

Vesicle formation induced by layered double hydroxides in the catanionic surfactant solution composed of sodium dodecyl sulfate and dodecyltrimethylammonium bromide

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Abstract In this paper, it is reported that positively charged Mg_3Al layered double hydroxide (LDH) nanoparticles can induce the spontaneous formation of vesicles in micelle solution of sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) with a mass ratio of 8:2. The formation of vesicles was demonstrated by negative-staining transmission electron microscopy observations. The size of the vesicles increased with the increase in the concentration of Mg_3Al -LDH nanoparticles. A composite of LDH nanoparticles encapsulated in vesicles was formed. A possible mechanism of LDH-induced vesicle formation was suggested. The positively charged LDH surface attracts negatively charged micelles or free amphiphilic molecules, which facilitates their aggregation into bilayer patches. These bilayer patches connect to each other and finally close to form vesicles. It was also found that an adsorbed compound layer of SDS and DTAB micelles or molecules on the LDHs surface played a key role in vesicle formation.

Keywords Vesicle · Surfactant · Layered double hydroxides · Composite

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Introduction

There are large numbers of clay minerals on the earth, and mineral surfaces have several important properties related to the origin of life. The mineral surfaces may offer an interface to adsorb organic solutes and then concentrate them. Ferris [1] has explored the ability of montmorillonite, one kind of smectite clay, to organize and even catalyze the synthesis of RNA from chemically activated mononucleotides. RNA polymers up to 50 nucleotides in length can be produced in this action. One more interesting experimental result from Hanczyc et al. [2] was that negatively charged montmorillonite particles can accelerate the spontaneous conversion of fatty acid micelles into vesicles, and in turn, some montmorillonite particles and molecules (fluorescently labeled RNA oligonucleotide) on their surfaces often become trapped in these vesicles. The vesicles consisting of amphiphilic molecules could have existed in the prebiotic environment. More recently, they extended their analysis of mineral-mediated vesicle catalysis to include other natural minerals (such as aluminum silicate, alumina, and glass microspheres) and synthetic surfaces (silica spheres) of varying shapes, sizes, and (negatively) charge densities. Their results showed that such mineral-assisted vesicle assembly appears to be a remarkably general phenomenon, which might play a key role in the organization and formation of the first cell-like structures on the early earth [3]. Although this is an interesting and attractive topic, there is not much related research [2, 3] on the phenomenon of vesicles induced by minerals and the interactions between vesicles and minerals except some articles focusing on the adsorption of amphiphilic molecules on mineral surfaces [4, 5]. The direct images of the interactions between clay particles with Aerosol OT (AOT) vesicles in aqueous suspensions have been obtained by Davis et al. in 1995 [6]

for the first time by cryogenic transmission electron microscopy (cryo-TEM). They found that the stability of the clay–AOT suspension was heightened, and some clay particles were encapsulated in vesicles. We [7] reported recently a structurally positively charged synthetic clay—layered double hydroxides (LDHs) that induced vesicle formation in a mixture of a zwitterionic surfactant (dodecyl betaine) and a double chained anionic surfactant (AOT). Moreover, parts of LDH particles were encapsulated in vesicles to form a composite. In order to understand the mechanism of LDH-induced vesicle formation and study the generalization of this phenomenon in different systems, in this paper, we investigated the spontaneous formation of vesicles induced by LDHs in an aqueous cationic surfactant solution composed of sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB). The anionic surfactant used in this study is a common single chained surfactant. The mechanism of LDH-induced vesicle formation was explored through the effect of different mixing orders of two kinds of surfactant solutions with LDH sol. In particular, it is confirmed that the vesicle formation was indeed induced by the LDH particles themselves, neither by the presence of soluble metallic salts accompanying LDHs nor by the change of pH value in the preparation process of the surfactant–LDH mixtures.

LDHs, also known as anionic clays or hydroxide-like compounds, are a class of layered inorganic materials that consist of structurally positively charged layers and exchangeable anions in the interlayer gallery for charge balance [8, 9]. The general formula is $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-} \cdot mH_2O$, where M^{II} and M^{III} are di- and trivalent metal cations, A^- is interlayer anions (or gallery anions) of charge n , x is the molar ratio of $M^{III}/(M^{II}+M^{III})$, and m is the number of moles of co-intercalated water per formula weight of the compound. LDHs have widespread applications in many areas such as anion adsorbents, catalyst supports, catalysts, and membranes. More recently, LDHs are attracting much attention in drug delivery and gene therapy because of their biocompatibility, anion-exchange property, and nontoxicity [10]. On the aspect of the origin of life, Arrhenius [11] reviewed many of the areas where LDH minerals are relevant to origin of life studies. Greenwell and Coveney [12] suggested that the LDHs not only catalyzed reactions of important prebiotic molecules, but also provided a superior coding environment relative to the cationic clays and could have served as prebiotic “ribozymes”, ultimately allowing the first RNA materials to be produced. However, the studies on the LDH-mediated organized molecular assembly were not reported by other researchers. The investigations of vesicle formation induced by LDHs may help to get a better insight into the origin of life. In addition, the composite of vesicle-encapsulated LDH nanoparticles may be expected to be potentially used in drug delivery and

gene therapy because both vesicles and LDHs may be used in controlled drug or DNA release [13–16], respectively. Therefore, the studies on the phenomenon of vesicles induced by LDHs may be of fundamental and practical importance.

Experimental section

Materials

SDS and DTAB were purchased from J&K Chemical Ltd and used as received. Other reagents were A. R. grade purchased from Sinopharm Chemical Reagent Co., Ltd. Ultra pure water was used in all cases.

Preparation of Mg_3Al -LDHs

Mg_3Al -LDHs ($Mg/Al=3:1$, molar ratio) were synthesized by the coprecipitation method [17]. Aqueous solutions of $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ were mixed at a molar ratio of 3:1 with the total metal ion concentration of 0.5 M. Then, the coprecipitation agent, diluted ammonia water (6 wt.%), was put into the mixed solution under stirring at a speed of 25 ml/min till the final pH value reached 9.5. The precipitate was aged for 45 min in the mother solution at room temperature and then filtered and washed with ultra pure water to remove NH_4Cl and the excess ammonia. The filter cake held in a glass bottle was peptized at 80 °C in an oven for 24 h to obtain Mg_3Al -LDH sol sample. The XRD patterns of the Mg_3Al -LDH sample (see [Supplementary Information](#)) exhibit all characteristic diffractions of hydroxide (JCPDS card no. 51-1528), indicating that the Mg_3Al -LDH sample is of a well-crystallized structure.

Preparation of surfactant–LDH mixtures

The stock surfactant solution of SDS and DTAB at a mass ratio of 8:2 with total original concentration of 2 wt.% was prepared by dissolving weighed amounts of dried substances in ultra pure water. A given volume of the stock surfactant solution and a given volume of LDH sol were vortex-mixed with different solid concentrations. The obtained surfactant–LDH mixtures were equilibrated in a thermostatic bath at 25 °C for at least 24 h prior to further experiments except absorbance measurements.

Determination of the morphology of organized assemblies

The morphology of organized assemblies was examined by transmission electron microscopy (JEM-100CXII). The negative-staining (with uranyl acetate in water solution)

technique was used for TEM sample preparation. Specimens for cryo-TEM were prepared in a controlled environment vitrification system at 25 °C and 90% relative humidity. A drop of the sample solution was placed on a copper grid. Immediately after blotting with two pieces of filter paper to obtain a thin film suspended on the mesh holes, the sample was quickly plunged into a reservoir of liquid ethane (cooled by the nitrogen) at −165 °C. The vitrified samples were then stored in the liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined with a JEOL JEM-1400 TEM (120 kV) at about −174 °C. The phase contrast was enhanced by underfocus. The images were recorded on a Gatan multiscan CCD and processed using DigitalMicrograph.

Dynamic light scattering measurement

The diameter of the vesicles was determined by dynamic light scattering (DLS) which was performed with a spectrometer of standard design (Brookhaven model BI-200SM goniometer and model BI-90000AT correlator) and a 300-mW Ar laser (488 nm wavelength). All measurements were made at the scattering angle of 90° at 25 °C, and the intensity of the function was analyzed by the method of CONTIN. The particle size distribution of aggregation in the solution was obtained from the scattering light intensity $I \cdot G(I)$ as a function of hydrodynamic radius R_h .

Absorbance measurement

After the mixed systems of the surfactant solution and Mg_3Al -LDH particles were prepared, absorbance measurements were immediately performed at 25 °C with a Hewlett Packard 8453 spectrometer at 500 nm.

Results and discussion

Macroscopic appearance

The phase behavior of aqueous mixtures of SDS and DTAB was investigated and described by Kaler et al. in 1993 [18]. The phase diagram provided by the authors indicated that hydrated crystals of 1:1 anion/cation surfactants dominate the phase behavior while vesicles only exist in a very narrow composition range, without a region of coexistence between small micelles and vesicles (see [Supplementary Information](#)). In this study, the surfactant concentration was 1 wt.% and the anionic/cationic weight ratio was 8:2 which remained constant throughout all the experiments. This surfactant solution is in the micelle region according to the phase diagram [18].

Figure 1 shows the macroscopic appearances of mixed systems, and the initial SDS/DTAB solution of 1 wt.% without Mg_3Al -LDHs is transparent and isotropic, corresponding to the micelle region of the phase diagram [18], which is also confirmed by the later DLS measurements (Fig. 2). After adding Mg_3Al -LDH particles, the given systems turn to bluish and turbid to the naked eyes in the range of Mg_3Al -LDH concentration from 1 to 3.5 g/L. After the Mg_3Al -LDH concentration was higher than 5 g/L, white cloudy precipitation (or flocculation) emerged in the systems. These results imply that a stable composite system is formed with LDH particles and SDS/DTAB solution at an appropriate composition.

Examination of assembly formation

In order to examine the formation of possible assemblies, negative-staining TEM (NS-TEM) was employed. Figure 3 shows the NS-TEM images of the mixed systems at a final surfactant concentration of 1 wt.% with various LDH concentrations. As a comparison, the NS-TEM image of Mg_3Al -LDH sol is also shown in Fig. 3. The Mg_3Al -LDH particles (Fig. 3a) are of hexagonal plate-like shape with the lateral size of 40–60 nm. For the mixed systems in the LDH concentration range of 1–2 g/L, a large number of vesicles with a vivid bilayer are observed and their size is in the range of 50 to 430 nm. Additionally, the average size of the vesicles is increasing as a function of LDH concentration. In particular, as shown in panels c and d of Fig. 3 where some larger vesicles encapsulate Mg_3Al -LDH particles (as directed by black arrows), on the contrary, we do not find the same phenomenon in the smaller vesicles. The size of the encapsulated objects in the larger vesicles is 40 to 60 nm, consistent with the scale of Mg_3Al -LDH nanoparticles. In order to corroborate the structures of the obtained composite, cryo-TEM was introduced into our experiments. Figure 4 shows the cryo-TEM image of the

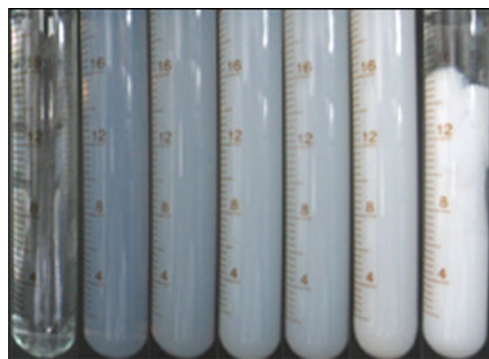


Fig. 1 Macroscopic appearance of mixed systems of Mg_3Al -LDHs and SDS/DTAB solution with various LDH concentrations. The LDH concentrations from *left to right* are 0, 0.5, 1, 2, 3.5, 5, and 10 g/L (pictures taken after equilibrated for 2 months)

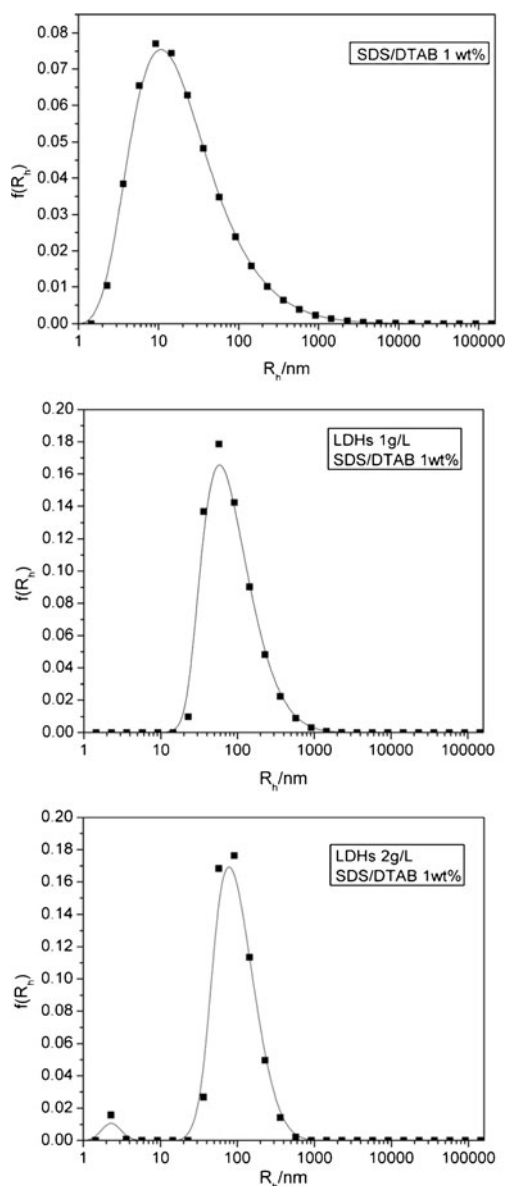


Fig. 2 Hydrodynamic radius (R_h) distributions of the composites of Mg_3Al -LDHs and SDS/DTAB solution

composite of Mg_3Al -LDHs and SDS/DTAB (1 wt.%) solution with Mg_3Al -LDH concentration of 2 g/L. We can see a series of composites of plate-like LDHs encapsulated in vesicles (as directed by black arrows). The size of the vesicles is around 150 nm and the size of the encapsulated LDHs is around 60 nm, consistent with the NS-TEM and DLS observations at this mixing ratio.

At a lower Mg_3Al -LDH concentration of 0.5 g/L, no vesicles but only some LDH particles are observed (see [Supplementary Information](#)). At Mg_3Al -LDH concentration of 3.5 g/L, some vesicles and aggregates coexist (see [Supplementary Information](#)). At Mg_3Al -LDH concentration higher than 5 g/L, no vesicles are observed with NS-TEM in both supernatant and precipitation.

Based on the above results, we conclude that spontaneous formation of vesicles can be induced by positively charged Mg_3Al -LDH nanoparticles in an aqueous cationic surfactant solution composed of SDS and DTAB. Moreover, the formation of vesicles is dependent of LDH particle concentration. In particular, the composites of LDHs encapsulated in vesicles could be obtained.

Hydrodynamic radius measurement of vesicles

DLS measurements were performed to determine the apparent hydrodynamic radius (R_h) of vesicles. As a comparison, the SDS/DTAB solution was also examined with the DLS method. The results are shown in Fig. 2. The average R_h value of SDS/DTAB solution of 1 wt.% is about 10 nm, which is a typical value of a micelle system [19]. For the LDHs/SDS/DTAB systems, the average R_h values are 57, 71, and 90 nm when the LDH concentrations are 1, 1.5, and 2 g/L, respectively. The average R_h is getting larger with LDH concentration increasing, and we presume that the rise of the vesicle radius with LDH concentration can be attributed to more and more Mg_3Al -LDH particles encapsulated in vesicles.

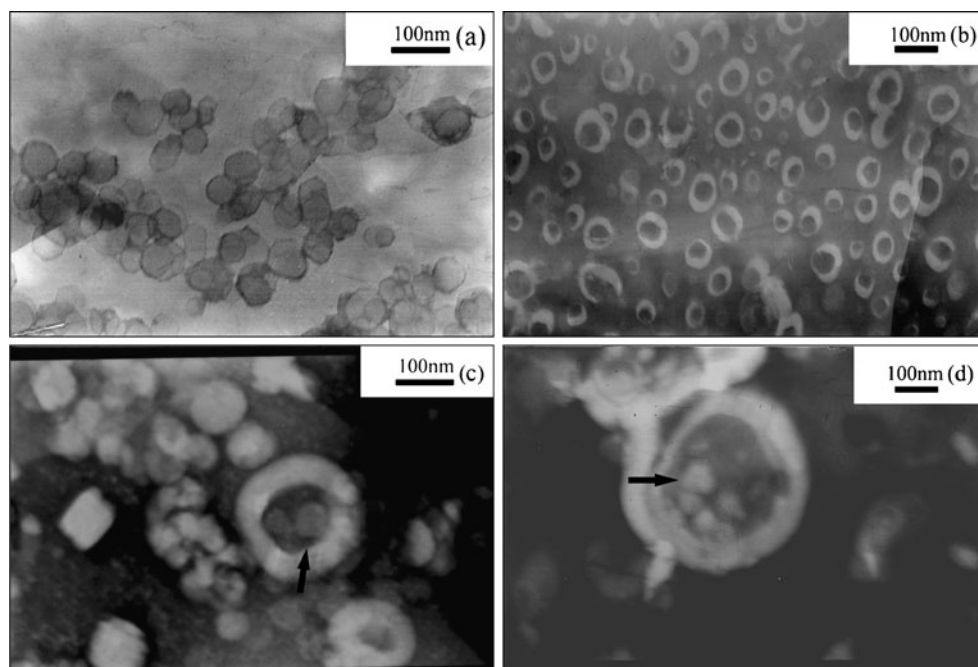
Aging effect on vesicle size

It was found that the average R_h values of surfactant-LDH mixtures vary with aging time. For example, at LDH concentration of 1.5 g/L, Fig. 5 shows that in the initial 5 min after mixing surfactants and LDHs, only a few vesicles are formed, and on the subsequent half hour to 1 h, a sharp peak indicating more vesicles with similar size is obtained. After 24 h, the size of partial vesicles increases to more than 100 nm; afterwards, their size almost remains constant. The results obtained by the DLS method are in agreement with the NS-TEM observations (Fig. 6). With the aging time from 5 min to 24 h, the average R_h increased from 28 to 71 nm. The change of vesicle size illustrated the process of vesicles growing.

Mechanism of vesicle formation

As we have known, the presence of salts [20] or the change of pH for a surfactant solution [21] may also induce the formation of vesicles possibly. In order to verify that the LDH particles themselves induced the formation of vesicles, first we determined whether the presence of soluble metallic salts accompanying LDHs induced the formation of vesicles. Mg_3Al -LDH sol of 5 g L⁻¹ was prepared and the particles were separated from the supernatant by centrifugation at 12,000 rpm. The fine particles were removed by passing the supernatant through 0.2- μ m syringe filters. Both particles and supernatant were

Fig. 3 Negative-staining TEM images of Mg_3Al -LDHs (**a**) and the composites of Mg_3Al -LDHs and SDS/DTAB (1 wt.%) solution with different Mg_3Al -LDH concentrations, respectively. **b** 1 g/L, **c** 1.5 g/L, and **d** 2 g/L



used in vesicle formation tests. It was found that only the solid particle fraction was able to induce vesicle formation, whereas there was no vesicle formation in the mixture of the filtered supernatant and surfactant solution (see [Supplementary Information](#)). Then, we tested whether the vesicle formation was induced by the change of pH value in the mixing process of SDS/DTAB solution and LDH sol. The pH value of the SDS/DTAB solution was 7.26 while that of the mixed system was 10.55. After the pH value of the SDS/DTAB solution was adjusted to 10.55 by adding 20 mM NaOH solution, the surfactant solution was still transparent and no large aggregates were found in NS-TEM (see [Supplementary Information](#)). Thus, we conclude that the formation of the vesicles does not result from soluble salts nor a change in the pH of the solution. Mg_3Al -LDHs themselves were the cause of the formation of vesicles.

It is acceptable that vesicle formation should be induced by the cooperation of surfactants and LDHs. About the mechanism of the spontaneous vesicle formation induced by minerals, Hanczyc et al. [2, 3] suggested that the mineral surfaces that are intrinsically negatively charged may directly stimulate membrane formation, while in other cases, an adsorbed layer of amphiphiles may coat the mineral particle and serve as the catalyst for subsequent vesicle formation. In our experiment, the concentrations of both surfactants are much higher than their CMC, and rod-like mixed micelles should abound in the cationic surfactant solution [22]. The electrostatic attraction between micelles and LDHs would increase the local concentration of the LDH surface, and the surfaces of LDHs can provide sites for hydrophobic association of micelles or molecules. Because of the hydrophobic interactions, the micelles will assemble to form more packed metastable intermediates

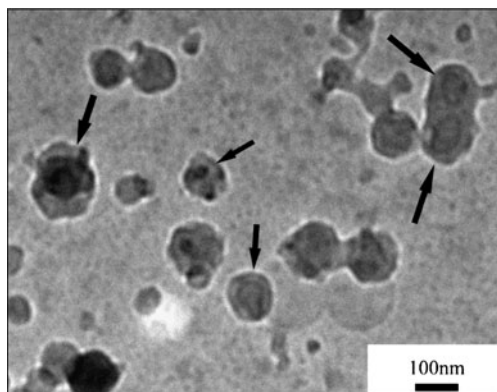


Fig. 4 Cryo-TEM image of the composites of Mg_3Al -LDHs and SDS/DTAB (1 wt.%) solution with Mg_3Al -LDH concentration of 2 g/L

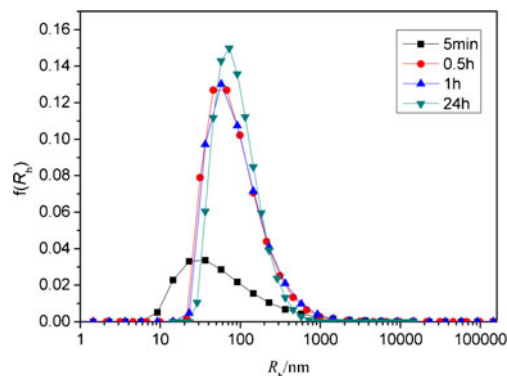
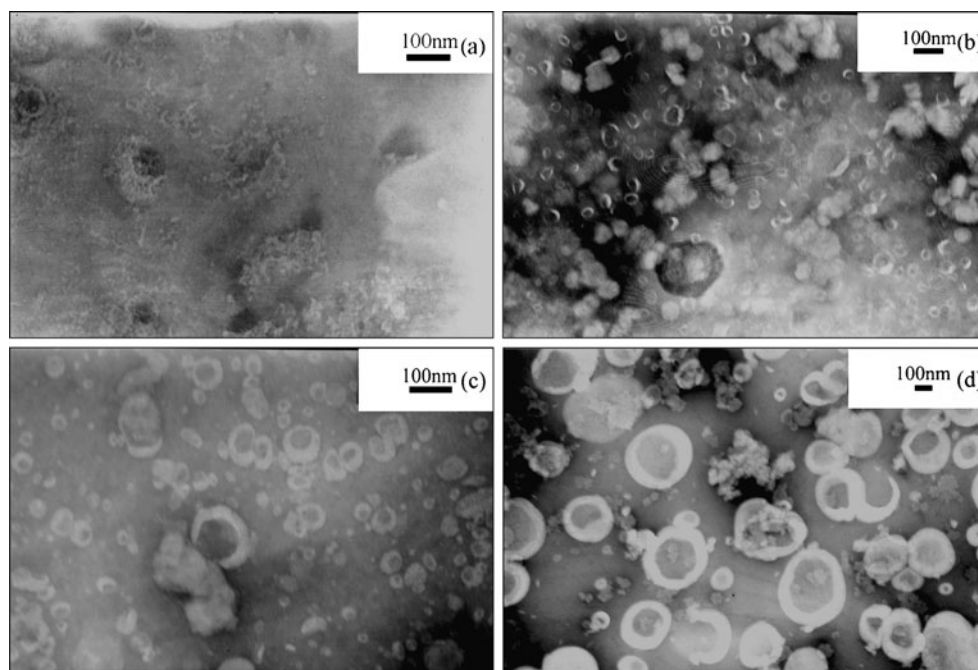


Fig. 5 Time change of hydrodynamic radius (R_h) distributions of the composites of Mg_3Al -LDHs (1.5 g/L) and SDS/DTAB solution (1 wt.%)

Fig. 6 Negative-staining TEM images of the time change of composites of Mg_3Al -LDHs (1.5 g/L) and SDS/DTAB (1 wt. %) solution. **a** 5 min, **b** 0.5 h, **c** 1 h, and **d** 24 h



which are larger than themselves. These metastable intermediates are not well-defined structures, but may be thought of as bilayer patches like elongated or flexural rod-like micelles that change with time (see Fig. 7a). With the micelles associating more and more on some sites of LDHs, the bilayer patches continue to grow and connect to each other, and finally close to form vesicles. If the patches curve toward the LDH particles, the composites of Mg_3Al -LDHs encapsulated in the vesicles are formed (see Fig. 7b).

Effect of the mixing order of two surfactants with LDHs

The effect of the mixing order of two kinds of surfactant solutions with LDH sol on vesicle formation was examined. In the first series, the SDS solution and LDH sol were first mixed to form an SDS–LDH mixture in a thermostatic bath

at 25 °C for 24 h to reach equilibrium. Afterwards, the DTAB solution was added into the mixtures equilibrated in a thermostatic bath at 25 °C for another 24 h. The final LDH concentration was 1.25 g/L and the final total surfactant concentration was 1 wt.%, which was under the same condition with the forenamed experiment. White cloudy flocculation immediately appeared when LDH sol and the SDS solution mixed together (see [Supplementary Information](#)), and this might be attributed to the intense electrostatic interaction between positively charged LDHs and ionic surfactant. Besides, some aggregations were found in the NS-TEM observation (Fig. 8a). Upon adding DTAB solution into the system, part of the flocculation dissolved, and then, vesicles could be observed in the system under NS-TEM (Fig. 8b). For the second series, the DTAB solution instead of the SDS solution was mixed with

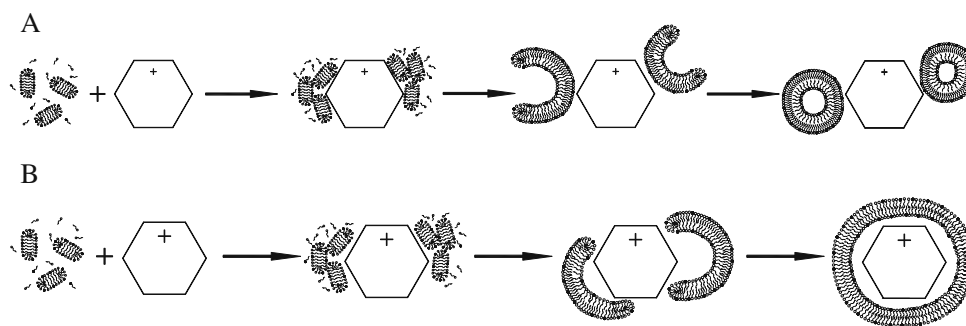
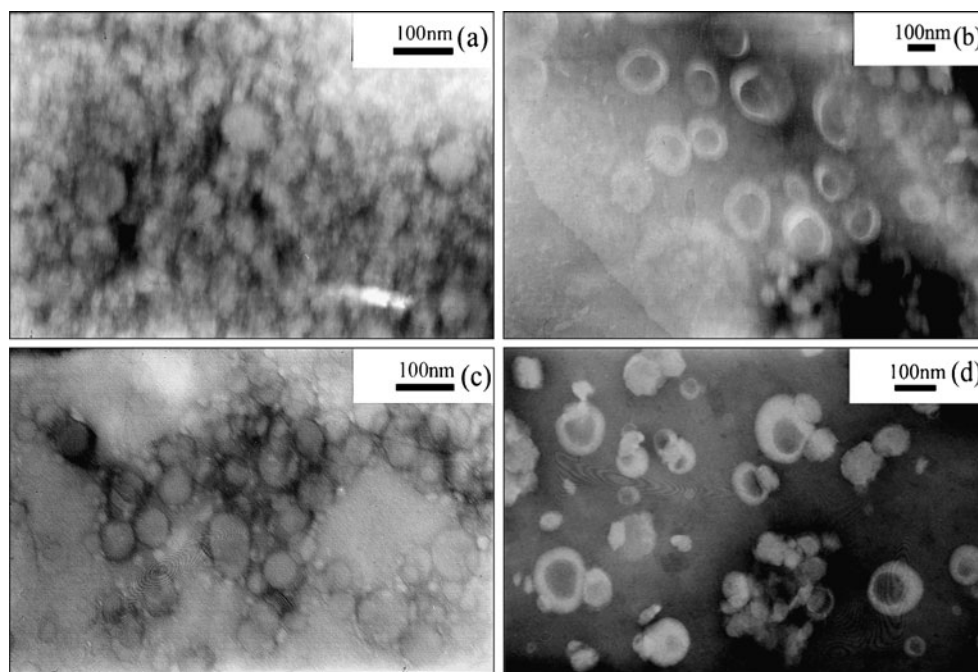


Fig. 7 Schematic illustration for the vesicle formation induced by layered double hydroxides. **a** Bilayer patches grow and connect to each other, and finally close to form vesicles; **b** bilayer patches curve

toward the LDHs particles, and the composites of Mg_3Al -LDHs encapsulated in the vesicles are formed

Fig. 8 Negative-staining TEM images of **a** LDH–SDS mixture, **b** mixed system of LDH–SDS mixture and DTAB solution, **c** LDH–DTAB mixture, and **d** mixed system of LDH–DTAB mixture and SDS solution



the LDH sol. Then, the SDS solution was added to the mixture in the next step. All the samples were equilibrated in a thermostatic bath at 25 °C for 24 h as before. The final composition of the second series is the same with the first one. It was found that the DTAB–LDH mixture was stable and only LDH particles were observed under NS-TEM observation (Fig. 8c). Nevertheless, vesicles appeared as soon as the SDS solution was added (Fig. 8d). The time-dependent curves of absorbance at 500 nm of the mixed systems were measured to examine the change of microstructures in the systems (Fig. 9). As to be expected, the absorbance values of Mg_3Al -LDH sol and the SDS/DTAB solution were kept almost constant during the studied time interval (Fig. 9 D, E). After mixing of Mg_3Al -LDH sol and

SDS/DTAB solution, the absorbance of the primal mixed system increased gradually in the initial 5 h and then reached a plateau (Fig. 9 B). In the case of the first series (Fig. 9 A), the absorbance of LDHs/SDS mixed system was much higher than that of the primal mixed system, which arises from the formation of the aggregation. After adding of the DTAB solution, the absorbance of the system decreased. However, the final value of the absorbance was also higher than that of the primal mixed system in the studied time interval. This means that aggregations and vesicles coexist in the system. That is to say, only partial aggregations could be transferred to vesicles. In the case of the second series (Fig. 9 C), the absorbance of the LDHs/DTAB mixed system was almost constant in the initial 24 h. After the SDS solution was added, the absorbance increased and finally approached to that of the primal mixed system. This means that the microstructures obtained with the second series method are the same as those of the primal mixed system.

To explain the results above, we try to analyze the processes of the vesicle formation. On one hand, in the mixture of cationic DTAB and LDH particles, DTAB micelles or molecules are adsorbed on the LDH surface. After adding SDS, the SDS micelles or molecules are more easily adsorbed on the LDH surface to form a compound layer of SDS and DTAB and then form vesicles. On the other hand, in the mixture of SDS and LDH particles, the anionic SDS micelles or molecules adsorbed on the LDH surface; furthermore, the intense electronic attraction results in the flocculation of particles. After adding cationic DTAB, the DTAB micelles or molecules are difficult to be adsorbed on the LDH surface, and only a few amounts

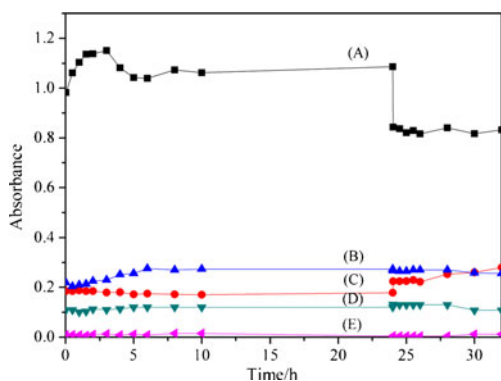


Fig. 9 Time-dependent changes of absorbance at 500 nm of various systems. **A** First series, LDH–SDS mixture and, after 24 h, the DTAB solution was added. **B** The primal mixed system of LDHs/SDS/DTAB solution; **C** in the second series, the LDH–DTAB mixture and, after 24 h, the SDS solution was added; **D** 1.25 g/L Mg_3Al -LDH sol; **E** SDS/DTAB solution (1 wt.%)

of DTAB micelles or molecules adsorb onto the LDHs surface; thus, only partial aggregations can be transferred into vesicles. The above discussion shows that the formation of the compound layer of SDS and DTAB on the LDH surface plays a key role on vesicle formation.

Conclusions

Structurally positively charged LDH nanoparticles can induce the formation of vesicles in a mixed micelle solution of an anionic surfactant (SDS) and a cationic surfactant (DTAB) at fixed ratios. A possible mechanism of LDH-induced vesicle formation is that the positively charged LDH surface attracts negatively charged micelles or free amphiphilic molecules, facilitating their aggregation into bilayer patches. Moreover, the bilayer patches connect to each other and then finally close to form vesicles. An adsorbed compound layer of SDS and DTAB micelles or molecules on the LDH surface plays a key role in the formation of vesicles. We anticipate that this work will make some advances in the field of clay nanoparticles inducing self-assembly transitions and the interactions between layered double hydroxides and surfactants. The composites of vesicle-encapsulated LDH particles might provide a new drug delivery system with controlled release properties.

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