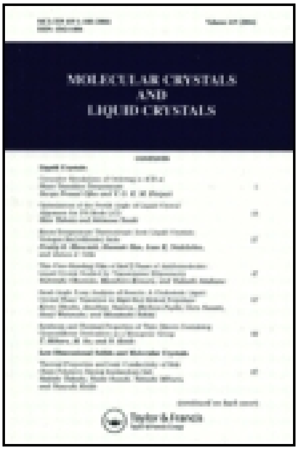

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Nematic Lyotropic Liquid Crystals as Media for Chemical Reactions

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NEMATIC LYOTROPIC LIQUID CRYSTALS AS MEDIA FOR CHEMICAL REACTIONS

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INTRODUCTION

An old theme in liquid crystal research, first introduced by Svedberg in 1916, is the examination of how chemical reactivity is modulated by the anisotropy of the medium to result in changes in rates of reaction or structures of product. We have recently returned to this problem by examining reactions in aqueous lyotropic nematic media. One can identify systems in which phase transitions occur from rod to disc to spherical aggregates of amphiphiles as functions of either temperature or concentration of surfactant, cosurfactant, or electrolyte, and study model reactions occurring through these phase transitions. One can orient the lyotropic medium in a magnetic field and assess the degree of ordering of reactant and product and their penetration into the micellar media by spectroscopic methods.

There are dramatic discontinuities in reaction rates occurring at the phase transitions from lamellar (N_L) to cylindrical (N_C) to spherical (I) micellar structures. We have examined several model reactions of both a bimolecular and unimolecular nature such as: catalyzed ester and phosphinate ester hydrolyses in a cationic surfactant; bromination of an olefin in an anionic surfactant; unimolecular photoisomerization of a merocyanine to a spiropyran in anionic surfactants. These results are summarized below.

Bromination of *trans*-stilbene in SDS lyomesophase[1]

It was the strategy of this study to investigate the kinetics of a typical bimolecular reaction through the rod-disc-sphere (N_C-N_L-I) phase transitions in order to ascertain the effects of environment on the reactivity. The reaction chosen was the bromination of *trans*-stilbene, since there already existed a careful study of this system in aqueous micelles and vesicles.[2] The lyomesophase system was sodium decylsulfate (SDS) since in the ternary phase diagram of SDS, 1-decanol and water, as a sensitive function of either concentration or temperature, transitions occur between the N_L, N_C and I phases.[3]

Pseudo-first order rate constants for the bromination of *trans*-stilbene in SDS lyomesophase aggregates were determined. Plots of k as a function of temperature and as a function of concentration through the N_C, N_L and I phases are shown in Figs. 1 and 2 respectively. On each plot, the experimental values for the phase transition temperatures determined optically are indicated. The rates of bromination are significantly lower in the N_C phase. Activation energies, enthalpies, and entropies all show pronounced changes through the phase transitions; for example, $\Delta H^{\#}$ = 63, 39, and 12 Kcal mol^{-1} for N_L, N_C, and I phases respectively. However, because of the small temperature ranges accessible, these values are inherently inaccurate. It is clear from these observations that changes in the shape of the aggregate alter the solubilization, orientation, or local motions of guest molecules leading to substantial reactivity changes.

Reactions Studied in Lyomesophase Aggregates of SDS, KL and MTAB

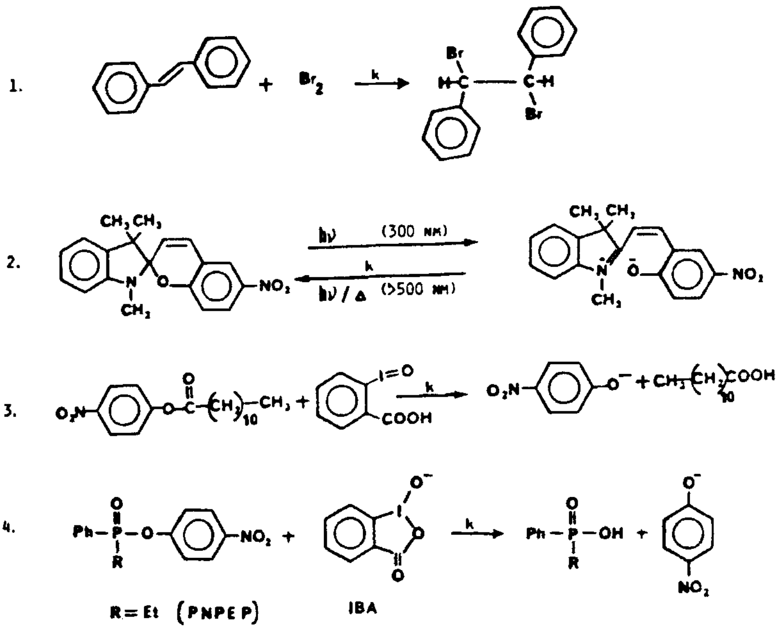

Table I. Reactions Studied in Nematic Lyomesophases

Reaction	Lyomesophase	Pseudo first order rate constants k (s^{-1})		
		N_L	N_C	I
Bromination of trans-stilbene	SDS/Dec/H_2O	1.8×10^{-3}	4.5×10^{-4}	2.1×10^{-3}
Unimolecular isomerization of merocyanine to spiropyran	SDS/Dec/H_2O	2.2×10^{-4}	4.4×10^{-4}	8.4×10^{-4}
	KL/Dec/H_2O	4.4×10^{-4}	8.2×10^{-4}	12.0×10^{-4}
	MTAB/H_2O	--	1.1×10^{-3}	4.0×10^{-3}
	MTAB/Dec/NH_4Br/H_2O	6.7×10^{-4}	--	--
p-nitrophenyl laurate (PNPL) cleavage by o-iodosobenzoic acid	MTAB/H_2O	--	1.3×10^{-3}	1.8×10^{-3}
	MTAB/Dec/NH_4Br/H_2O	3.0×10^{-4}	--	1.8×10^{-3}
p-nitrophenylethyl(phenyl) phosphinate (PNPEP) cleavage by o-iodosobenzoic acid	MTAB/H_2O	--	4.2×10^{-4}	5.3×10^{-4}
	MTAB/Dec/NH_4Br/H_2O	$<2.5 \times 10^{-7}$	--	2.3×10^{-4}

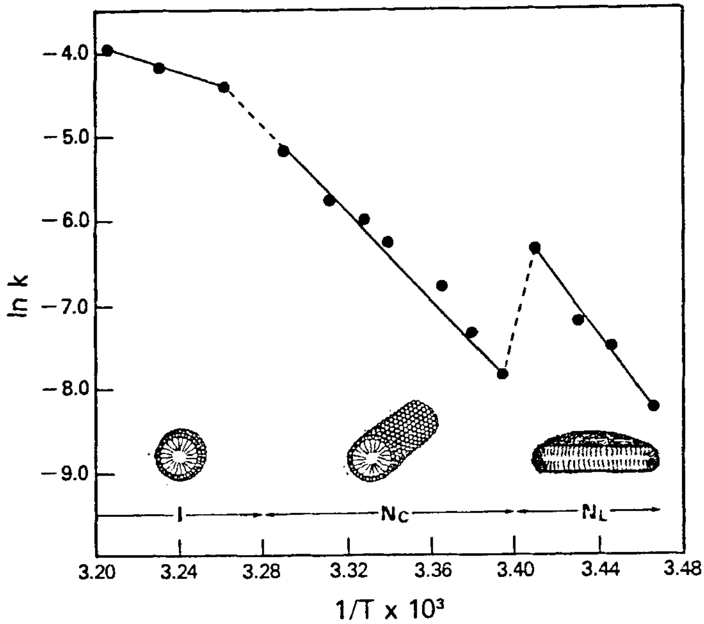

Fig. 1. Arrhenius plot of the bromination of trans-stilbene in the N_L, N_C and I phases of SDS/water/1-decanol::35/58/7 wt %

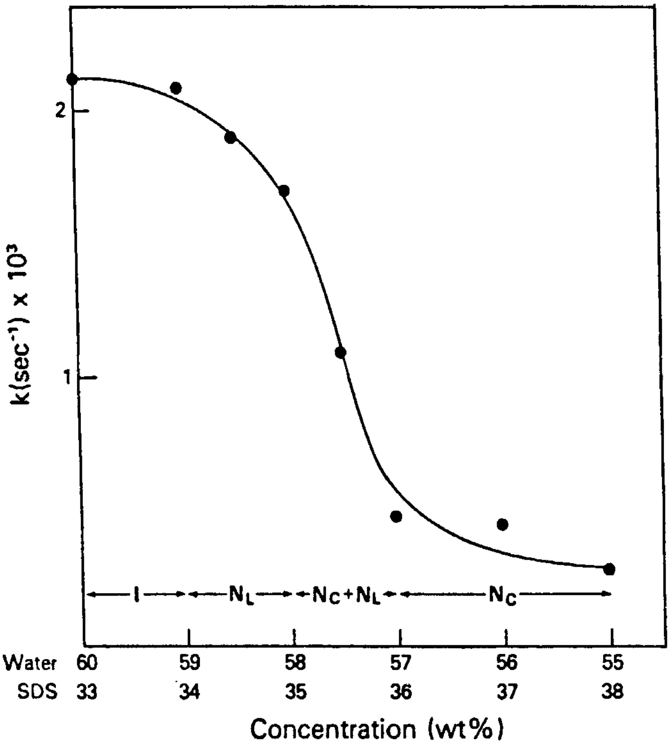

Fig. 2. Pseudo-first order rate constants $k(s^{-1})$ for the bromination of <u>trans</u>-stilbene as a function of SDS/water concentration at 20°C, and constant 1-decanol concentration (7 wt %)

Unimolecular isomerization of merocyanine to spiropyran[4]

In order to assess the extent to which disc-rod-sphere phase transitions in nematic lyotropics might influence the reactivity of unimolecular processes, the unimolecular isomerization of a photochromic merocyanine 1 to an indolinospiropyran 2 was studied in the nematic lyophases formed by potassium laurate[5] (KL), myristyltrimethylammonium bromide[6] (MTAB), or SDS with 1-decanol and water.

Not only were the rate constants (k) of the isomerization measured, but we were also able to determine the "order parameter" S of both the reactant and product. In addition, to ascertain the micropolarity encountered by 1 in the N_L, N_C and I phases, we measured the absorption maxima for merocyanine in these phases and compared them with solvents of known polarity. Since no shift in λ_{max} was observed for merocyanine in the N_L, N_C and I phases, it is obvious that merocyanine molecules experience similar micropolarity in the three phases.[7]

Plots of isomerization rate constants k, as a function of temperature (Arrhenius plots) and as a function of concentration for the KL lyomesophase are depicted in Figs. 3 and 4. The experimental values for the phase transition temperatures determined optically are indicated on each plot. The striking observation is that there are marked discontinuities in reaction rates as a function of concentration or temperature which correspond to the phase transitions from disc- to rod- to sphere-like aggregates. Of particular significance is the retardation in isomerization rate by the N_L phase. While the rate of isomerization is affected by the nature of the surfactant aggregate, no significant changes in activation energy through the

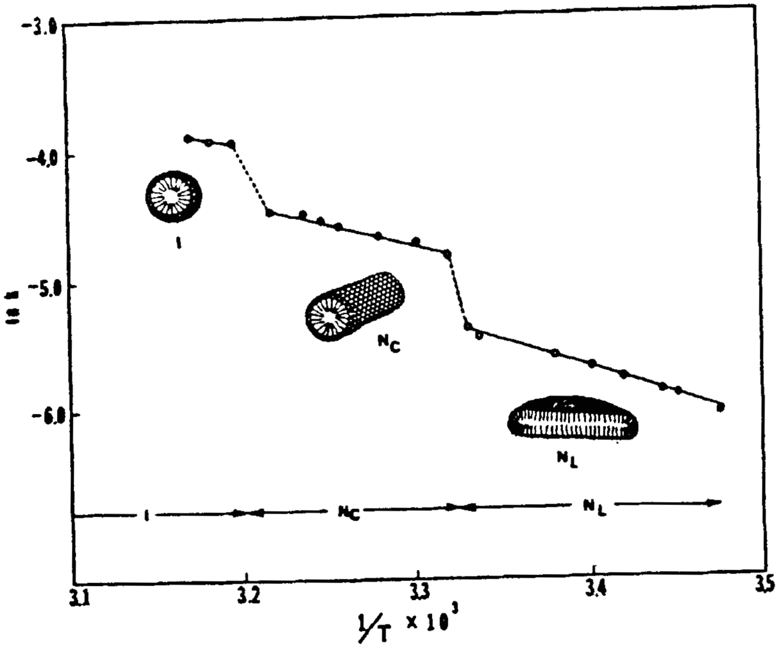

Fig. 3. Arrhenius plot of the merocyanine to spiropyran isomerization in the N_L, N_C and I phases of KL/water/1-decanol::26.0/66.76/6.24 wt %

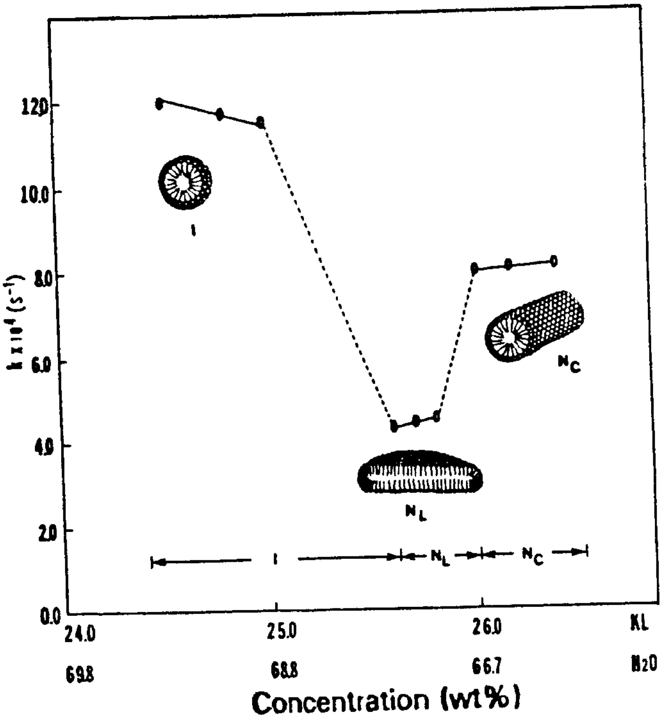

Fig. 4. Isomerization rate constants k(s^{-1}) as a function of KL/water concentration at 28°C and at constant 1-decanol concentration (6.24 wt %)

phase transitions are observed. For example, E_{act} is $\sim$ 8.5 k cal mol^{-1} in KL and $\sim$ 13.3 k cal mol^{-1} in SDS regardless of whether the phase is N_L, N_C or I.

Order parameter values (S) were determined by polarized absorption spectroscopy for both spiropyran and merocyanine in the N_L and N_C phases of SDS and KL. Low S values for spiropyran (S = -0.002) and high S values for merocyanine (S = -0.099) are an indication that the degree of orientational ordering for the globular spiropyran molecules is low, while that for the rod shaped merocyanine molecules is much higher. Further, the large change in S, in going from $\underline{1}$ to $\underline{2}$, is indicative of the significant molecular motion required during the reaction. Therefore, the constraints offered by the local order encountered by $\underline{1}$ in the aggregate cannot be ignored. Since rates of $\underline{1} \rightarrow \underline{2}$ isomerization are lowest in the N_L phase, it is obvious that the bilayer nature of the disc like aggregate offers the most constraint to ring closure. This could most probably arise due to the rod-like merocyanine molecules being effectively "incorporated" within the bilayer matrix preventing facile ring closure. In fact, a similar explanation has been advanced to explain the retardation of isomerization rates of $\underline{1}$ in the smectic B phase of n-butylstearate.[8]

The internal or microviscosity arising from restricted segmental motions of the hydrocarbon chains in the vicinity of merocyanine molecules plays a significant role in determining the rates and mechanism of the isomerization.[9] Although the bulk viscosities of N_L and N_C phases are not very different, microviscosities are probably quite different. This difference coupled with the changes in local order encountered by the merocyanine molecules are most likely explanations for the rate changes at the phase transitions.

o-Iodosobenzoic acid catalyzed cleavage of carboxylate[10] and phosphinate esters[11]

The kinetics of o-iodosobenzoic acid (IBA) catalyzed cleavage of carboxylate and phosphate esters in cationic detergent systems have been explored in detail.[12] Significant rate enhancements were observed upon micellization of the esters. We envisioned that this would be an ideal reaction to investigate in lyomesophase aggregates to study the influence of the nature of surfactant aggregate on bimolecular reactivity. Moreover, micelle bound IBA catalyzed cleavage is an important process in the detoxification of organophosphorous compounds. Myristyltrimethylammonium bromide (MTAB), a cationic surfactant, which forms both a nematic cylindrical and lamellar lyophase depending on the concentrations of water, ammonium bromide and 1-decanol was employed as the lyomesophase medium.[6]

Results of this study are summarized in Table I. The pseudo first order rate constant (k) for the cleavage of p-nitrophenyl laurate (PNPL) in the lamellar N_L phase was observed to be approximately 5 times lower than in the N_C phase.[10] The effect of the nature of the surfactant aggregate is more dramatic in the phosphinate ester cleavage (p-nitrophenylethyl(phenyl)phosphinate, PNPEP), where, a more than 3 order of magnitude difference is found between the rate constants in the N_L and N_C phase. Dilution of the N_L to the I phase causes a pronounced enhancement in the rate of cleavage.

The observed trends in reactivity suggested that changes in the nature of the surfactant aggregate alters the solubilization sites, orientation and local motions of the aggregate bound esters leading to substantial reactivity changes. An FTIR study on PNPEP solubilized in the N_L, N_C and I aggregate of MTAB was undertaken to ascertain whether the microenvironment experienced by PNPEP is different in the lamellar, cylindrical, and spherical aggregates.

Fig. 5 depicts the FTIR spectra of a 3.4×10^{-3}M solution of PNPEP in the N_L, N_C and I phases of MTAB. Fortunately the liquid crystalline host matrix has no infrared absorption bands in the region 1380 cm^{-1} to 1066 cm^{-1} making it accessible for investigating the absorption bands of the guest PNPEP. Three striking observations are:

(1) The symmetric stretching frequency of the $-NO_2$ group shifts by ∿ 10 cm^{-1} in going from the lamellar (1345.3 cm^{-1}) to the cylindrical aggregate (1336.7 cm^{-1}) (Fig. 6).

(2) The relative intensities of the in-plane aromatic C-H rocking bands at ∿ 1122 cm^{-1} and 1100 cm^{-1} are different in the three phases.

(3) The symmetric stretching frequency of the $-NO_2$ group appears at 1336.7 cm^{-1} for the isotropic phase derived from both the N_L and N_C phases.

Since in KBr, CCl_4, and n-hexane solvents, the symmetric stretching band of the $-NO_2$ group appears at 1345.3 cm^{-1} and the relative intensities of the bands at 1122 cm^{-1} and 1110 cm^{-1} are similar to that in the N_L phase, one can conclude that PNPEP is solubilized in the hydrocarbon interior of the lamellar N_L aggregate. The

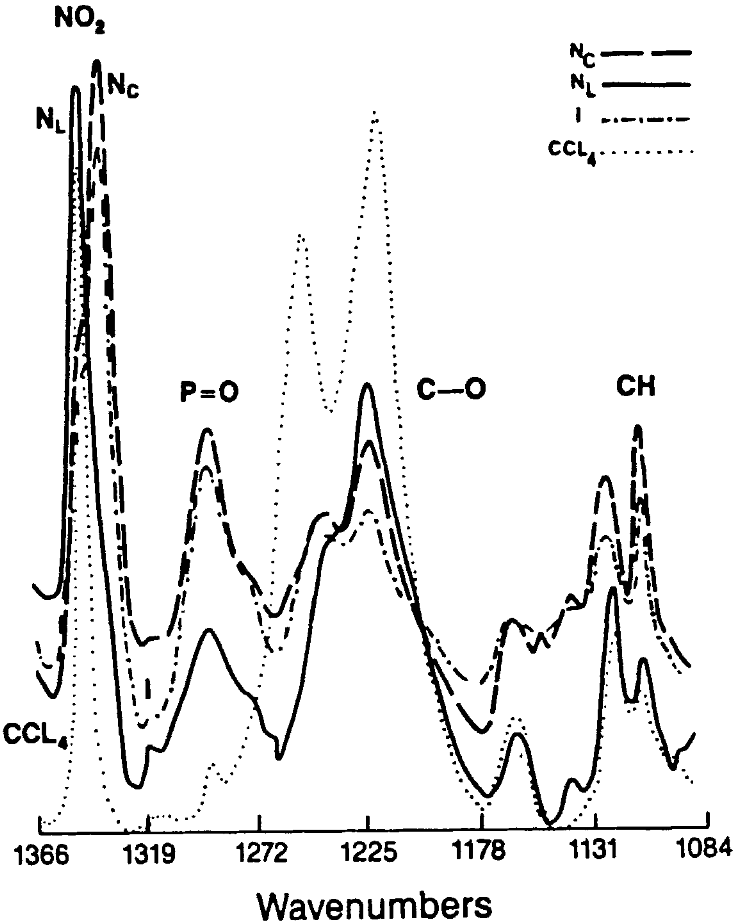

Fig. 5. FTIR spectra of PNPEP in the N_L, N_C and I phases of MTAB and CCl_4

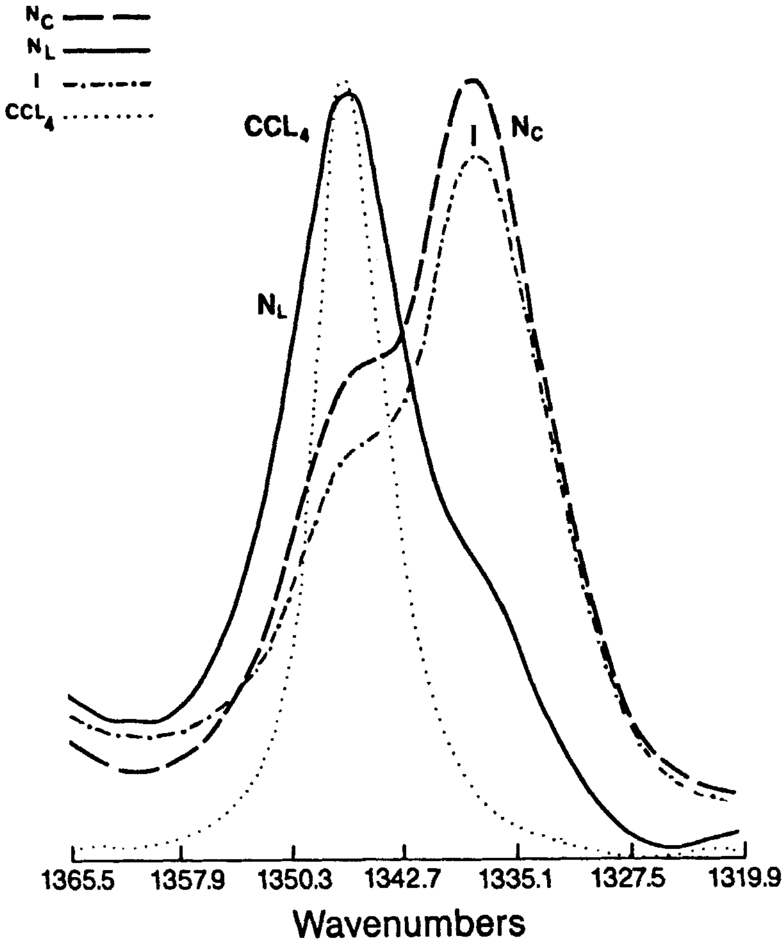

Fig. 6. FTIR spectra of PNPEP in the N_L, N_C and I phases of MTAB and CCl_4 depicting the nitro group symmetric stretching band

∿ 10 cm^{-1} shift of the 1345.3 cm^{-1} band can be attributed to a change in the site of solubilization of PNPEP in the N_C and I aggregates. It is most likely that PNPEP is located in the polar interface region in the cylindrical and spherical aggregates.

The order parameter (S) for the symmetric stretching band of the NO_2 group of PNPEP in the N_L and N_C phases determined by polarized FTIR spectroscopy was found to be -0.15 and -0.02 respectively. The negative sign for (S) implies that the $-NO_2$ group of PNPEP lies perpendicular to the nematic director or parallel to the hydrocarbon chains. The higher magnitude for (S) in the N_L phase indicates that, on the average, the PNPEP molecules are more ordered within the hydrocarbon chains in the N_L phase than in the N_C phase.

The role of electrolytes in inhibiting anion-molecule reactions in micellar medium has been investigated.[13] Rate retardations have been attributed to the exclusion of the nucleophile by the anion of the added salt. Since the N_L phase has and requires NH_4Br as one of its components, the "electrolyte effect" in screening the hydrocarbon solubilized substrate from attack by IBA is important.

Based on the observed kinetic and spectroscopic data we propose the following model: PNPEP molecules are solubilized in the hydrocarbon regions of the lamellar aggregates, are fairly well ordered with respect to hydrocarbon chains in their vicinity, and are effectively screened from the aqueous regions by the electrolyte. In the cylindrical and spherical aggregates PNPEP is located nearer to the interface region. As a consequence, IBA-nucleophilic attack on PNPEP is more facile in the cylindrical and spherical aggregates than in the lamellar aggregate. Consequently, the rates of cleavage are much higher in the N_C and I phases than in the N_L phase.

CONCLUSIONS

It now appears that it is quite general that the N_C-N_L transition affords reactivity control in organic reactions. For those bimolecular processes occurring at the interface, one might expect there to be cases where this control is quite dramatic. Indeed, in the case of IBA cleavage reactions the N_C phase allows the solutes to be exposed at the aqueous interface, whereas the N_L phase functions as a protective environment for the same solutes. In unimolecular processes, rate control is still afforded as a consequence of the differences in microviscosity and micropolarity between the two phases. In all the cases studied, the rod-sphere transition is considerably less dramatic in its effect on reactivity.

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