A study on organized assemblies in the sodium alkylcarboxylate/ fatty alcohol/water systems

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The phase behavior and evolution of self-organized assembling structures in the sodium alkylcarboxylate/fatty alcohol systems were investigated by TEM. With increasing concentration of fatty alcohol, the micelles transform into lamellar L_α phase, sponge L_3 phase, multilamellar vesicle, and transform back to lamellar L_α phase. At higher alcohol concentration, a stable two aqueous phase coexisting region has been observed in this kind of systems after aged two months. Unilamellar vesicles were found both in two separated phases but the vesicle density of the upper phase is much higher than that of the bottom phase.

Keyword   Self-organized assembly, micelle-vesicle transformation, two aqueous phase coexistence

Introduction

     Amphiphiles in solution form a wide range of self-assembling structures, such as the micelle L_1, lamellar phase L_α, the vesicle L_4 and the sponge L_3, which have been widely used as model membranes of biomembrane and microreactors in recent years.[1-3] It is well known that the structure of organized assemblies is directly related to the function or application of the system. Therefore, it is interesting from the viewpoint of fundamental research and application to construct self-assembly system possessing a desired structure and morphology. In some cases, pH variation and addition of cosurfactant seemed to be an effective method to the transformation of organized assemblies in solution.[4-7] However, the answer is not unique even between the similar systems such as sodium dodecyl sulfate(SDS)/octanol/brine system and

SDS/octanol/water system.[8,9] Thus more efforts are needed to explore the methods for controlling the formation and transformation of various assemblies in aqueous solutions. In our previous report, the influences of pH and salt on the microstructure formed in alkylammonium chloride systems were investigated.[10] In this paper, fatty alcohol as cosurfactant was added to the sodium alkylcarboxylate system to adjust various organized assemblies formation and transformation. In particular the evolution of the self-assemblies structures including micelle, sponge L_3, multilamellar vesicle and lamellar phase was shown.

Experimental

Material

     Sodium alkylcarboxylates ($C_nH_{2n+1}COONa$, $n = 9, 11$) were prepared by neutralizing the corresponding carboxylic acid ($C_nH_{2n+1}COOH$) with NaOH in ethanol, then the solvent was removed and $C_nH_{2n+1}COONa$ was dried in vacuum. $C_9H_{19}COOH$ was doubly distilled and $C_{11}H_{23}COOH$ was recrystallized five times from ethanol-water mixture (mp 43—44℃). Fatty alcohols (n-octanol, n-decanol) were purchased from Beijing Chemical Co., A.R. Grade. Water was deionized water treated with $KMnO_4$ and distilled.

Methods

     The pH of the solutions studied was adjusted to 13

by using NaOH in order to prevent the hydrolysis of sodium laurate. Samples for transmission electron microscopy (TEM) observation (JEM-100CXII) were prepared by negatively staining method with 2% uranyl acetate solution or freeze-fracture method as described in Ref. 11 using a Hitachi Hus-5GB device. The experimental temperature was kept at about 30℃ and the mixing CS/S ratio is the molar ratio of fatty alcohol/surfactant.

Results and discussion

Organized assembly formation in decanol/sodium laurate system was investigated. The concentration of sodium laurate was fixed at 0.04 mol/L. According to the TEM and light scattering results, micelles are the main form of organized assemblies in this case (pH = 13, without decanol addition). However, with decanol addition, various types of organized assemblies gradually appeared by TEM observation. The first kind of organized assemblies is lamellar phase. Fig. 1 shows a TEM picture from a sample at decanol/sodium laurate (CS/S) molar ratio = 0.033 and a typical texture for a lamellar phase—the stacks of parallel bilayers was shown. As the concentration of decanol increases, the structure of the assembly is completely different. The sponge L_3 phase which consists of a multiconnected but self-avoiding folded bilayer[12,13] is clearly observed at CS/S = 0.066 (Fig. 2).

Fig. 1 Negative staining micrograph of decanol/sodium laurate (CS/S = 0.033) system, the lamellar L_α structure (enlarged by 180000 times).
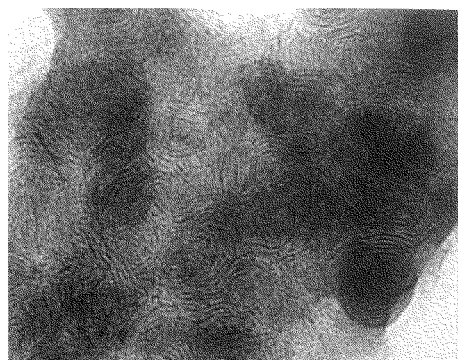

Fig. 2 Negative staining micrograph of decanol/sodium laurate (CS/S = 0.066) system, the sponge L_3 structure (enlarged by 240000 times).

It is worthy to note that the sponge L_3 structure gradually transforms into multilamellar vesicles with the further increase of concentration of decanol. Fig. 3a shows the break-up of the multiconnected bilayers (CS/S = 0.131). However, the sponge L_3 structures still exist at this stage (see Fig. 3b). When the CS/S ratio increases to 0.262, the formation of multilamellar vesicle is clearly observed (see Fig. 4) although some multilamellar vesicles are not so regular. This may be attributed to the result of the transition structures between the sponge phase and monodispersed multilamellar vesicle (Fig. 5). Further increasing the decanol concentration, the multilamellar vesicles break up and transform into stacks of bilayers (Fig. 6). If decanol/sodium laurate is higher than 0.6, the solution become multiphase region and some precipitations could be observed. Thus the evolution of the assembly structures in decanol/sodium laurate in homogeneous solution is: L_1-L_α-L_3-L_4-L_α.

The influence of decanol addition on the evolution of organized assemblies may be explained by curvature variation of the oriented molecular layer. According to the geometry rule proposed by Isrealachivili,[14] molecular packing parameter P can be used to describe the organized assembly formation in amphiphilic solution. P was defined as: $P = V_c/l_c a_0$, where V_c and l_c are the volume and length of the stretched hydrocarbon chain and a_0 is the appropriate area for the hydrophilic group. At pH 13, hydrolysis was almost completely reduced and $C_{11}H_{23}COONa$ was the dominant amphiphilic species in sodium laurate system. Thus micelles with high curvature were the main form of assemblies. With the increase of decanol, the electric repellence was reduced and the average molecular area was smaller. Consequently the
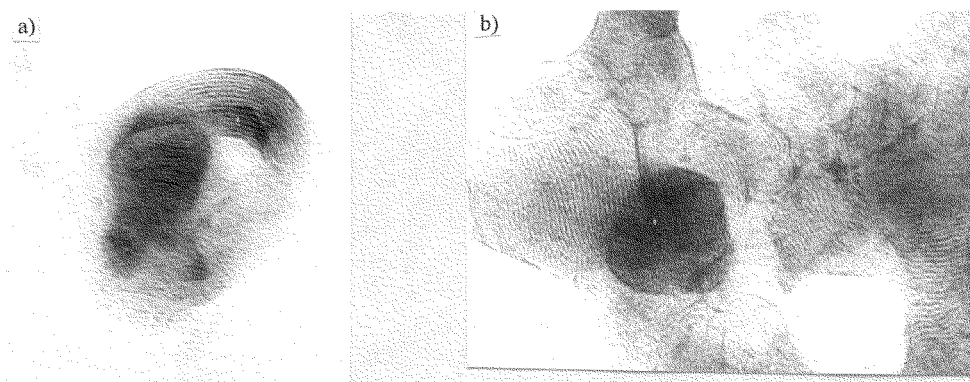
Fig. 3 Negative staining micrograph of decanol/sodium laurate (CS/S = 0.131) system: (a) the break up of the sponge L_3 structure, (b) the coexisting sponge L_3 structure (enlarged by 180000 times).
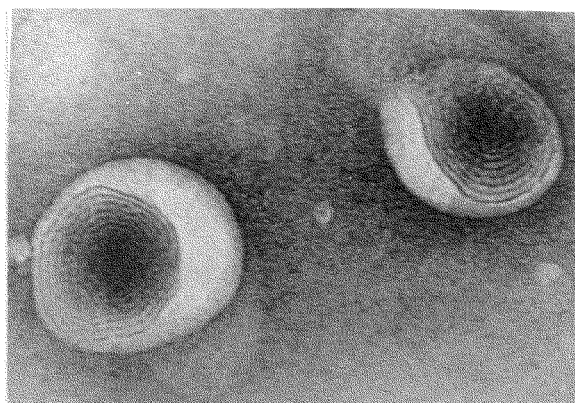

Fig. 4 Negative staining micrograph of decanol/sodium laurate (CS/S = 0.262) system, the L_4 multilamellar vesicle (enlarged by 240000 times).
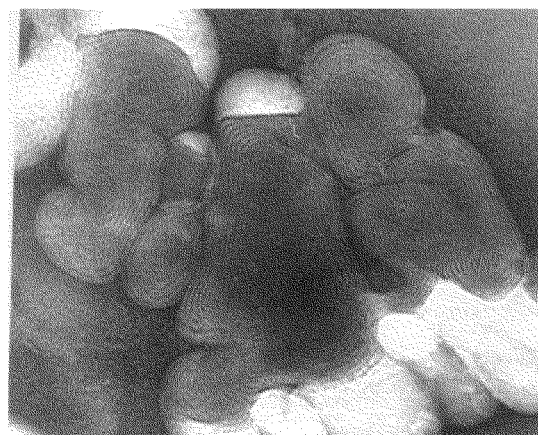

Fig. 5 Negative staining micrograph of decanol/sodium laurate (CS/S = 0.262) system, the coexisting unregular multilamellar structure (enlarged by 240000 times).
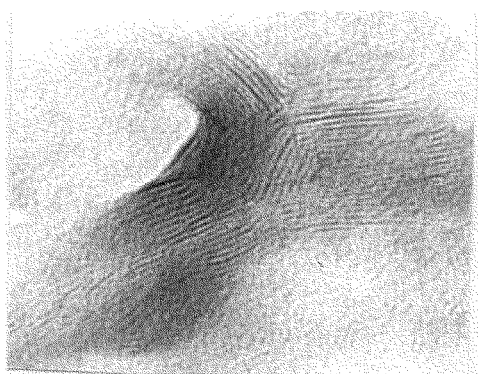

Fig. 6 Negative staining micrograph of decanol/sodium laurate (CS/S = 0.524) system, the lamellar L_α structure (enlarged by 240000 times).

micelles grew and changed to lamellar structure. Bilayer lamellae further aggregated to form sponge L_3 structure and then transformed to the multilamellar vesicles. They stacked parallel to each other in the middle part and were curved and closed at the edge or end of multilamellar vesicles. Similar results were also observed in alkylammonium chloride systems with hydrocarbon chain length of 10 or 12 while the pH varied from 0.5 to 8.[10] The difference was just that hydrolysis is controlled at lower pH and alkylamine replaces the fatty alcohol to adjust the assembly structures in alkylammonium chloride systems. With the more decanol added the curvature of the oriented molecular layer further changed since the hydrophobic effect may be reduced by the ratio of sodium laurate/decanol decrease, hence the lamellar phase become the main form of organized assemblies in the system. This fact is similar to the Dufourc's result which

demonstrates that the multilamellar vesicles and stacks of flat parallel bilayers exist within the region of lamella phase in the water/SDS/octanol system by use of NMR and TEM.[9]

The influences of the hydrocarbon chain length in surfactants and fatty acids were also studied. TEM observation showed that in the homogeneous phase area no vesicle was formed after octanol was added to the sodium laurete system (pH = 13 and 0.04 mol/L surfactant concentration). It demonstrated that fatty acid of shorter hydrocarbon chain has lower ability to adjust the structure transformation of organized assembly in this kind of systems. For the aqueous solution of sodium decanoate (pH = 13 and 0.04 mol/L surfactant concentration), the addition of fatty alcohol seemed to have no obvious effect to the formation of the new kind of organized assemblies even dodecanol was used to replace decanol. This result is different from that in alkylammonium chloride systems, in which surfactants of the hydrocarbon chain length of 10 or 12 carbons can form vesicle after the pH varied from 0.5 to 8.[10] This difference may be attributed to that $C_9H_{19}COONa$ is of just 9 carbons in the hydrocarbon chain and consequently with weaker organized assembling capability due to the hydrophobic effect.

While the fatty alcohol concentration is very high (usually higher than the surfactant concentration), the mixed solutions of fatty alcohol/sodium alkylcarboxylate become turbid. It is interesting to note that a steady two aqueous phase coexisting region could be reached in some systems after aged two months later at room temperature. The two aqueous phase coexisting region was observed in the following systems: dodecanol/sodium laurate (CS/S is 1.11, 1.67, 3.34, respectively. The surfactant concentration is fixed at 0.04 mol/L.); decanol/sodium laurate (CS/S is 1.32, 1.98, 2.64, re-

spectively. The surfactant concentration is fixed at 0.04 mol/L.); octanol/sodium laurate (CS/S = 2.38, the surfactant concentration is 0.04 mol/L); decanol/sodium decanoate (CS/S = 0.79, the surfactant concentration is 0.2 mol/L).

The interface between the two phases is very clear and the volume ratio of the two phases is about 1 : 1. Usually the upper phase is turbid and the bottom phase is clear except for the octanol/sodium laurate system, in which the upper phase is clear and the bottom phase is turbid. There is no precipitation observed in these turbid phases. Since the volume of the turbid phase is much larger than that of the pure alcohol ever added, the reason of two aqueous phase formation can not be attributed to the unsolved alcohol floating on the solution surface.

In order to study the microstructure of the two separated phases, two systems were selected as the model system: decanol/sodium laurate (CS/S = 1.32) and decanol/sodium decanoate (CS/S = 0.79). The TEM observations by freeze-fracture technique clearly show the difference of the assembling structures in the upper and bottom phases. For the decanol/sodium laurate system, the upper phase consists of densely packed unilamellar vesicles (Fig. 7a) and stacks of bilayers (Fig. 7b), while the bottom phase just consists of sparsely unilamellar vesicles. For the decanol/sodium decanoate system, the upper phase also consists of densely packed unilamellar vesicles (Fig. 8a) and the sparsely unilamellar vesicles in the bottom phase (Fig. 8b). It is the density difference of densely packed unilamellar vesicles and sparsely unilamellar vesicles that produced the phenomenon that the two aqueous phases coexist in the fatty alcohol/sodium carboxylate. This fact is very similar to the situation observed in the cationic-anionic surfactant systems.[15]
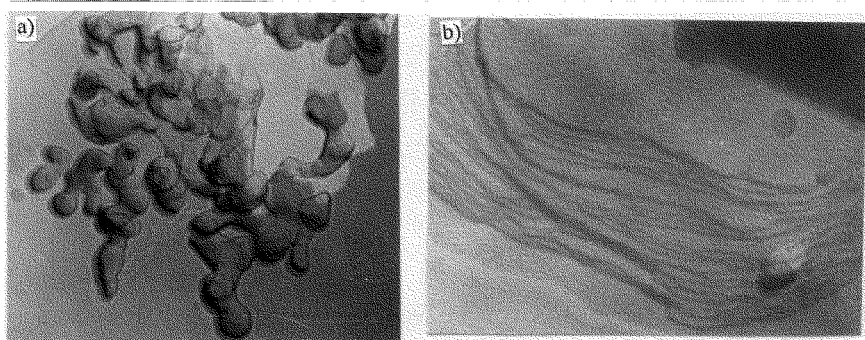

Fig. 7   Freeze fracture micrograph of the upper phase of the decanol/sodium laurate (CS/S = 1.32) system: (a) the densely packed vesicles (enlarged by 81000 times), (b) the stacks of parallel bilayers (enlarged by 120000 times).
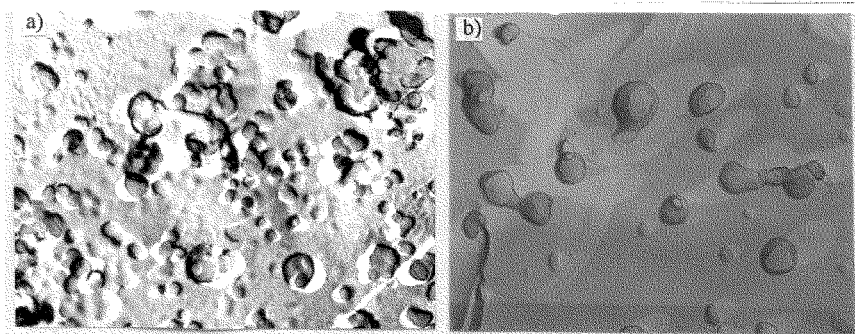
Fig. 8 Freeze fracture micrograph of the decanol/sodium decanate (CS/S = 0.79) system: (a) the densely packed vesicles formed in the upper phase (enlarged by 81000 times) (b) the sparsely dispersed vesicles formed in the bottom phase (enlarged by 33000 times).

Conclusion

The sodium laurate and decanol molecules self-assemble into bilayer aggregates with a morphology that strongly depends on the decanol concentration. The self-assembling structure evolution of L_1—L_α—L_3—L_4—L_α has been identified. The influences of the hydrocarbon chain length in surfactants and fatty acids were also studied. At high alcohol concentration, a steady two-phase coexisting region was observed in some fatty alcohol/sodium alkylcarboxylate systems. The densely packed unilamellar vesicles and sparsely unilamellar vesicles are the main forms of organized assemblies in the separated upper phase and bottom phase, which produce the two aqueous phase coexisting phenomenon as that in cationic-anionic surfactant mixed systems.

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