Mono- and Bilayer Equilibria of Stearate Self-Assembly Formed in Hydrotalcite Interlayers by Changing the Intercalation Temperature

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The self-assembly of sodium stearate and its homologs ($>C_{12}$) in hydrotalcite (LDH) interlayers was found to change reversibly between mono- and bilayer structures with a ratio changing continuously within a range of 70 °C and 5 °C in stoichiometric intercalations in aqueous dispersion. The bilayer structure was more stable than the monolayer, judging from the fact that bilayer aggregations were formed even in high temperatures with the addition of excess amounts of guest stearates over the anion exchange capacity (AEC). Hydrophobic interaction was determined to be the key factor for the formation of a bilayer assembly.

Hydrotalcite, i.e., layered double hydroxide (LDH), is able to intercalate various anionic molecules in its interlayers because of its anion-exchange properties.[1-4] This characteristic capacity enables the fabrication of organic-inorganic hybrid materials which are able to accommodate functional molecules in its interlayers.[5,6] In the case of mineral ions, larger ionic valency and smaller ionic radius are favorable to the ion exchange intercalation. However, the anion exchangeability of organic anions depends on the extent of intermolecular interactions rather than on the valency and size of the guest molecules. Especially in aqueous solutions, hydrophobic interactions of guest molecules acts as one of the driving forces of the intercalation reaction in addition to the electrostatic interactions.[3] Amphiphilic compounds, possessing both hydrophilic and hydrophobic moieties, are able to form molecular assemblies such as micelles, vesicles, and lamellae in aqueous solution. The formation of these assemblies is responsible for the hydrophobic interaction, and the aggregation forms were found to be affected by the concentration and temperature. In this paper, we have studied the effects of the intercalation temperature and degree on the aggregation structures of aliphatic acid surfactants in LDH interlayers. Although there are several reports on the effects of the thermal change of conformational structures of alkyl chains, kink-blocks and gauche-blocks in layer compounds[7] and LDH,[8] the present work is the first report on LDH-intercalated molecular assemblies which shows that the aggregation structure is strongly affected by the intercalation temperature as well as degree. It can be seen that the self-assembly structure of the stearate in LDH is reversibly changed between mono- and bilayer depending on the intercalation temperature.

The LDH clay employed in present work, Alcamac, manufactured by Kyowa Chemicals Ltd, contains chloride as the exchangeable anion in its interlayers, i.e., $[\ Al_2Mg_{4.5}(OH)_{13}\ ]Cl_2 \cdot 4H_2O$, the anion exchange capacity (AEC) of which is 350 mequiv/100 g. Clay-intercalated samples were prepared by mixing 5 mmol dm^{-3} aqueous solutions of sodium stearate with appropriate amounts of the clay powder, then stirred for 1 day at several temperatures (5, 30, 50, and 70 °C). The suspensions were filtered using a membrane filter (Tokyo Roshi Co., pore size 0.45 μm) and the filtrated clays were dried in vacuo at room temperature for 2 h. The intercalation states were elucidated by X-ray diffraction and infrared spectroscopy. The degree of intercalation was measured using the following procedures. To decompose clay layers, the filtrated clay was acidified with concentrated HCl (5 cm^3), inducing precipitation of free carboxylic acids. The acidified solution was extracted with several 50 cm^3 portions of $CHCl_3$, followed by methylation with CH_2N_2, drying over anhyd. Na_2SO_4, and then condensation in vacuo to produce a white powder. Finally, the amount of intercalated fatty acid was estimated by GLC.

Figure 1 shows the X-ray diffraction patterns of the stearate-clay composite powders which were intercalated at several temperatures. At 70 °C, broadened diffraction peaks caused by (00n) spacing were observed, the interlayer distance (d) of which is 32.0 Å (state A ; shown by open circle). New diffraction peaks appeared at d = 52.5 Å (state B ; filled circle) with a decrease in the temperature. State B has very sharp peaks compared with state A, indicating that the intercalation structure of state B is much more densely and regulated than that of state A. Since no other peaks besides state A and B could be detected, it can be deduced that the stearate is only able to be accommodated in either or both two types of intercalation states within the LDH clay interlayers, while the ratio of state A and B is reversibly changed by the change in temperature for the intercalation reaction. The gallery heights of these states from the d-spacing, calculated by taking the 4.8 Å thickness of hydroxide layer, were 27.2 Å and 47.7 Å, respectively. Configurations of the alkyl chains of the stearate in clay interlayers were measured by infrared spectroscopy. The C-H asymmetric and symmetric stretching vibrations were observed at 2917 and 2849 cm^{-1} for all samples. These results indicate that the alkyl chains exist in trans configurations. Judging from the molecular length of stearate which was 24.2 Å, the aggregation structures of stearate molecules in state A and B were expected to be monolayer and bilayer, respectively. However, the equilibrium was not observed with intercalated LDH in dry powder form,

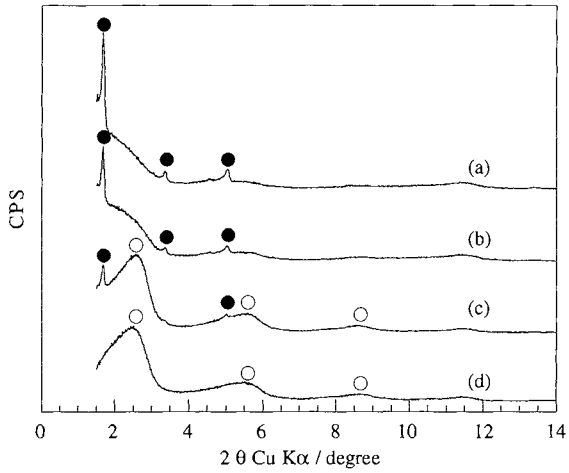

Figure 1. X-ray diffraction patterns of stearate-clay composite. The temperature of intercalation in °C : 5 (a), 30 (b), 50 (c) , and 70 (d).

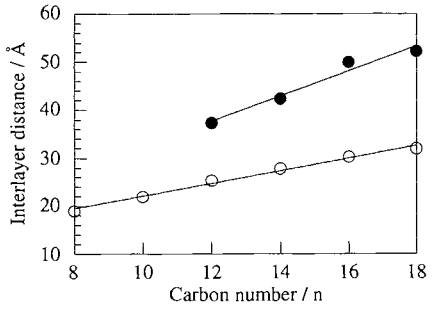

Figure 2. Plots of Interlayer distance versus carbon number of state A (○) and B (●).

implying the mobility of the guests through bulk solutions.

Investigation were carried out under similar conditions for liner fatty acids, the carbon number of which is n = 8 - 16. Intercalation did not occur for n = 8 and 10 at low temperature because of its rather high hydrophilicity. The plots for the interlayer distance against the carbon number are shown in Figure 2, in which open and filled circles represent state A and B, respectively. The slope of state B, 2.6 Å/n, which was twice as large as that of state A, 1.3 Å/n, supports the proposed mono- and bilayer structures for each state, since the C-C distance of alkyl chain is 1.27 Å.

Figure 4 shows X-ray diffraction patterns of clay-intercalated compounds prepared at 70 °C by mixing with varying amounts of sodium stearate from 100 to 300% based on the AEC. GLC analysis revealed that intercalation degree far exceeded the AEC at any temperature. State A shows a diffraction pattern which is characteristic to the existence of only a monolayer assembly in the stoichiometric intercalation. However, a peak for a bilayer assembly appears at d = 52.5 Å and state A begins to disappear with an increase in the percentage of the intercalation up to 300%. Diffraction at d = 52.5 Å is in good agreement with that of state B. Hence, the bilayer structure formation at low temperature was found to be due to the non-electrostatic interaction of the stearate over the AEC, indicating that the packing arrangement of the bilayer structure is much tighter than that of the monolayer structure. It have, therefore, found that the bilayer contains much more stearate molecules in each interlayer (Figure 3). Each anionic site was completely exchanged by stearate ions in the monolayer structure, but there remained half as many vacant sites in the bilayer structure as in the AEC. X-ray analysis indicates that there are no second-stage intermediates[9] which are alternatively stacked due to absence of any reflections (00n) for the sum of the bilayer and vacant layers. It can, therefore, be concluded that the bilayer formation is caused by hydrophobic interaction among the stearate alkyl chains. Assuming Al^{3+} is distributed homogeneously in the clay layer, the

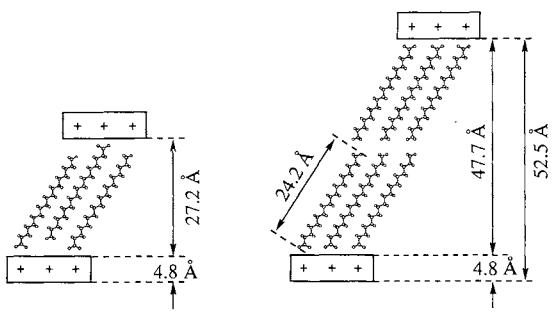

Figure 3. Models of mono- and bilayer structure.

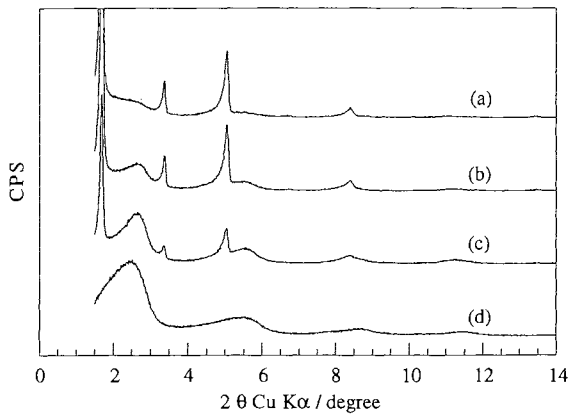

Figure 4. X-ray diffraction patterns of stearate-clay composite intercalated at 70 °C. Amount of Sodium stearate v.s. AEC in % : 300 (a), 200 (b), 150 (c), and 100 (d).

area occupied by each anion exchangeable site is 25.3 $Å^2$. Since guest molecule can be adsorbed on both side of the clay layer, one guest anion occupies 50.6 $Å^2$ (2 x 25.3 $Å^2$). The alkyl chain cross section is known to be 20 $Å^2$ in a closely packed monolayer.[10] The muximum intercalation degree of stearate was 2.5 times as much as the AEC. One stearate molecule can occuppy 20.2 $Å^2$ (50.6 $Å^2$/2.5) in accordance with the cross section of stearate. Therefore, the bilayer consists of a closely packing structure of stearate in its interlayers which is evidenced by the sharp diffraction patterns in a X-ray analysis.

The formation of a bilayer structure can be explained by hydrophobic interaction of stearate molecules. In methanol solutions without any hydrophobic interactions between adjacent stearates, no temperature effect could be observed for the intercalation, while the X-ray diffraction patterns at any temperature were the same as for those in 70 °C in aqueous solution. Furthermore, no matter how much sodium stearate was added over AEC, intercalation always occurred at a degree of 100%. In clay interlayers, the hydrophobic interaction works as the driving force to form a bilayer structure which allows more stearate molecules to be intercalated into one interlayer than with a monolayer structure.

In conclusion, the present study is unprecedented in showing that the aggregation structure of stearates in hydrotalcite clay interlayers is greatly affected by the intercalation temperature and degree. Furthermore, the bilayer structure is caused by the hydrophobic interaction of the stearate molecules, showing the significant effects of controlling the aggregation structure in clay interlayers.

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