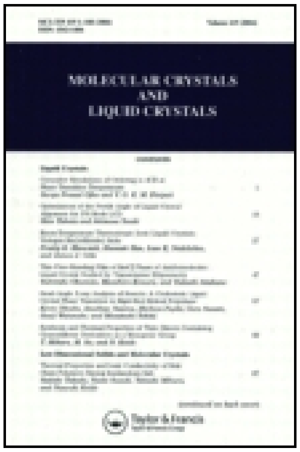

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Decarboxylation of 6-Nitrobenzisoxazole - 3 - Carboxylic Acid Through Phase Transitions in Lyotropic Liquid Crystals

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DECARBOXYLATION OF 6-NITROBENZISOXAZOLE - 3 - CARBOXYLIC ACID THROUGH PHASE TRANSITIONS IN LYOTROPIC LIQUID CRYSTALS

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Abstract Kinetics of the spontaneous decarboxylation of 6-nitrobenzisoxazole-3-carboxylic acid have been studied in the lyophases formed by anionic, cationic and nonionic surfactants: sodium dodecyl sulfate (SDS), myristyltrimethylammonium bromide (MTAB) and pentaethylene glycol mono-n-dodecylether ($C_{12}E_5$) respectively. This substrate was chosen for study because of the large amount of data available on its behavior in micellar solution. Without surfactants the reaction proceeds slowly in both acidic (pH 4.0) and alkaline (pH 9.0-11.0) water solutions, with the reaction rate $\sim 0.7\times10^{-5} s^{-1}$ (at 25 °C). Anionic SDS has no catalyzing effect on the reaction. Cationic MTAB significantly accelerates the reaction in all phases: isotropic, lamellar or cylindrical nematic. Nonionic $C_{12}E_5$ is the only surfactant which shows a catalyzing effect dependent on the type of the lyophase. The reaction goes ~1.5 times faster in the lamellar as compared to the isotropic phase.

INTRODUCTION

Concentrated micellar solutions exhibiting a variety of ordered liquid crystalline phases have been the subject of research for many years, and more recently this work has been extended to examine modulation of the chemical reactivity of guest molecules by the structure and anisotropy of their liquid crystalline aggregates.[1-3] The goal of these studies is twofold: (I)-to explore the possibility of enhancing micellar catalysis in anisotropic concentrated surfactant media and (ii)-to investigate the morphology of the self-assembled surfactant aggregates employing known reactions as probes of their microenvironment. Unimolecular reactions which allow one to avoid complications due to incorporation of more than one reactant, afford a possibility of putting into perspective the nature of the lyophase.

In a previous study in this laboratory, the isomerization of a photochromic merocyanine to indolinospiropyran in anionic and cationic lyophases was investigated and marked discontinuities in the reaction rate have been observed as a function of concentration or temperature which cause phase transitions from disc- to rod- to sphere-like aggregates.[1,2] To test the generality of this phenomenon and develop a microscopic understanding of the reasons for reactivity control by various lyophases, another well known unimolecular reaction, decarboxylation of 6-nitrobenzisoxazole-3-carboxylic acid (NBCA), which is strongly catalyzed by cationic cetyltrimethylammonium bromide (CTAB) micelles at pH>9.0,[4] was chosen for study. The kinetics of the spontaneous decarboxylation of NBCA have been studied in the lyophases formed by cationic, anionic and nonionic surfactants: CTAB, myristyltrimethylammonium bromide (MTAB), sodium dodecyl sulfate (SDS), pentaethylene glycol mono-n-dodecylether ($C_{12}E_5$) respectively.

EXPERIMENTAL

NBCA was synthesized following the procedures previously described.[4-6] Surfactants MTAB, CTAB and SDS, purchased from Aldrich, were recrystallized prior to use from ethanol/water. $C_{12}E_5$ (Sigma) was used as received.

Lyotropic phases were prepared by mixing appropriate surfactants (electrolytes and cosurfactants were added when needed) with a buffer followed by thorough stirring and centrifugation. Buffers consisting of a 0.01 M HCl solution containing various amounts of NH_3 to give pH in the range of 4.0 to 9.0 were employed. Phase diagrams of the systems based on SDS, MTAB, CTAB and $C_{12}E_5$ have been reported in detail.[7-11] Ternary SDS/1-decanol/water and quaternary MTAB/ammonium bromide/1-decanol/water systems both afford easily accessible rod-like N_C, disc-like N_L and sphere-like isotropic I phases at convenient temperatures and concentrations.[2,7,8] There is a narrow region in the binary phase diagram of CTAB/water where one can go from isotropic to nematic to hexagonal phase as a function of concentration.[9] The binary system of $C_{12}E_5$/water exhibits a rich variety of lyophases depending on concentration or temperature.[11,12] Phase transitions were identified by examining the samples under a Nikon polarizing microscope on a Mettler FP-52 hot stage.

Kinetics of the NBCA decarboxylation were followed spectrophotometrically using a Perkin-Elmer 330 spectrophotometer with a thermostated cell holder.[1,3] The integrated first order rate constant **k** was obtained from computer-generated correlations of $\ln(OD_t - OD_\infty)$ with time, where OD_t and OD_∞ are the optical densities at any given time and at completion of the reaction respectively. Estimated errors in the rate constants were ±8%.

RESULTS

NBCA undergoes a slow spontaneous decarboxylation forming 2-cyano-5-nitrophenol (CNPH) with equal rates of $0.75\times10^{-5}s^{-1}$ at 27 °C at both acidic and basic pH in water. In acidic solutions (pH 4.0), the absorption band of the protonated product lies at ~ 340 nm; in basic solutions the anion absorbs at ~ 400 nm. The activation parameters, calculated from the rate constants determined at temperatures 27, 45 and 60°C are: $\Delta H^{\ddagger} = 27.5$ Kcal·mol^{-1}, $\Delta S^{\ddagger} = 6.6$ eu.

Both cationic (MTAB and CTAB) and nonionic ($C_{12}E_5$) surfactants significantly catalyze the reaction. Cationic micelles accelerate the reaction approximately 80-90 times, whereas nonionic micelles accelerate the reaction about 60 times and show some concentration dependence. The absorption band of the reaction product shifts from ~ 400 nm in water solution to ~ 413 nm in cationic lyophase (pH 9.0) indicating a change in the polarity of the reaction environment.

Within experimental error, all MTAB phases have the same catalyzing effect on the reaction (Table I). The reaction rate is also invariant to the type of lyophase in the binary CTAB/water system: the rate constants determined at T=33°C were 1.45×10^{-3}, 1.50×10^{-3} and 1.58×10^{-3} s^{-1} in isotropic (CTAB/H_2O, 20:80), nematic (CTAB/H_2O, 25:75) and hexagonal (CTAB/H_2O, 30:70) phases respectively.

In MTAB lyophases both NBCA and CNPH retain their deprotonated form at acidic pH. For example, in MTAB/water 35:65 isotropic lyophase at pH 5.5, the product CNPH absorbs at 413 nm corresponding to its deprotonated form. At pH 4.5, two peaks are observed at 341 and 413 nm, and only at pH 4.0 does there appear to be a single absorption peak at 341 nm. The MTAB catalysis (MTAB/water 5:95, 25 °C) is about 6 times slower at pH 4.0 ($k=9.6\times10^{-5}$ s^{-1}) than at pH 9.0 ($k = 58.5\times10^{-5}$ s^{-1}). The activation parameters for the reaction in MTAB/water 35:65 are $\Delta H^{\ddagger} = 23.0$ Kcal·mol^{-1} and $\Delta S^{\ddagger} = 4.2$ eu.

TABLE I Rate constants for the decarboxylation of NBCA at 27°C in MTAB aggregates. [NCBA]=2.5×10^{-4} mol·l^{-1}, pH 9.0.

Phase	MTAB	H_2O	1-decanol	NH_4Br	10^5k, s^{-1}
N_C	42	58	-	-	69.0
N_C	41	59	-	-	64.5
N_L	29	61	3.8	6.2	68.4
N_L	30	60	3.8	6.2	73.9
N_L	31	59	3.8	6.2	71.4
I	33	57	3.0	7.0	64.0
I	35	61	1.9	3.1	65.3
I	39.5	60.5	-	-	71.0
I	38.4	61.6	-	-	68.8
I 3	5	65	-	-	65.3

SDS has no catalyzing effect on the reaction at low concentrations. At higher concentrations, corresponding to a nematic lyophase (SDS/1-decanol/water, 37:7:56), the reaction rate is even slower than in pure water : 8.5×10^{-5} s^{-1} and 14.5×10^{-5} s^{-1} respectively

(t = 45°C). As in the MTAB lyophases, the reaction rate is invariant with respect to phase.

Nonionic $C_{12}E_5$ is the only surfactant which shows a catalyzing effect dependent on the type of the lyophase. As shown in Table II, the reaction goes ~1.5 times faster in lamellar as compared to isotropic phase. $C_{12}E_5$ /water binary systems do not exhibit nematic phases. One can go from isotropic (spherical micelles) to hexagonal to lamellar phase at a constant temperature (below 20°C) by increasing the concentration of $C_{12}E_5$ in water, or proceed from hexagonal to isotropic to lamellar phase by raising the temperature of a system with fixed composition.

TABLE II Rate constants for the decarboxylation of NBCA in $C_{12}E_5$ aggregates. T =45°C; pH = 7.0.

Phase	PEO	H_2O	10^4k, s^{-1}
Isotropic (L_1)	35	65	36.0
	40	60	33.0
	45	55	29.0
	50	50	35.0
Lamellar (L_α)	55	45	52.7
	57	43	48.0
	60	40	53.0
	70	30	60.0

At a constant temperature of 17°C, the isotropic-hexagonal phase transition occurs at concentrations of $C_{12}E_5$ above 37.5%; this phase persists to ~58 wt.% of $C_{12}E_5$ and the lamellar phase appears above 60 wt.% of $C_{12}E_5$ in water. Reaction rates determined at 17°C in the isotropic (30 wt.% $C_{12}E_5$), hexagonal (50 wt.% $C_{12}E_5$) and lamellar (65 wt.% $C_{12}E_5$) phases were 7.5×10^{-5}, 8.3×10^{-5} and 15.0×10^{-5} s^{-1} respectively. For the composition of 50 wt.% $C_{12}E_5$ in water the hexagonal phase melts to isotropic (spherical micelles) at ~ 22°C, and on further heating an isotropic-lamellar transition occurs at 52°C. The Arrhenius plot was found to be linear on going through these phases. The rate constants, 10^4k (s^{-1}), at 17, 30, 35, 45, 55, and 60 °C are 0.83, 5.50, 14.3, 35.2, 111.0 and 171.0, respectively. The activation parameters were calculated as $\Delta H^{\ddagger} = 22.8$ Kcal·mol^{-1} and $\Delta S^{\ddagger} = 2.2$ eu.

DISCUSSION

The lack of reaction rate sensitivity towards the change in shape and size of MTAB or CTAB aggregates can be rationalized by the dominant role of strong electrostatic attractions in the interaction between an anionic reactant and a cationic MTAB or CTAB micelles, so that structural factors become less significant. The fact that both the reactant and product retain their deprotonated form in these media even at pH 4.5 favors the assumption that cationic micelles incorporate NBCA molecules deeply into the micellar pseudophase, effectively screening them from external ions. NBCA decarboxylation in cationic micelles is somewhat unusual in the sense that this catalysis is enhanced by some salts.[4] It has been argued that the effect could be attributed to several factors, one of them being an increase in the aggregation number of micelles. It is reasonable to assume that larger micelles afford more complete incorporation providing the NBCA molecules a somewhat better environment for reaction. Apparently, above a certain critical point, further increase in the size and changes in the shape of "large" micelles (such as those which form MTAB lyonematic phases) have no effect on the reaction.

An attempt at reducing the electrostatic interaction between NBCA and cationic aggregates so as to reveal other factors governing the kinetics of the reaction has been made by performing the reaction at low pH, where NBCA molecules remain in a nonionized form. Although the MTAB catalysis was reduced 6 fold at pH 4.0 as compared to pH 9.0, no dependence of the reaction rate on the type of the lyophase was observed under these conditions either, indicating that electrostatic interactions still remain dominant.

Diluted micellar solutions of SDS have no effect on the rate of the reaction since the repulsive forces between similarly charged micelles and substrate prevent substrate molecules from penetrating. At higher concentrations of SDS, the reaction goes more slowly than in water, because solute molecules confined in the aqueous media encounter stronger repulsion from adjacent anionic aggregates and appear to be in a more polar environment due to the increased ordering of dipolar water molecules at the water-micellar interface.

The only surfactant which shows a catalyzing effect dependent on the type of the lyophase is nonionic $C_{12}E_5$. A possible reason for the different behavior of the reaction through the phase transitions in these uncharged aggregates is the increased proportion of the contribution from structural factors in the free energy of the initial and transition states. It is known that NBCA decarboxylation is favored by factors which stabilize the transition state by interactions between the aryl group and the polar heads of micelles, and which selectively destabilize the initial state by increasing dipolar interactions with the CO_2 group.[4] With increased concentration of surfactant, the transition from spherical micelles to the lamellar phase might force a closer association of the oxyethylene head groups on the bilayer-water interface and increase their association with substrate. This increased beneficial association must be reflected in a lowering of the free energies of both the initial and transition states, but the transition state is stabilized because it has a negative charge density delocalized into the ring. Thus, the lamellar phase should promote the decomposition of NBCA. As to the isotropic - hexagonal phase transition, the degree of association of the surfactant head groups on the surface of spheres and cylinders seems to be very similar, and hence no effect on the rate of the reaction is observed.

In spite of the pronounced increase in the rate of the reaction in lamellar phase observed at the hexagonal-lamellar (17°C) and isotropic-lamellar (45°C) phase transitions, no discontinuity was observed in the Arrhenius plot on going from the isotropic to the lamellar phase. Although the enthalpy of the reaction in $C_{12}E_5$/water systems is equal to that in the MTAB lyophases (~ 23 Kcal·mol^{-1}), the entropy is less (2.2 vs 4.2 eu) which implies that the substrate molecules lose some degree of freedom. This is quite consistent with the observed dependence of the reaction rate on the structural changes in nonionic aggregates; but its relationship to micelle-substrate interactions requires further investigation.

CONCLUSIONS

NBCA decarboxylation catalyzed by cationic MTAB/1-decanol/water and CTAB/water aggregates proceeds with the same rate in the isotropic, lamellar and cylindrical nematic lyophases. It appears that strong Coulombic forces between ionic micelles and anionic reactant dominate other types of interaction, and therefore make the reaction rate invariant to the changes in size and shape of the ionic surfactant/water aggregates.

Nonionic $C_{12}E_5$/water lyophases afford some control of the rate of this reaction as a consequence of structural changes in their aggregates, showing approximately a 1.5 fold increase in the lamellar phase with respect to the isotropic L_1 phase.

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