

Supporting Information for

Structure of Hydrated Crystal (L_c), Tilted Gel ($L_{\beta'}$),
and Liquid Crystal (L_α) Phases of Linear
Alkylbenzene Sulfonate (LAS) Studied by X-ray
Diffraction and Molecular Dynamics Simulation

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Crystal Structures of Other than the Monohydrate System.

The crystal structure of LAS under the ambient conditions was found to be the monohydrate. However, recent studies on SDS reported that different crystalline polymorphs can be produced by performing temperature drop experiments at various temperature conditions.³ Therefore, the structures of the other hydrates might be observed depending on the conditions. In this Section, we describe the crystal structures other than the monohydrate system did not match the present experimental XRD pattern. Table S1 shows the area per molecule S in the x - y plane, the tilt angle of the alkyl group φ , and the lamellar repeat spacing d_L for each hydrated crystal structure. Here, φ is defined as the angle between a vector connecting C1 to C18 carbon atoms (noted in Figure 1) and the z -axis, and averaged over simulation time and LAS molecules. As increasing the hydration number, S and φ both increased. d_L for anhydrate and tetrahydrate systems are larger than those observed in the other systems. The mechanisms of these differences are understood by captured images and number density profiles of each atom along the z -axis as summarized in Figure S1. In the case of anhydrous crystals, the sodium ions are mainly located at the space between lamellae along the bilayer normal (Figure S1a and b), whereas in higher hydrated system, sodium ions are also more frequently found in the vicinity of sulfonate group along the lamella plane (Figure S1c - j). Most water molecules exist near the benzene ring in hemihydrate and monohydrate systems (Figure S1c - f), while stoichiometrically-excess water in dihydrate and tetrahydrate systems, were located between lamellae with forming a thin aqueous layers (Figure S1g - j). The oxygen atoms of water located

near the benzene ring uniformly coordinates to sodium ions (Figure S1a, c, e, g, and i). Based on these observations, we judged that the increase in S originates from the local configuration in which sodium ions or hydration waters are located near the hydrophilic group. An increase in φ is caused in order to fill the additional free volume generated by the increase in S . We consider that the water molecules near the benzene ring contribute to stabilize the crystal structure by (1) filling free spaces around the benzene rings with realizing closer atom packing in the crystal, and (2) making energetically-favorable interactions of the polar functional group of LAS (charge-dipolar interaction) with sodium ions, as suggestion by Laughlin.¹ The trend of increases in S and φ , accompanied by decrease in d_L , with hydration number of the crystals is consistent with the trend observed in the anhydrides and monohydrates of SDS crystals reported by Smith *et al.*² Therefore, the trend is a common between LAS and SDS, and might be observed for other ionic surfactants systems. Figure S2 provides another beneficial information about local configuration in the LAS hydrated crystals. The benzene rings are randomly oriented in the monohydrate system, while those have higher periodic structure in the dihydrate and tetrahydrate systems. In the dihydrate system, benzene rings exhibited the “Herringbone Pattern” with two adjacent molecules of LAS as an asymmetric unit. In tetrahydrate system, they formed another kind of periodic structure with five molecules of LAS as an asymmetric unit. The observed many diffraction peaks in the XRD pattern (see Figure 4), which do not originate from the lamellar interval and the packing period of the alkyl chain in dihydrate and tetrahydrate crystals, may be assigned to these lateral long period structures of benzene rings. As described above, the experimental XRD pattern shows the best

match to the XRD pattern calculated from MD trajectory in the monohydrate system. It implies that the in-plane orientation of the benzene ring is relatively disordered in the LAS sample at 298 K.

Table S1 Area per molecule S , the lamellar repeat spacing d_L and tilt angle of the alkyl group φ of LAS crystal

	S (Å ²)	d_L (Å)	φ (°)
0 H ₂ O	23.0 ± 0.1	41.5 ± 0.1	33 ± 4
1/2 H ₂ O	26.3 ± 0.2	37.2 ± 0.1	43 ± 4
1 H ₂ O	27.2 ± 0.1	36.3 ± 0.1	46 ± 2
2 H ₂ O	27.6 ± 0.1	38.8 ± 0.2	45 ± 3
4 H ₂ O	27.7 ± 0.1	41.5 ± 0.1	48 ± 2

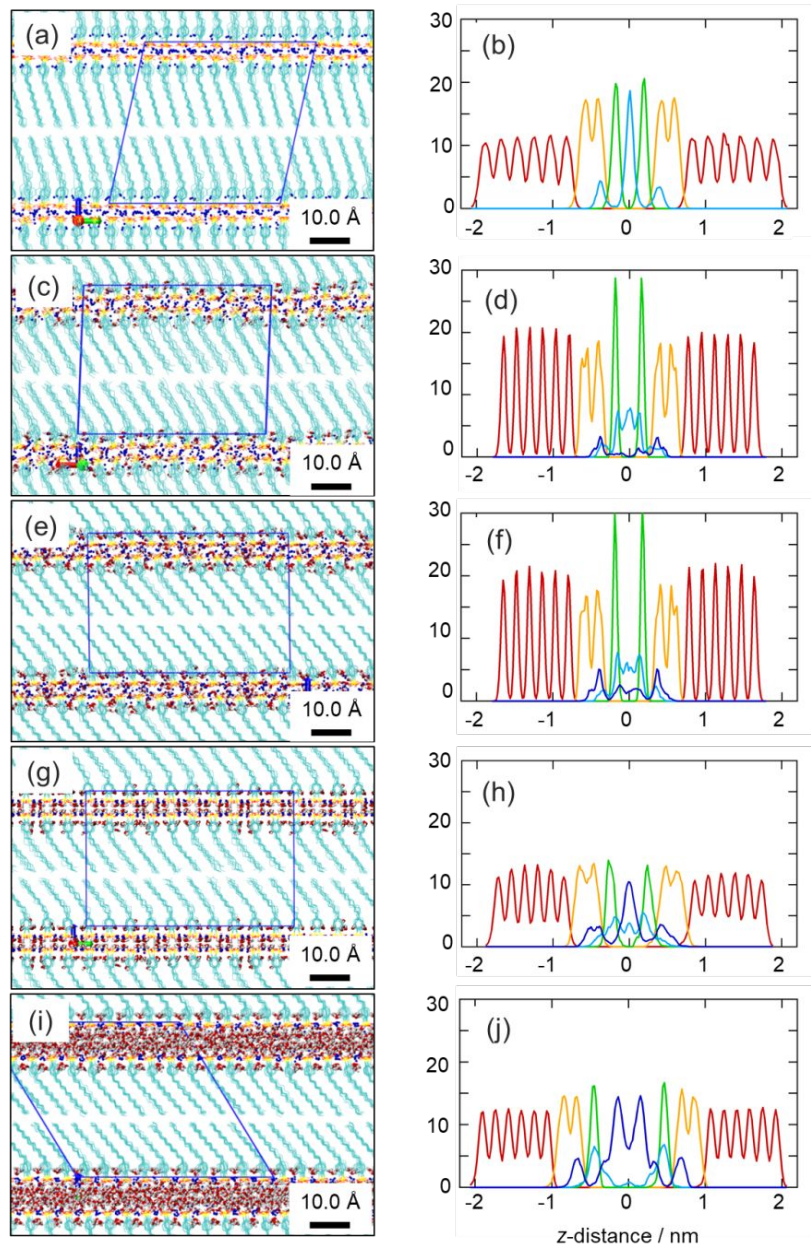


Figure S1 Side views of MD calculation unit cell for the (a) anhydrate, (c) hemihydrate, (e) mono-hydrate, (g) di-hydrate, and (i) tetra-hydrate systems at 300 K, and number density profiles of atoms for (b) anhydrate, (d) hemihydrate, (f) mono-hydrate, (h) di-hydrate, and (j) tetra-hydrate systems. Difference in line colors of the number density profiles indicate

difference in atom kinds; red: aliphatic carbon, yellow: aromatic carbon, green: sulfur, cyan:
sodium, blue: oxygen of water.

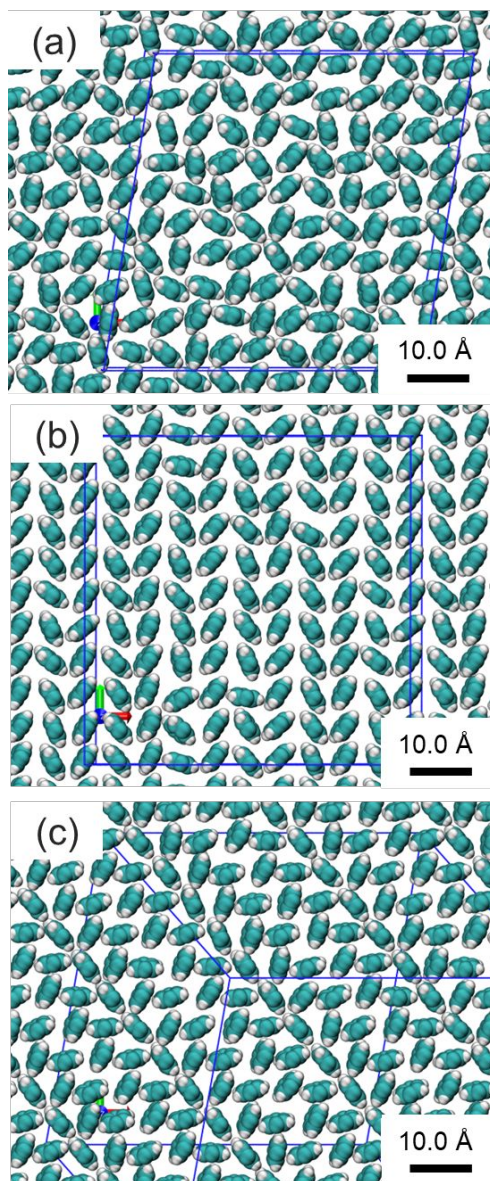


Figure S2 Arrangement of the benzene rings of LAS projected on the x-y plane for (a) monohydrate, (b) dihydrate and (c) tetrahydrate systems.

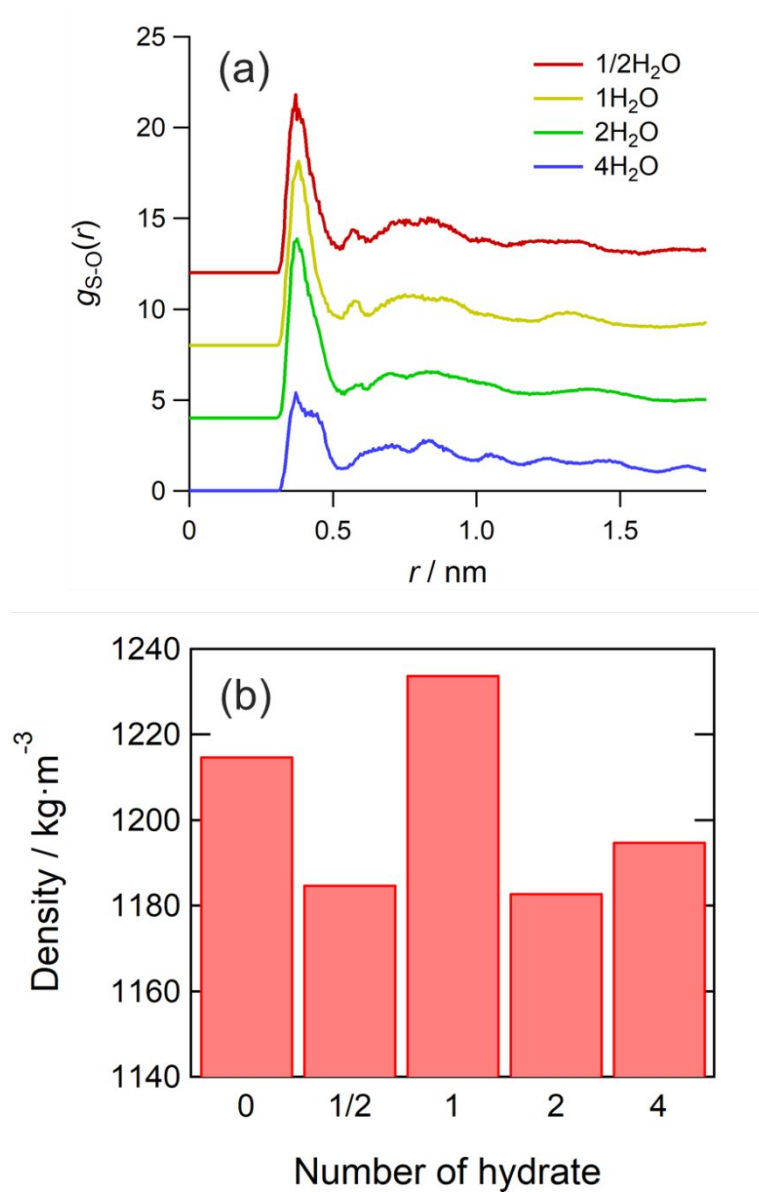


Figure S3. (a) Radial distribution function $g(r)$ between sulfur atom of LAS and oxygen atom of water in four systems with different hydration levels. Peak shape of the monohydrate system is relatively sharp with other systems. (b) System density at each hydration level including anhydrate.

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