

A Study on Organized Assemblies in the Aqueous Systems of Alkylammonium Chlorides

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Various types of organized assemblies, including micelle, planar multi-bilayer, bent multi-bilayer, fingerprint-like multi-bilayer, and multilamellar vesicles, were found in the aqueous system prepared by only one simple surfactant—alkylammonium chloride with a hydrocarbon chain length of 10 or 12. Electron microscopic images of the assemblies are provided. The properties of the system were characterized by DSC, fluorescence, and absorption probing techniques. It was found that the structure and shape of molecular assemblies in this system can be adjusted by very simple physico-chemical measures, such as pH adjustment and alcohol or salt addition. The mechanisms of formation and transformation of various molecular assemblies were discussed based on the mixing effect of the cationic amphiphile and the nonionic amphiphile which is only a hydrolysis product of the former. © 1999 Academic Press

Key Words: alkylammonium salt; organized assembly; micelle; multi-bilayer; multi-lamellar vesicles.

Organized assemblies from surfactants, such as micelles, vesicles and liquid crystals, have been widely used as model membranes of biomembranes, as capsules for agents in assays and drug delivery (1), and as microreactors and templates for synthesizing fine particles with particular sizes and shapes (2, 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 and important in science and technology to construct a self-assembly system possessing a desired structure and morphology. Thus, the self-assemblies in the aqueous systems of primary alkylamines were investigated in this work.

Primary alkylamine and alkylammonium chlorides are common compounds and have been used as collectors in flotation (4). Their properties have been studied rather fully (4–7). In recent years, they were used as one of the additives in the preparation of some functional materials, such as aluminophosphate and tin sulfide, with a mesostructure of lamellae (8–10), coaxial cylindrical bilayers (10), or honeycomb-like patterns (11). It is well known that lamellae, vesicles, and other mesostructures were usually formed in the system of amphiphiles with complicated structure, e.g., double-chained amphi-

philes (1, 12–14). The formation of vesicles from alkylamine was even considered to be theoretically unexpected (9, 11). Thus, the role of alkylamine in the formation of functional materials with the special mesostructures mentioned above is still vague. Besides, alkylamine has a much simpler structure than the amphiphiles used to form mesostructures, and it is cheaper and easier to obtain. It has been thought that providing the various structures of organized assemblies in such a surfactant system would be an attractive project. However, so far there has not been systematical report on the formation and properties of organized assemblies from alkylamine and its salt.

In the present work, microstructures formed in alkylammonium systems under various physico-chemical conditions were investigated. The influences of alkyl alcohol, salt, acid, alkali, and the length of hydrophobic chain of alkylammonium chloride on the organized assemblies were studied. The mechanism of structural variation of assemblies was proposed, and the measures for controlling the formation of various assemblies were explored.

EXPERIMENTAL

Materials

Primary alkylammonium chlorides (C_mNH_3Cl , $m = 8, 10, 12$) were synthesized from alkylamine by reaction with hydrochloric acid. Alkylamines were fractionated by vacuum distillation before use. The products of alkylammonium chlorides were recrystallized three times from a mixed solvent of ethanol–ethyl ether and three times from ethanol. Their purities were proved by the absence of a minimum in the surface tension vs concentration curve.

The hydrochloric acid, sodium hydroxide, and sodium chloride were products of Beijing Chemical Reagents Factory, China, A.R. degree, and used as received.

Water was redistilled from potassium permanganate-deionized water solution.

Methods

Solution preparation. The systems investigated were the aqueous solutions of C_mNH_3Cl ($m = 8, 10$ and 12) at various

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pH. The pH of the liquid phase was adjusted by addition of sodium hydroxide or chloric acid solution and was monitored with a pH meter (type PHS-2, Shanghai 2nd Analytical Instruments Factory, China). In consideration of the solubility of alkylammonium chlorides, particularly that of $C_{12}H_{25}NH_3Cl$, the experimental temperature was kept at about 30°C.

Observation by transmission electron microscopy (TEM). Samples were prepared by the negative staining method with 2% uranyl acetate solution (13) or by the freeze-fracture method as described in Ref. (14), using a Hitachi HUS-5GB device. They were then observed on an electron microscope (JEM-100CXII).

Differential scanning calorimetry (DSC). DSC was performed on Universal V1.10B TA instruments at a heating rate of 2°C/min.

Micropolarity measurement. Two probes were used in this work. (a) Pyrene was used as a fluorescence probe to measure the micropolarity of the organized assemblies. The fluorescence spectra of pyrene was recorded on a Hitachi F-4500 Fluorescence Spectrophotometer with scan speed 2400 nm/min and slit(ex/em) 5.0 nm/2.5 nm. The concentration of pyrene was 3×10^{-7} mol/L. The ratio of intensities of the first to the third vibronic peaks of the fluorescence spectrum of pyrene (I_1/I_3) was determined. This value provides an estimate of the polarity sensed by pyrene in its solubilization site (15, 16). (b) Methyl Orange (MO) was used as an absorption probe. Recently, the maximum absorption wavelength of MO in solution was found to be a function of the micropolarity of the environment that MO encountered (17). The absorption spectrum was recorded on a Shimadzu UV-250 UV-Visible Recording Spectrophotometer; each reference sample was the same as that measured, except without MO. The concentration of MO was 2.5×10^{-5} mol/L.

RESULTS AND DISCUSSION

Formation of the Organized Assemblies

Assembly formations in aqueous systems of alkylammonium chlorides were investigated. The concentrations of C_8^- , C_{10}^- , and C_{12}^- ammonium chlorides were fixed at 0.60, 0.10, and 0.05 mol/L, respectively. Each was a few times higher than its own cmc. The cmcs of C_8^- , C_{10}^- , and C_{12}^- ammonium chlorides in neutral aqueous solution at 303 K are 0.18, 0.06, and 0.015 mol/L, respectively, determined according to the inflection point in surface tension curves. These cmc values are in good coincidence with those in the literature. Aggregates of various shapes and structures, including micelle, planar multi-bilayer, bent multi-bilayer, fingerprint-like multi-bilayer, and multilamellar vesicles, were found in the aqueous system of alkyl-ammonium at various physico-chemical conditions. The results are shown in Figs. 1 and 2, where A, B, C, and D denote planar multi-bilayer, bent multi-bilayer, fingerprint-like multi-bilayer and multilamellar vesicles, respectively. It is known

that these structures of assembly have been found separately in the systems of amphiphiles with complicated molecular structures, e.g., double long-chained amphiphiles and those with a rigid group in the hydrophobic chain (1, 12–14). Particularly, it is very rare that so many types of assemblies appear in a system prepared by a very simple amphiphile and can be controlled by very simple physico-chemical measures. It should be mentioned that the formation of vesicles from alkylammonium salts was even considered to be unexpected in theory (8, 10).

The influence of pH was as follows. The solutions of C_mNH_3Cl ($m = 8, 10, \text{ and } 12$) at neutral pH (~ 5.2) were clear, but they were translucent at higher pH, the value of which varied with the hydrocarbon chain length of the amphiphile. TEM images of alkyl-ammonium chloride solutions at various pH are shown in Fig. 1. The images provided here are of the samples prepared by the negative staining method, which is similar to the counterpart obtained by the freeze-fracture method, as shown in Figs. 2a and 2b, but in more detail.

In the pH range 0.1 \sim 9.0, various microstructures were observed, and they are listed in Table 1. There are multi-bilayer (MBL) structures with different shapes (A and B in Figs. 1a, 1b, 1d, 1e), multilamellar vesicles (MLV) with 50 \sim 100 nm diameter (D in Figs. 1c, 1d, 1f), and some fingerprint-like aggregates (C in Fig. 1f). It is seen that the bilayer is the basic unit for various assemblies observed. The thickness of it may be estimated from the images. Thicknesses of about 4 nm in the $C_{12}NH_3Cl$ system and slightly less in the $C_{10}NH_3Cl$ system were found. These results are in good agreement with the length of the bimolecular layer of the amphiphiles. To our knowledge, this is the first time the fine structures of so many kinds of organized assemblies in a simple conventional surfactant system have been revealed, although these structures have been found in various systems of complex amphiphiles (12, 13) separately. For example, MBL and MLV were formed from many single-tailed amphiphiles with rigid segments and termed as disk-like structures and multiwalled vesicles, respectively, by Kunitake *et al.* (12).

From Table 1, it is obvious that MBL and MLV structures appear only when the number of carbons in the hydrophobic chain of alkylammonium is 10 or larger. This is in accordance with the results found previously in other surfactant and lipid systems (18, 19).

The microstructure varied with pH. At very low pH (< 1), MBL and a sparse amount of MLV (Fig. 1a, 1d) were observed. As pH increased to pH 2 \sim 5 in the $C_{12}NH_3Cl$ system and to pH 2 \sim 7.5 in the $C_{10}NH_3Cl$ system, no structure of bilayers or vesicles was observed. However, as pH increased further, MBL occurred again. Then, MLV appeared in large amounts and the system looked translucent. It is seen from Table 1 that the pH values at which MBL, MLV, and translucence appear decrease with the increase of chain length, i.e.,

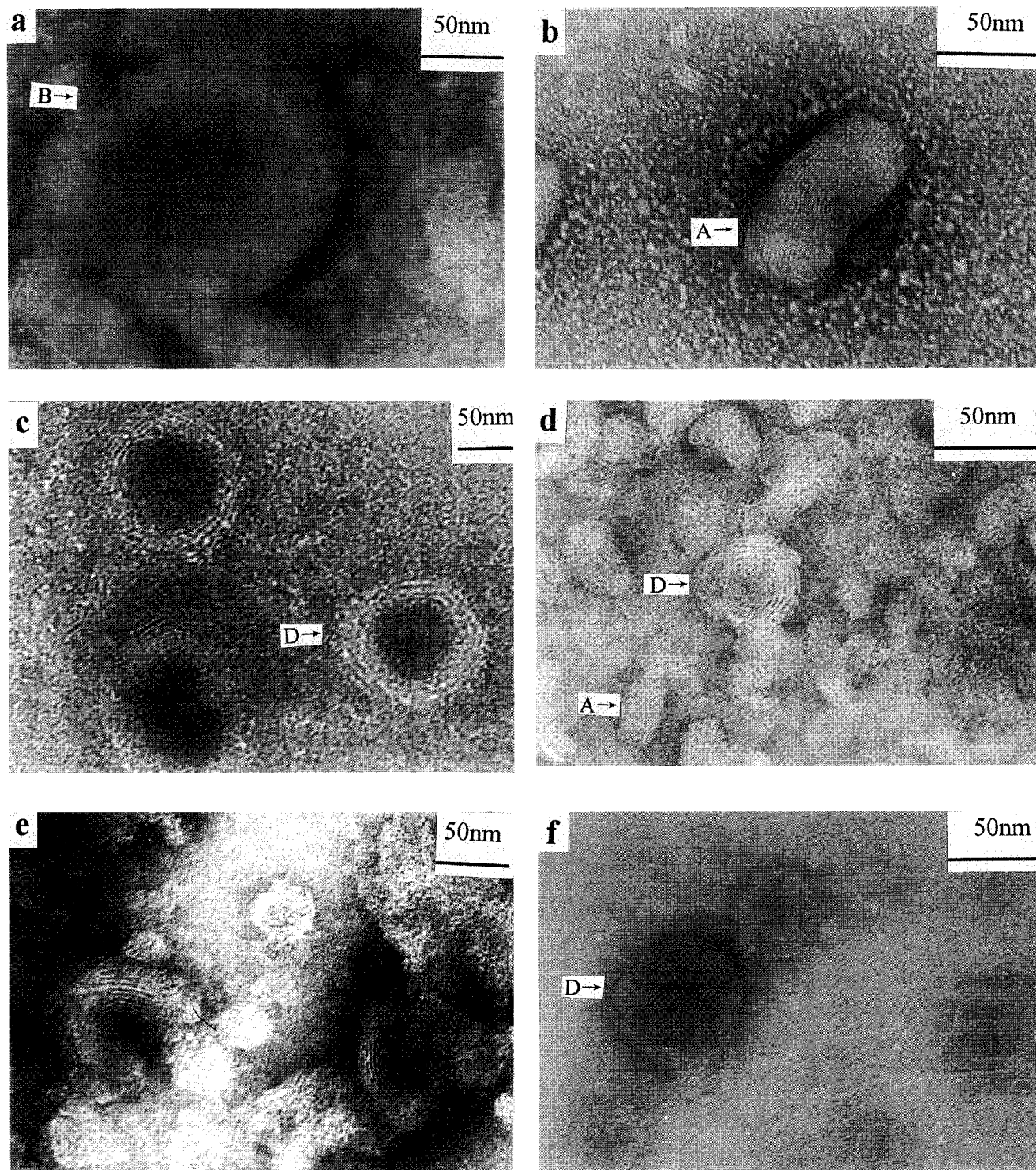


FIG. 1. Negatively stained TEM images of alkylammonium chloride systems at various pH. (a) $C_{12}NH_3Cl$, pH 0.5; (b) $C_{12}NH_3Cl$, pH 5.2; (c) $C_{12}NH_3Cl$, pH 7.1; (d) $C_{10}NH_3Cl$, $[HCl] = 1.25$ mol/L; (e) $C_{10}NH_3Cl$, pH 8.2; (f) $C_{10}NH_3Cl$, pH 8.6. A, B, C, and D represent planar multi-bilayer, bent multi-bilayer, fingerprint-like multi-bilayer, and multi-lamellar vesicles, respectively. The concentration is 0.050 mol/L in the $C_{12}NH_3Cl$ system and 0.10 mol/L in the $C_{10}NH_3Cl$ system.

approximately pH 8.0, pH 8.5, and pH 8.0 for the $C_{10}NH_3Cl$ system and pH 5.2, pH 7.1, and pH 7.3 for the $C_{12}NH_3Cl$ system.

The phenomena mentioned above show that alkylammonium salt is an interesting system in which a variety of self-assemblies, including micelles, bilayers, and vesicles, are

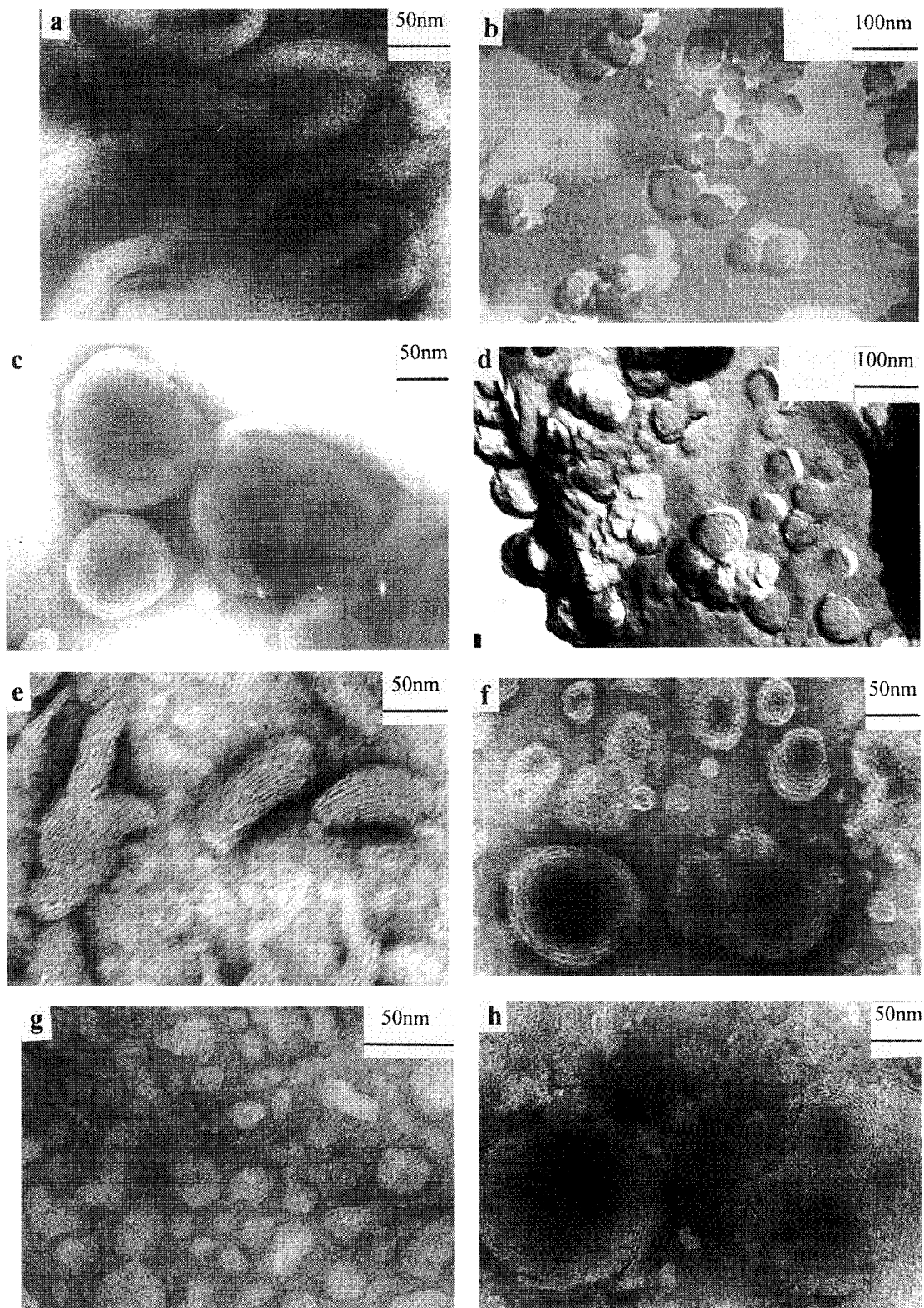


FIG. 2. Negatively stained and freeze-fractured TEM images of alkylammonium chloride systems at pH 3.0 with fatty alcohol and NaCl addition. (a) $C_{12}NH_3Cl-C_{12}OH$ (5%); (b) the same as (a), freeze-fractured TEM; (c) $C_{12}NH_3Cl-C_{12}OH$ (22%); (d) the same as (c), freeze-fractured TEM; (e) $C_{10}NH_3Cl-C_{10}OH$ (8%); (f) $C_{10}NH_3Cl-C_{10}OH$ (33%); (g) $C_{10}NH_3Cl$, $[NaCl] = 0.1$ mol/L; (h) $C_{10}NH_3Cl$, $[NaCl] = 0.2$ mol/L. The total concentrations of surfactant and alcohol were 0.050 mol/L ($m = 12$), 0.10 mol/L ($m = 10$).

TABLE 1
MBL and MLV in the Dispersion of C_mNH_3Cl
($m = 10, 12$) at Various pH

pH:	<1	2 ~ 4	5.2	7.1	7.5	8.0	8.5	9.0
C_{10}	MBL MLV	—	—	—	—	MBL,t	MBL MLV,t	—,t
C_{12}	MBL MLV	—	MBL	MBL MLV	MBL MLV,t	MBL MLV,t	MBL MLV,t	—,t

Note. (MBL) multibilayer; (MLV) multilamellar vesicles; (t) translucent solution; (—), no bilayer structure. Concentrations: 0.050 mol/L ($m = 12$), 0.10 mol/L ($m = 10$), 0.60 mol/L ($m = 8$).

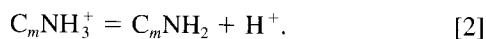
formed. Particularly, the microstructure of the system can be adjusted through the pH—a very simple measure. This specificity is important for both theory and application and is worth investigating further.

It is well known that simple single-chained ionic surfactants are micelles forming amphiphiles, and they can not form bilayer or vesicle structures, due to the relatively large area occupied by the charged hydrophilic headgroup (20). Isrealachvili (21) adopted molecular packing parameter P to describe this characteristic of the surfactant in the system. P was defined as

$$P = V_c/l_c a_0, \quad [1]$$

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. As a rule, micelles would be preferred when $P < 1/3$, while bilayers and vesicles would be preferred at $0.5 < P < 1$. It is seen, among the quantities determining the value of P , i.e., V_c , l_c , and a_0 , only a_0 has the character of varying with the physico-chemical environment of the system. Obviously, for a definite amphiphile, any factor which can make a_0 decrease must be beneficial in the transformation of the molecular assembly from micelles to vesicles. For example, neither an anionic nor a cationic surfactant with a single tail can form vesicles in aqueous solution, but their mixture can (18).

Alkylammonium chloride is a kind of ionic surfactant with a single tail; hence its a_0 is quite large and should form micelles in a solution of concentration higher than its cmc. In fact, this is true only in the solution of lower pH, because the alkylammonium ion undergoes hydrolysis in water to form alkylamine:



The pK_a is ~ 10.63 (5); thus

$$[C_mNH_2]/[C_mNH_3^+] = Ka/[H^+]. \quad [3]$$

Here $[C_mNH_2]$, $[C_mNH_3^+]$, and $[H^+]$ are the concentration of C_mNH_2 , $C_mNH_3^+$, and H^+ , respectively. Obviously, the lower the pH, the more alkylammonium ions appear. At pH 1 ~ 9, the ratios of alkylamine to alkylammonium ions in solution ($[C_mNH_2]/[C_mNH_3^+]$) were calculated to be $2.3 \times 10^{-10} \sim 2.3 \times 10^{-2}$. That is to say, in this range of pH, $[C_mNH_2]$ is very low and cationic $C_mNH_3^+$ dominated in the system. In our observations, at an acidic solution of pH 2 ~ 5 for $C_{12}H_{25}NH_3Cl$ and pH 2 ~ 7.5 for $C_{10}H_{21}NH_3Cl$, the organized assemblies were mainly in the form of micelles which could not be observed by TEM, just as in the case of the micellar solution of alkyltrimethylammonium salt (12). Micelle formation in the solution of $C_{12}H_{25}NH_3Cl$ at pH 2 ~ 6 was also reported in the literature (5, 22).

It is worth noting that although the equilibrium concentration of alkylamine is very low, and even can be neglected, its effect on aggregation is stronger than expected based on its concentration in the bulk phase. This is due to the much stronger surface activity of neutral alkylamine compared with that of the corresponding cation, as well as to the possibility of hydrogen bond formation between the headgroups of $C_mNH_3^+$ and C_mNH_2 in the oriented molecular layer of the organized assemblies. These effects decrease the energy level of the organized molecular layer and make it stable. Actually, the system is a mixed surfactants system and not a simple one, although only one surfactant was used to prepare the system. Hence mixed assemblies of alkylamine and alkylammonium chloride resulted. With the increase of pH, the amount of nonionic C_mNH_2 increased; meanwhile cationic $C_mNH_3^+$ decreased. The nonionic amphiphiles participate in the oriented molecular layer, reducing the electrostatic repulsion among ionic surfactants and enhancing the density of amphiphiles in the oriented molecular layer. Accordingly, the average a_0 of the mixed system goes down, which is beneficial to lamella or vesicle formation. Therefore, it is understandable that the alkylammonium chlorides form bilayers and vesicles in the system at higher pH. This is similar to the situation in the aqueous system of carboxylate (19), except that the carboxylate is an anionic amphiphile and lower pH would be beneficial for its vesicle formation.

TABLE 2
MBL and MLV in the C_mNH_3Cl System ($m = 10, 12$) at pH 3.0
with Various Amounts of Alcohol and Salt

	C_mOH (%)						NaCl (mol/L)	
	0	5	8	10	20	70	0.1	0.2
$m = 10$	—	—	MBL	MBL,t	MBL MLV,t	MBL MLV,t	MBL	MBL MLV
$m = 12$	—	MBL	MBL MLV,t	MBL MLV,t	MBL MLV,t	MBL MLV,t	MBL	MBL MLV

Note. See note to Table 1.

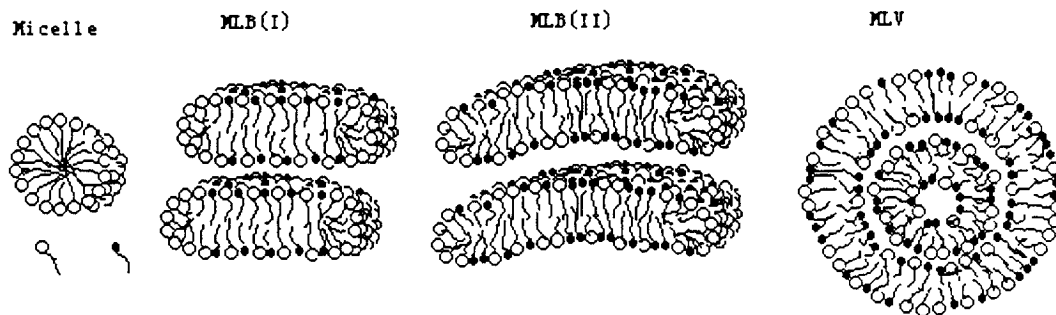


FIG. 3. Schematic illustration of the organized assembly variation with the increase of nonionic C_mNH_2 or C_mOH : (open circles) C_mNH_3Cl , (filled circles) C_mNH_2 or C_mOH .

According to the above analysis, the fact that vesicles and bilayers were not observed in the system at pH 3.0 would be attributed to the lack of nonionic amphiphile, the alkylamine. If this is true, addition of nonionic amphiphile should induce bilayer or vesicle formation. It was considered that since alkyl alcohol has a molecular structure similar to that of alkylamine, a similar effect on the formation of MBL or MLV would be brought about by alkyl alcohol addition. In addition, alcohol has the advantage that its concentration in the aqueous system of alkylammonium salt can be adjusted independently, regardless of the pH of the system. Therefore, alkyl alcohol C_mOH was added into the aqueous systems of C_mNH_3Cl at pH 3.0 and the systems were observed by TEM. The experimental results are shown in Fig. 2, and the microstructure change with the addition of alcohol is shown in Table 2. It is seen that the ratios of alkyl alcohol to total amphiphiles at which MBL and MLV formed are about 5% (MBL) and 8% (MLV) in the $C_{12}NH_3Cl$ system and 8% (MBL) and 20% (MLV) in the $C_{10}NH_3Cl$ system. The fundamental structural units of MBL and MLV in these systems are also bilayers with a thickness of about 4 nm. No bilayer structure was found in the C_8NH_3Cl – C_8OH system, which is similar to the case of pH adjustment and should be attributed to too weak a hydrophobic interaction of the amphiphiles. These results support our inference very well.

It is strange that the MBL and MLV structures also appeared in both $C_{12}NH_3Cl$ and $C_{10}NH_3Cl$ systems at pH < 1. According to the hydrolysis equilibrium, the amount of nonionic alkylamine in these cases should be much less than that in the same systems at pH 2 ~ 4. Obviously, there should be not enough alkylamine for bilayer and vesicle formation. However, it is well known that ionic strength has a significant effect on the self-assembly of ionic surfactants (23) through counterion binding. The addition of an inorganic salt of a common counterion always strengthens the counterion binding to the assemblies and decreases the repulsion between the amphiphiles in the oriented molecular layer, which results in a smaller a_0 , and hence a stronger tendency of the assembly to transform from micelles to bilayers or vesicles. This would be right for the case occurring in the C_mNH_3Cl system at pH < 1, since when the pH is less than 1, a large amount of HCl exists in the system,

making the ionic strength quite high. The headgroup area of alkylammonium chlorides was obviously lowered by the counterion binding at high ionic strength. This is beneficial for bilayer and vesicle formation, similar to the effect of salt on ionic surfactant (23). To support this explanation, the effect of sodium chloride was investigated. Addition of sodium chloride into both $C_{10}NH_3Cl$ and $C_{12}NH_3Cl$ systems at pH 3.0, where no vesicles or bilayers could be found, did induce MBL and MLV formation. The MBL appeared at a NaCl concentration of 0.1 mol/L and MLV at 0.2 mol/L. TEM images of these solutions are shown in Figs. 2g and 2h. The microstructures of these systems are listed in Table 2.

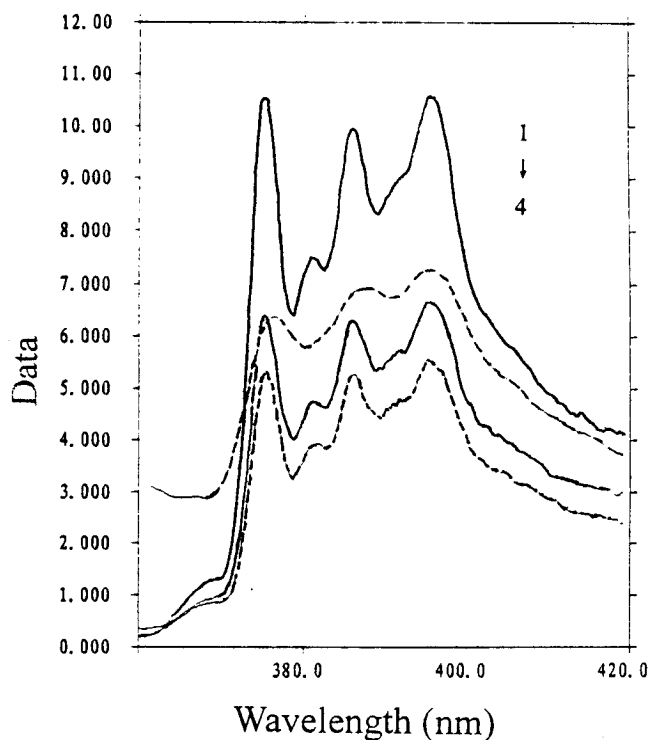


FIG. 4. The fluorescence spectra of pyrene in the $C_{10}NH_3Cl$ system at various pH: (1) pH 3.0, (2) pH 8.9, (3) pH 7.9, (4) pH 8.2.

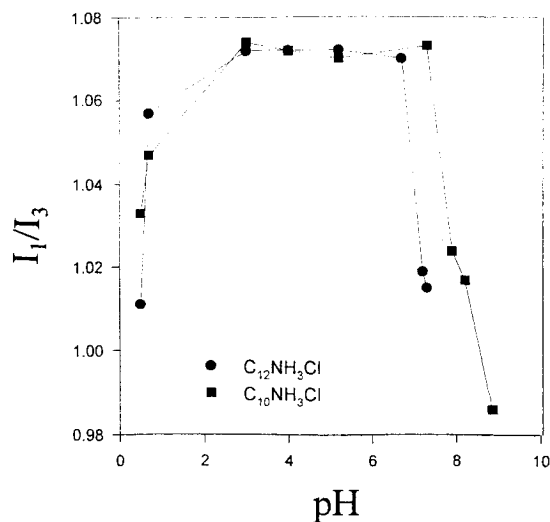


FIG. 5. I_1/I_3 of fluorescence spectra as a function of pH in the C_mNH_3Cl system ($m = 10, 12$).

It is worth noting that in addition to the methods of pH adjustment and alkyl alcohol addition, sodium chloride addition is another simple method to get the desired organized assemblies in an aqueous system of C_mNH_3Cl .

Oliver *et al.* (8) and Sayari *et al.* (9, 10) showed similar results. They prepared lamellar aluminium phosphorate using alkylamine as an additive. A lamellar structure (similar to the MBL structure here) and a coaxial cylindrical bilayer (similar to MLV in Fig. 1d (D) and Fig. 2h) were obtained from a mixture of alkylamine and phosphoric acid. It should be noticed that under their experimental conditions, alkylamine was almost totally transformed into alkylammonium salt.

Detailed examination of the microstructure shown in Figs. 1 and 2 and Tables 1 and 2 provided more information. With the increase of pH and alcohol addition, the structure and shape of self-assemblies in the system at pH 3.0 change, from micelle to planar multi-bilayer (MBL(I)) to bent multi-bilayer (MBL(II)) to multilamellar vesicles (MLV), as shown in Fig. 3.

The influences of various factors on the transformation of micelles to bilayers and vesicles can be explained by the curvature variation of the oriented molecular layer. Micelles with high curvature were the main form of assemblies at pH 3.0, because in this case $C_mNH_3^+$ was the dominant amphiphilic species, which exhibited a large value of a_0 due to the electric repulsion between the headgroups. With the increase of pH, the amount of nonionic species C_mNH_2 increases while that of $C_mNH_3^+$ decreases, resulting in weaker electric repulsion and hence smaller average molecular area a_0 . Consequently, the micelles grew and changed to lamellar structure. Bilayer lamellae further aggregated to form MBL. They stacked parallel to each other in the middle part and were curved and closed at the edge or end of MBL. Obviously, the curvature of the oriented molecular layer would be different at the two parts of the same aggregate. To satisfy the curvature requirement at

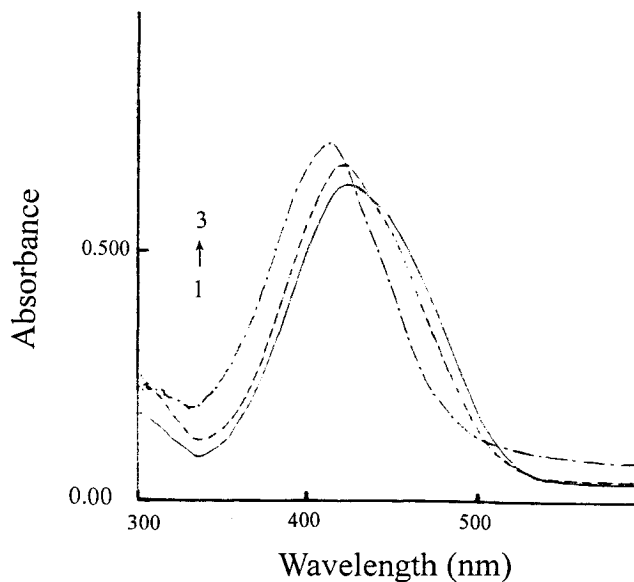


FIG. 6. The absorption spectra of MO in the $C_{10}NH_3Cl$ system: (1) pH 5.2, (2) pH 7.9, (c) pH 8.9.

each part, more ionic amphiphiles would exist in the curved part than in the planar part. As for MBL (I) and MBL (II) both are aggregates of bilayers, except MBL (I) is smaller and more rigid while MBL (II) is larger and more flexible. The radical difference between MBL (I) and MBL (II) can be thought of as a difference in average curvature. In other words, they have different ratios of the planar part to the curved part. At lower pH, lower concentration of alkyl alcohol, or lower ionic strength, the ratio of alkylammonium cations to nonionic amphiphiles is larger; hence the average a_0 and the average curvature of the oriented molecular layer are larger too. As a

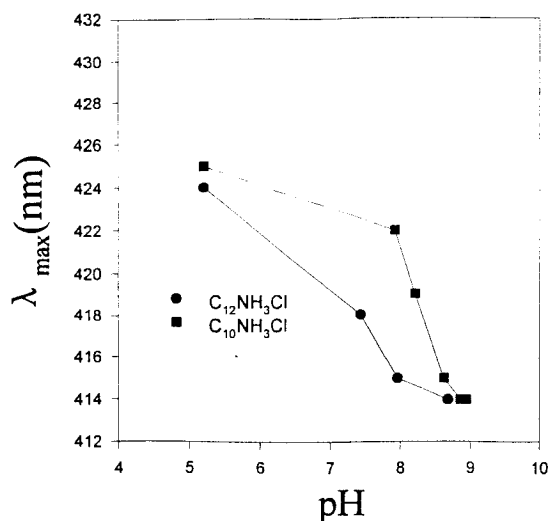


FIG. 7. The λ_{max} in MO absorption spectra as a function of pH in the C_mNH_3Cl system ($m = 10, 12$).

TABLE 3
The Micropolarity in the $C_{12}NH_3Cl$ System at pH 3.0
as a Function of Alkyl Alcohol and NaCl

	$C_{12}OH$ (%)					[NaCl] (mol/L)	
	0	5	10	15	50	0.1	0.2
I_1/I_3	1.072	1.011	0.993	0.956	0.956	1.020	1.012
λ_{max} (nm)	424	422		414	414	420	418

result, the molecular assemblies have a larger area of high curvature and MBL (I) will be preferred. At higher pH, higher concentration of alkyl alcohol, or higher ionic strength, the amount of nonionic amphiphiles increases, resulting in a larger planar part and a smaller curved part in the assemblies. Thus, MBL (II) will be preferred. As MBL (II) becomes larger and larger, it will be flexible enough for the ends of the same MBL (II) to combine with each other to take advantage of the reducing area of higher curvature. Then, closed bilayers or MLV forms. In other words, a system containing a lesser amount of the cation is suitable for MLV formation. This is right in the case of the alkylammonium chloride systems at higher pH or alcohol concentration.

It can be seen from Figs. 1 and 2 and Tables 1 and 2 that the pH value and alcohol (C_mOH) quantity required for the formation of MBL and MLV, and for the appearance of translucence in the C_mNH_3Cl system, increase with the decrease of the hydrocarbon chain length of alkylamine chlorides and alcohols. This is similar to findings revealed by Hargreaves and others for a system of fatty acids (19). In their case, vesicle formation appeared at higher pH with the increase of the hydrocarbon chain length of fatty acids, which was attributed to a higher packing density of amphiphiles also. They explained that the higher packing density of amphiphilic ions created a higher surface charge density, and thus a greater shift in the apparent pK_a occurred for the assembled fatty acids. In another word, at a certain pH, the longer the chain length of the hydrocarbon is, the higher the packing density is, and the larger the amount of nonionic fatty acids. Things would be similar for the alkylammonium salt system, except the amphiphilic ions are oppositely charged. Therefore, the apparent pK_a should vary with the hydrocarbon chain length of alkylamine in a mode contrary to that of fatty acids. As a result, MBL, MLV, and translucence would occur at lower pH with the increase of the hydrocarbon chain length of alkylamine.

The Properties of the Organized Assemblies in the C_mNH_3Cl System

Micropolarity of the organized assemblies. Pyrene is a hydrophobic compound, usually used as a fluorescence probe to measure the polarity of its environment. When pyrene is solubilized in assemblies of amphiphiles, the micropolarity of the

assemblies can be probed according to the I_1/I_3 value of the fluorescence spectra of pyrene. It has been shown that different micropolarities probed in an aqueous solution of surfactant would indicate a difference in microstructure. For example, it is well known that the I_1/I_3 values are always different at the concentrations lower and higher than the cmc, since the structure of the solution changes from molecular to micellar.

The fluorescence spectra of pyrene and I_1/I_3 as a function of pH in the C_mNH_3Cl system are shown in Figs. 4 and 5.

It can be seen that the I_1/I_3 value increased first and then decreased with the increase of pH. The highest I_1/I_3 value corresponds to pH range 3 ~ 6.7 in the $C_{12}NH_3Cl$ system and pH range 3 ~ 7.4 in the $C_{10}NH_3Cl$ system. These results are in agreement with those for the transformation of microstructure observed by TEM.

As described above, in the pH range 3 ~ 6.7 in the $C_{12}NH_3Cl$ system and the pH range 3 ~ 7.4 in the $C_{10}NH_3Cl$ system, the organized assemblies are mainly in the form of micelles, while beyond this pH range MBL and MLV structures formed in large numbers. It is seen that the results from the fluorescence spectra of pyrene provide the same information.

Recently, the maximum absorption wavelength of MO in solution was found to be a function of the micropolarity of the environment too (17). The absorption spectra of MO and the maximum wavelength (λ_{max}) in the MO absorption spectra as a function of pH in the C_mNH_3Cl system are shown in Figs. 6 and 7. It was found that the λ_{max} of the MO absorption spectrum did not change in aqueous solution within the pH range 5 ~ 12, but it shifted to 500 nm at pH below 4 because of the formation of an acidic type of MO molecule in acidic solution. Thus, in our experiments MO absorption spectra were measured only in C_mNH_3Cl systems with pH higher than 5.

It can be seen from the results that λ_{max} decreased with pH increase, indicating that the micropolarity of the organized assemblies decreased. The pH range at which micropolarity

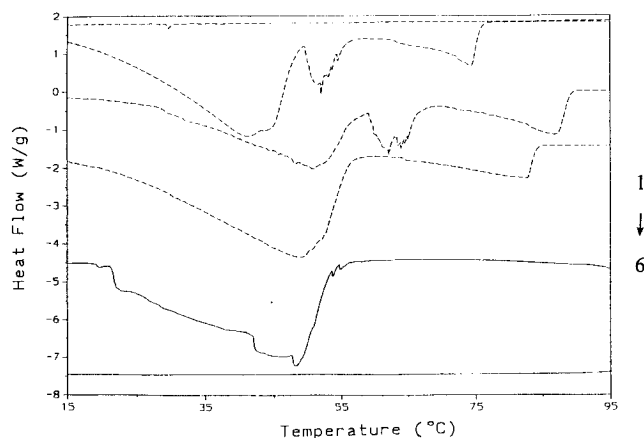


FIG. 8. DSC chart of the $C_{12}NH_3Cl$ (---) and $C_{10}NH_3Cl$ (—) systems with various pH: (1) pH 0.7, (2) pH 6.7, (3) pH 7.3, (4) pH 7.4, (5) pH 8.9, (6) pH 8.2.