

Synthesis of a Series of Long Chain Lamellar Inorganic/Organic Iron(II) Alkylsulfonate Hydrates

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Abstract

A series of the long-chain iron(II) alkylsulfonate hydrates were synthesized via self-assembly of surfactant alkyl chains in aqueous medium. Reaction of iron(II) salts with n-alkylsulfonate yields lamellar $\text{Fe}(\text{C}_n\text{H}_{2n+1}\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$. These compounds show a layered structure, as determined by XRD, consisting of alternating organic alkylsulfonate layers and inorganic iron(II) hydrate layers, with interlayer distances of upto 3.2 nm. This lamellar structure may be attributed to the amphiphilic nature of the surfactants, mediating the coordination and H-bonding interactions, and the hydrophobic alkyl chains. An alkyl chain packing of present system are differ from those of similar Cu(II) series, which are attributed from the size of hydrated metal(II) ions.

Key words : organic-inorganic hybrids, lamellar, layered structure, self-assembly, model biomembrane

1. Introduction

The discovery of mesoporous materials^[1,2] with pore openings in the range from 2-10 nm has open the way to new class of inorganic oxides with a wide potential for applications in gas separation, sorption and catalysis. Generally, the synthesis involves the cooperative assembly of surfactant molecules with hydrolysable inorganic precursors into a mesostructured precipitate. By varying the surfactant head group, the kind of precursor and other synthetic parameters like temperature, addition of an acid or base etc., the preparation of metal oxide/surfactant composites has been achieved.^[3] Among these, materials with a lamellar structure have not attracted as much interest as their hexagonal or cubic variants. However, based on the special two-dimensional structure of the inorganic part, with nanometer-size dimensions in one direction, layered metal oxide-surfactant composites should exhibit special magnetic and optical properties with differ from those of the corresponding bulk oxides. Therefore, the field of organic/inorganic hybrid materials are attractive from both the theoretical and the application point of view. In particular, the abil-

ity to rationally design the hybrid materials with meso-scale periodicity is of particular interest, allowing for *structural control* on the molecular level.^[4]

Recently, we have reported a new example⁵ of organic/inorganic hybrids, $\text{Cu}(\text{C}_n\text{H}_{2n+1}\text{SO}_3)_2 \cdot z\text{H}_2\text{O}$ where $z=4$ for $n=10,12$ (group(I)) and $z=2$, for $n=14, 16, 18$ (group (II)), consisting of alternating an inorganic copper(II) hydrate layer and an long-chain alkylsulfonates layer with structural flexibility. It would be interesting to this system, which because of a structural packing variety which drastically depends on the length of alkyl chains.^[6] The layer to layer distance can be easily and rationally metered by choosing alkylsulfonates of different lengths; shorter alkylsulfonates (group (I)) yield an interdigitated structure with shorter periodicity, whereas longer alkylsulfonates (group (II)) yield a non-interdigitated structure with longer periodicity. The structure may be described as nice candidates for model biomembranes. In this extended work, we intend to report the synthesis of an another series of iron (II) alkylsulfonates (denoted as $\text{FeSO}_3\text{-C}_n$), and compares the structural difference on the chain packing of between two series.

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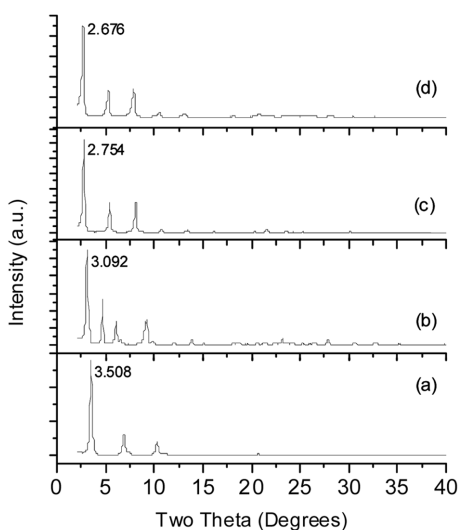


Fig. 1. Powder XRD patterns of the lamellar iron (II) alkylsulfonates, $\text{FeSO}_3\text{-C}_n$, (a-d: $n=10, 12, 14, 16$, respectively)

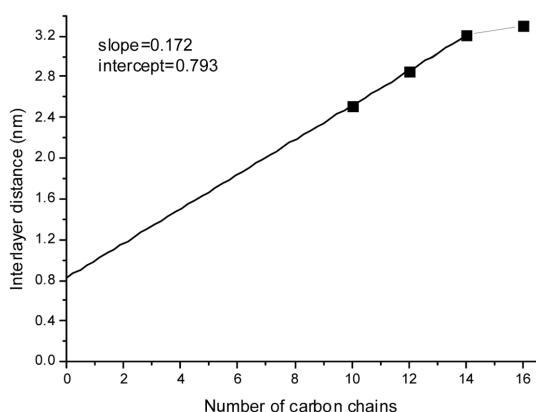


Fig. 2. The dependence of interlayer distance on the carbon number of the iron (II) alkylsulfonates, $\text{FeSO}_3\text{-C}_n$.

2. Syntheses and Their Characterizations

2.1. Syntheses

The $\text{FeSO}_3\text{-C}_n$ ($n=10, 12, 14, 16$) compounds were synthesized via self-assembly of surfactant alkyl chains in aqueous medium. All of the n -alkylsulfonate sodium salts ($\text{C}_n\text{H}_{2n+1}\text{SO}_3\text{Na}$, $n=10, 12, 14, 16$) were obtained from TCI Co. and used without further purification. The $\text{FeSO}_3\text{-C}_n$ compounds were simply prepared from by mixing 20 mL of dilute aqueous solution of sodium alkylsulfonate, $c=0.01\text{-}0.005$ M) with 20 mL of 0.01 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at room temperature. In all cases, shortly

after the solutions were mixed, precipitation occurs. The precipitate was filtered, washed and deoxygenated water, and dried under vacuum at room temperature.

2.2. Powder XRD studies

The powder X-ray diffraction (PXRD) patterns are shown in Fig. 1, The $\text{FeSO}_3\text{-C}_n$ ($n=10, 12, 14, 16$) compounds all exhibit a lamellar structure, as is evident from the powder XRD patterns exhibiting, in the low 2θ range, intense (00 l) reflections, corresponding to the stacking periodicity of the inorganic layers. Increasing the alkyl chain length, the lowering of peak position of (00 l) reflections are observed, which reflects the increasing of interlayer distances. Therefore, iron(II) alkylsulfonate series are successfully synthesized.

The alkyl chain packing from the XRD data can be understood through analysis of their variation in the fundamental layer spacing (d_{001}) with the alkyl chain length: $d(\text{nm})=d_0+\eta(0.127n \cos\theta)$, where $\eta=1$ or 2 depending on the chain packing and θ is the tilt angle of the chains.^[7] The d -spacing plotted against the number of carbon is represented in Fig. 2, which indicate a slightly greater slope (slope=0.172 nm/ carbon atom). Therefore, the $\text{FeSO}_3\text{-C}_n$ series are of a non-interdigitated bilayer structure with a tilt angle of 47° ($\theta=\cos^{-1}(0.172/0.254)$). The intercept ($=0.793$ nm) of the layer spacing versus the carbon chain length plot can be assigned to the thickness of the inorganic layers plus the sulfonate headgroup.

3. Discussions

All $\text{FeSO}_3\text{-C}_n$ series exhibit a layered structure, which crystal structures consist of alternating polar layers of the hydrated iron(II) ions interlinked by hydrogen bonds and non-polar layers of perfectly aligned alkyl chains, that similar with those of the copper(II) series. This two-dimensional inorganic/organic hybrid structure may be attributed to the cooperative amphiphilic nature of the surfactants, i.e., both the hydrophilic sulfonate head groups, mediating the coordination and H-bonding interactions, and the hydrophobic alkyl chains. However, an alkyl chain packing of present Fe(II) system are being a non-interdigitated bilayer independent of alkyl chain length whereas that of Cu(II) series are monolayer or bilayer depending on the alkyl chain length. An alkyl chain packing of present system are

differ from those of similar Cu(II) series, which are attributed from the size of hydrated metal(II) ions, which are attributed from the size of hydrated metal(II) ions (dedicated from the intercept of Fig. 2).

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