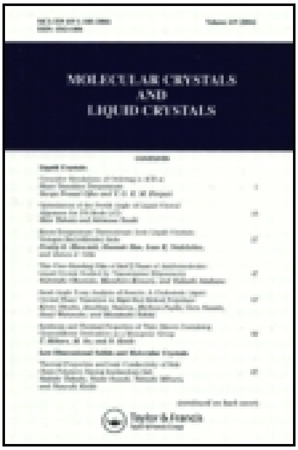

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Hydrolysis Reactions in Aqueous Lamellar Liquid Crystalline Media

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Introduction of a quarternary ammonium head group into aqueous dodecylammonium chloride solutions gives an optically clear lamellar mesophase. Inhibition in the rate of hydrolysis of benzylidene *t*-butylamine N-oxide is greater in the lamellar phase of the mixed amphiphile system than in a similar phase containing only dodecylammonium head groups. This suggests maximum inhibition of the reaction may not be due to electrostatic effects but to partitioning of the substrate into the less compact hydrocarbon regions.

INTRODUCTION

The organization of amphiphilic molecules in aqueous solution encompasses small micellar forms or large aggregates of liquid crystalline structures depending upon the concentration of the amphiphile. The lammellar phase is the most commonly formed liquid crystalline structure with its bilayer arrangement of molecules forming the fundamental structure of biological membranes.

Recent studies of the effect of changes in concentration of the amphiphilic molecule, dodeclyammonium chloride, DdAC, on the rate of hydrolysis of benzylidine *t*-butylamine N-oxide demonstrated that maximum inhibition of the reaction occurred when the lamellar mesophase is formed. We suggested the micellar aggregate structure of the lamellar packed liquid crystalline structure may show maximum electrostatic effect on the reaction and therefore maximum inhibition.[1] In this communication we report the characterization of a second lamellar system containing different polar head groups

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resulting in an alteration of the electrostatic influence and the resultant effect on the hydrolysis reaction.

Two important properties responsible for the formation of liquid crystalline phases are centered on the amphiphilic molecules. They include:

a) the magnitude of the repulsive forces between adjacent polar head groups at the amphiphile/water interface, as well as the degree of polar head group hydration, head group and alkyl chain steric requirements.

b) The amount of conformational disorder in the alkyl chain and the degree of alkyl chain/water contact. These are influenced by the number, length and degree of unsaturation of the alkyl chains. The effects of these factors on the formation of various structures are outlined below. As the amphiphile concentration, alkyl chain number and degree of unsaturation increases the phases proceed from left to right and at high amphiphile concentrations or with non-aqueous solvents the reverse phases are formed.

Micelles ⟷ Hexagonal ⟷ Lamellar ⟷ Reverse Hexagonal ⟷ Reverse Micelles

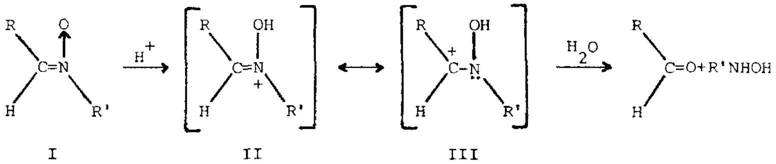
An observation in agreement is that weakly hydrated amphiphiles form extensive liquid crystal zones but may not form a micellar solution.[2] Not all the phases illustrated above will occur in any single system and most of the phases are concentration dependent. After the lamellar phase the hexagonal and reverse hexagonal phases are the most common liquid crystalline structures and the various cubic phases which are observed only over limited temperature and composition ranges, are the least common. The cubic phase may well be an intermediate in the transitions between the phases shown above.

An important characterization of amphiphiles was offered by Tartar[3] and Tanford.[4] This relation is between the cross-sectional area of the polar head, a_0, the length, b_0, and the volume, v_0, of the hydrocarbon moiety. For a given, b_0, a large, a_0, and a small, v_0, favors spherical or rod-shaped micellar aggregates, while a small a_0/v_0 ratios favors a lamellar structure. One method of changing a_0/v_0 ratios is by introducing a third component to the water-amphiphile system. A well known example of this component is a weak amphiphile such as a long chain alcohol in which the hydroxyl group can adhere to the aggregate surface with the alkyl chain in the interior of the aggregate.[5] When the alkyl chain is approximately the same as that of the amphiphile the effective a_0/v_0 ratio is decreased. If the amphiphile prefers a rod-shaped structure then the tendency to form a planar aggregate will increase upon the addition of an alcohol to the micellar solution. When a sufficient quantity of alcohol is added the lamellar liquid crystalline structure appears. Many ternary systems of water-amphiphile-long chain alcohol are reported by Ekwall.[6] The role of the alcohol in terms of specific interactions is to increase the hydrocarbon volume without increasing the area of the polar heads to the same extent.[5]

We have modified the lamellar mesophase of DdAC by the addition of didodecyldimethylammonium chloride, DdDMAC, which serves to lower the a_0/v_0 ratio, as well as altering the polar head groups of the surfactants. This aqueous mixed micelle system forms a lamellar mesophase stable at room temperature. This is in contrast to the lamellar phase of dodecylammonium chloride-water system in which two phases appear about 22°. Amphiphiles with different head groups form mixed micelles as readily as amphiphiles with the same head group[4] and the equilibrium in a system of mixed surfactants is established regardless of the order of addition. For example, lysophosphatidylcholine, a lipid with a single hydrocarbon chain is added to phosphatidylcholine, containing two hydrocarbon chains, a mixed micelle is formed with the lamellar structure.[7] Examination by electron microscopy indicates the lamellar bilayer structure is progressively disrupted presumably due to steric factors in packing the odd numbered hydrocarbon chains. Perhaps the addition of DdAC to the lamellar structure of DdDMAC may also disrupt the ordered core structure because the resulting lamellar structure now contains more hydrocarbon chains per polar group than in the case of DdAC.

The lamellar phase, also known as neat phase, has a structure in which the amphiphilic molecules are arranged in bilayers separated by water layers. In a given sample the thickness of each water layer is usually within ±0.5 Å. The water layer thickness can vary from ~8 Å to >100 Å depending on the water content while the amphiphile layer thickness is generally about 10–30%, less than the length of two all trans amphiphilic chains.[2] The hydrated polar groups and counterions within the water-amphiphile interface of the lamellar phase make up an interface similar to the Stern layer with a thickness about equal to that of the hydrated ionic heads. Beyond the Stern layer is also water containing the hydrated protons as well as the reaction substrate.

The acid hydrolysis of benzylidene *t*-butylamine N-oxide, I, in aqueous and micellar solutions was reported and the mechanism is shown below.[8,9]



$R = C_6H_5$; $R' = t\text{-}C_4H_9$

This reaction was selected because cationic surfactants inhibit acid hydration reactions[10] possibly through a long range electrostatic effect originating from the charged micellar interface.[9]

RESULTS AND DISCUSSION

The rate constants for the hydrolysis of *I*, shown in the Table is in agreement with the reported value[8] in water adjusted to pH 1.00 with hydrochloric acid. Also the rate of hydrolysis decreases as the concentration of sodium chloride or *n*-butylammonium chloride increases in aqueous solution, and the rate of inhibition is greater in the latter case. Although neither case shows the amount of inhibition caused by the lamellar phase of DdAC.[1]

The polar head group of DdAC is smaller than its counterpart in the mixed micelle system. The effect of the amphiphilic head group structure on the micelle molecular weight is evident in the cases of decylammonium bromide[11] surfactants and tetradecylammonium bromide surfactant.[12] For these surfactants the aggregation number increases as the size of the polar head group decreases. The counterion can approach the smaller head group more closely thus allowing for tighter packing between the amphiphilic molecules in the micelle and permitting larger micelles to be formed. This conclusion is consistent with surface area per head group data, namely as surface area per head group increases the amphiphilic molecules will be less tightly packed and the micelle molecular weight will decrease. We expect the micellar aggregate in the case of DdAC to have a more compact packing than the mixed micellar system; however, the molecular weight comparison data are not available.

The lamellar phase of the mixed amphiphilic molecules contain about one half the total amphiphile concentration as the same phase of DdAC, yet the rate of hydrolysis of *I*, is about one fourth as fast as the hydrolysis in DdAC. Based upon the difference in concentration of the amphiphile one calculates the surface area per polar group is larger in the mixed amphiphile system than in the same phase of DdAC. These observations suggest the rate of hydrolysis of *I*, in the lamellar phase of the mixed amphiphile system should be faster than in DdAC if the inhibition is due totally to the electrostatic effect.

The explanation for the slower rate of hydrolysis in the lamellar phase of the mixed surfactant system appears to be the greater partitioning of the substrate between the water and the hydrocarbon region of the lamellar structure. This is understandable since the lamellar phase of the mixed surfactant system contains a much larger hydrocarbon region, and its

TABLE I

Rate constants for hydrolysis of benzylidene *t*-butylamine *N*-oxide[a]

Solvent	H_2O	Aq NaCl				
M/L		.432	1.099	1.370		
Rate sec^{-1}	$3.37x10^{-3}$	$2.82x10^{-3}$	$2.57x10^{-3}$	$2.45x10^{-3}$		
Solvent	Aq $n\text{-}C_4H_9\overset{+}{N}H_3\overset{-}{Cl}$				Aq DdAC	Aq DdDMAC/DdAC
M/L	.100	.400	1.340	1.918	1.356	0.7374[b]
Rate sec^{-1}	$2.93x10^{-3}$	$2.47x10^{-3}$	$1.85x10^{-3}$	$1.47x10^{-3}$	$5.40x10^{-4}$	$1.42x10^{-4}$

[a] Pseudo First-Order rate constants at pH 1.00.

[b] Calculated as total amine.

structure is much less compact. The partition coefficient of *I*, in octanol-water solvent system determined from Beer's law relation in water saturated with octanol and the reverse gave a value of eleven. This result suggests that *I*, has a preference for the hydrocarbon environment[13] and presumably in the lamellar system a concentration of eleven times more of *I*, resides in the hydrocarbon region than in the water. Such unfavorable partitioning results in a decrease in the rate of hydrolysis in the lamellar phase of the mixed amphiphilic system.

The conductivity of hexagonal and lamellar phases of soap is somewhat insensitive to composition while values for the lamellar are lower than those of the hexagonal phase.[2] However, the effects of anisotropy and the lack of basic information on conductivity, care must be exercised in using such measurements to determine phase structures.[2] Identification of the lamellar mesophases for the mixed surfactants and for DdAC were determined by microscopy and shown in Figure 1.

We are presently determining the surface area per polar group for each lamellar structure to distinguish between expanding and non-expanding lamellar structures.[14] Interaction of the polar groups with themselves and with water molecules result in an increase in surface area per polar group with dilution, however, such interaction sometimes is so strong that the spacings remain constant or even diminish when the water content is increased.[15] The difference in the electrostatic effect on reactions in such lamellar phases has not been studied.

EXPERIMENTAL

Didodecyldimethylammonium chloride (DdDMAC) was prepared from the corresponding bromide (Eastman) from methanolic hydrogen chloride.[16] The crude chloride was recovered by evaporation of the methanol then recrystallized from acetone until the product is a white solid at room temperature.[17] The melting point of the hydrated solid surfactant (which corresponds to the Kraft point) is 38.3°C based on the DSC–2 analysis. The prepreparation and purification of dodecylammonium chloride (DdAC) and benzylidene *t*-butylamine N-oxide, *I*, were described previously.[1]

Lamellar phases were prepared by mixing 17.00 g (0.0407 M) of DdDMAC and 75.0 g deionized water then carefully heating with stirring to 95° until a smooth paste is formed. Then carefully add to the mixture at 60–70°, 8.0 g (0.0361 M) of DdAC and repeat the heating and stirring to 95° until the solution is optically clear. The solution was adjusted to a pH 1.00 by the addition of conc. hydrochloric acid using a Fisher Accumet pH Meter with an expanded scale, equipped with a Corning combination electrode. The

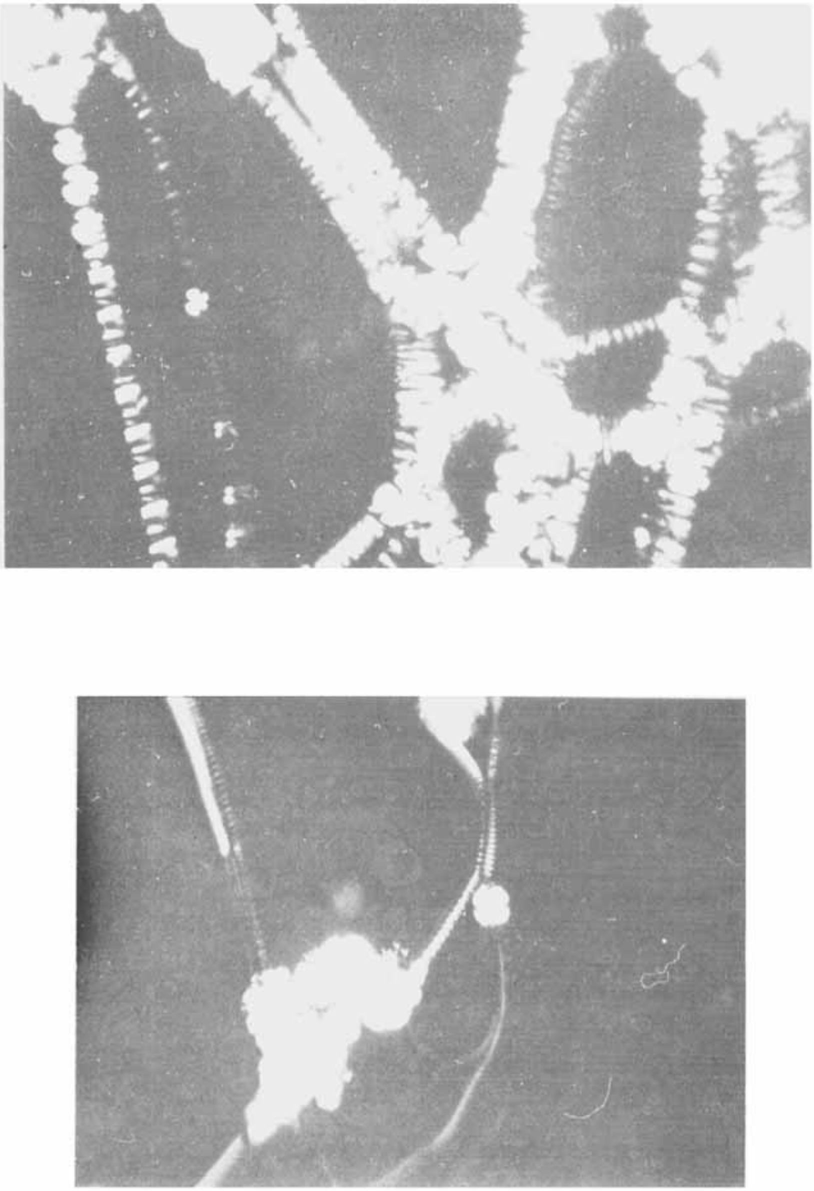


FIGURE 1 Pseudoisotropic textures and oily streaks of lamellar systems at pH 1.00 crossed-polarizers 96x. a) 1.36 M aqueous DdAC. b) 0.737 M aqueous mixed amphiphile system.

addition of conc. hydrochloric acid to the solution causes a precipitate to form which is dissolved by repeating the heating and stirring procedure. The optically clear solution was then sonicated at 40° for one hour with an Ultramet Sonication.

The hydrolysis of *I*, was followed by the consumption of reactant at 292 nm in thermostated 1 cm curvettes at 25.0 ± 0.05° with a Gilford recording spectrophotometer. The reaction was initiated by the injection of nine microliters of an aqueous solution of *I*, into the curvette and then stirring to insure homogeneous solution. The pseudo first-order plots are linear to greater than 90% reaction and the reproducibility is within 5%. The microscopy was done by introducing the solutions into rectangular optical capillaries with an optical pathlength of 200 μm by capillary action. The capillaries were then sealed with a fast setting resin and fastened to microscope slides. Observation was conducted by a Leitz polarizing microscope and equipped with a Mettlar heating stage and a camera.

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