membrane bound K^+ complex of nigericin. Quantitatively it is in fair agreement with our estimates of the stability constants of the Na^+ and K^+ complexes. It is noteworthy that when a similar experiment was performed with monensin, little effect was observed on the Na^+ transport rate when an equimolar amount of K^+ was present.[28] For monensin the Na^+ complex is observed to have the higher stability constant in nonaqueous solvents,[26] and one would therefore expect little effect on the Na^+ transport rate.

Acknowledgment. We thank the Science and Engineering Research Council for a grant to carry out this work and for an allocation of time on the high-field spectrometer in Edinburgh. We thank Dr. Stephen George of the NERC aquatic biochemistry unit of Stirling University for assistance with the electron microscopy.

Registry No. Na, 7440-23-5; K, 7440-09-7; nigericin, 28380-24-7.

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Dramatic Influence of the Nature of the Surfactant Aggregate on the Rate Constant for Hydrolysis of Phosphinate Esters in Aqueous Nematic Lyotropic Liquid Crystals

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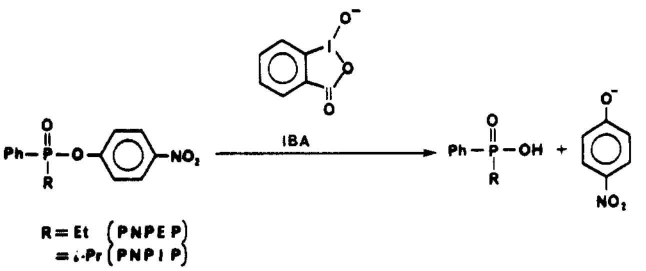
Abstract: The *o*-iodosobenzoic acid catalyzed hydrolysis of two organophosphinate esters has been studied in the lyotropic nematic phases of myrystyltrimethylammonium bromide in 1-decanol, ammonium bromide, and water. Depending on the concentration of these ingredients, three phases are observed at room temperature consisting of rod-like (N_C), disk-like (N_L), or sphere-like (I) aggregates. There is a three order of magnitude difference in the rate constant for hydrolysis between N_L and N_C phases. The N_L phase serves as a protective environment, preventing the hydrolysis of the ester, whereas the N_C phase allows the reaction to occur rapidly. Based upon infrared evidence, the phosphinate ester is solubilized in the hydrocarbon region of N_L aggregates, but in N_C and I aggregates the solute is nearer the aqueous interface.

It has recently been reported that the disk-like (N_L), rod-like (N_C), and sphere-like (I) phase of nematic lyotropic liquid crystals differ dramatically as solvent media for organic reactions.[1-3] One case of a hydrolysis reaction has been studied in detail: catalyzed ester hydrolysis of *p*-nitrophenyl laurate in myristyltrimethylammonium bromide (MTAB) lyomesophases.[2] The rate constant for hydrolysis in the lamellar N_L phase was lower by a factor of ~5 than in the N_C phase. Since the solubility of organic molecules in these concentrated surfactant phases are about 100-fold greater than the dilute micellar phases of the same surfactants, and since reactivity control can be afforded by varying the surfactant medium only slightly, it seems appropriate to extend this study to other hydrolytic processes.

In particular, the process of detoxification of organophosphorus compounds by hydrolytic cleavage has been the subject of considerable investigation.[4-10] Recently, Moss et al.[6-9] and Mackay et al.[10] have demonstrated that micelle solubilized *o*-iodosobenzoic acid (IBA) and its derivatives, in their preferred 1-hydroxy-1,2-benziodoxolin-3-one valence tautomeric form, are very efficient catalysts for phosphate cleavage.

In this work, the IBA-catalyzed hydrolyses of *p*-nitrophenyl ethyl(phenyl)phosphinate (PNPEP) and *p*-nitrophenyl isopropyl(phenyl)phosphinate (PNPIP) are studied in the dilute micellar and the N_L, N_C, and I phases of MTAB/1-decanol/ammonium bromide/water (Scheme I). Utilizing FTIR spectroscopy the nature of the solute solubilization in the N_L, N_C, and I phases are also determined. A more than three-order of magnitude difference is found between the rate constants in the N_L and N_C phases, and an explanation for the reactivity differences is proposed.

Scheme I



Experimental Section

Materials. PNPEP and PNPIP were obtained from Ash-Stevens, Inc. and used as received. IBA and MTAB were obtained from Aldrich Chemical Co. IBA was used as received, whereas MTAB was recrystallized twice from 95% ethanol/water and dried under vacuum. Triply distilled deionized water was used in the preparation of all samples.

Kinetic Studies. Solutions (2.0×10^{-4} M) of IBA in the liquid crystalline solvents MTAB/water (N_C) and MTAB/water/1-decanol/NH_4Br (N_L) and the isotropic micellar solution were prepared by stirring together for 10 h weighed amounts of IBA and the components forming the phases[11-13] (Table I). The N_L–I and N_C–I transitions were depressed by approximately 2 °C in these solutions. Samples were prepared so that

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Table I. Observed Pseudo-First-Order Rate Constants for the Cleavage of PNPEP and PNPIP by IBA at 24 ± 0.5 °C[a]

	wt % of components					k (s^{-1})	
phase	MTAB	H_2O	1-dec	NH_4Br	η (P)[b]	PNPEP	PNPIP
N_C	39	61			9.3	1.5×10^{-4}	1.9×10^{-4}
N_L	30	60	3.8	6.2	2.7	$<2.5 \times 10^{-7}$	$<2.5 \times 10^{-7}$
I	35	65			4.3	5.3×10^{-4}	8.0×10^{-4}
I	30	65	1.9	3.1	38.3	2.3×10^{-4}	8.8×10^{-4}
mic.	0.24	99.76			0.01	6.0×10^{-3}	4.2×10^{-3}

[a] Experimental conditions: pH 8.5 (0.02 M phosphate buffer); [PNPEP], [PNPIP] = 3.4×10^{-5} M; [IBA] = 2.0×10^{-4} M; ±10% errors in rate constants. [b] The viscosities of the lyomesophases are extremely sensitive to the composition of their components. Small changes in composition was observed to change η significantly.

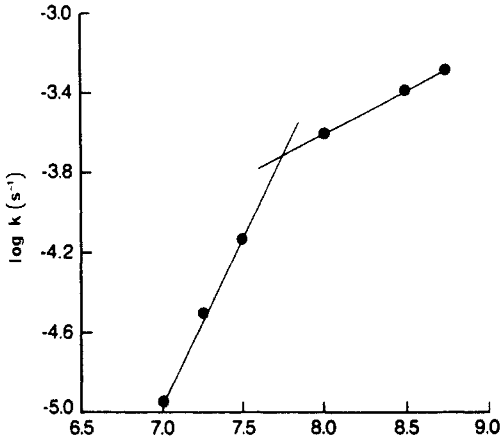

Figure 1. pH–rate profile for the cleavage of PNPEP by IBA in the N_C phase of MTAB.

they were in the N_L or N_C phases at room temperature (24 ± 0.5 °C). These phases could easily be observed by examining the samples under a Nikon polarizing microscope on a Mettler FP-52 hot stage. The N_C phase shows a typical nematic Schlieren texture, whereas N_L phases are best identified conoscopically because of their spontaneous homeotropic texture. A 1-mL portion of catalyst bound-aggregate solution was introduced into a 1-cm path length UV cuvette, and thermostated for 10 min at 24 °C. Phosphinate ester cleavage was initiated by injecting 20 μL of standard 1.7×10^{-3} M PNPEP or PNPIP solution prepared in acetonitrile and stirring vigorously for 20 s. It was observed that injection of 20 μL of acetonitrile into 1 mL of lyomesophase did not destroy the liquid crystalline phase. For higher concentrations of substrate a 1-mm path length UV cuvette was employed and 250 μL of surfactant solution was used. A Perkin-Elmer 330 spectrophotometer interfaced with a Model 3600 data station was used to monitor the appearance of *p*-nitrophenoxide ion at 400 nm. Pseudo-first-order hydrolysis rate constants (k) were obtained from computer-generated correlations of ln ($OD_\infty - OD_t$) with time, where OD_∞ and OD_t are the optical densities at time t = 15 h and at any given time t, respectively. At least three independent experiments were conducted and the mean value for k was determined. Reactions were followed to >85% completion and showed good pseudo-first-order kinetics ($r > 0.998$). Errors in k were estimated to be ±10%.

Viscosity Measurements. Viscosities were determined with a Cannon-Manning semimicroviscometer immersed in a constant-temperature bath (24 ± 1 °C). An average of at least three determinations are made for each sample.

FTIR Studies. Infrared spectra were recorded with a Nicolet 20 SX FTIR equipped with a liquid nitrogen cooled mercury–cadmium telluride (MCT) detector. A potassium bromide beam splitter was employed. The interferograms were accumulated 50–500 times by using an optical retardation of 0.5 cm and performing a Fourier transform to yield a resolution of 0.5 cm^{-1} with a high signal-to-noise ratio. The spectrometer was purged with dry air during the course of its operation.

Samples for FTIR studies were prepared in the following manner: the liquid crystalline (N_C and N_L) and the isotropic (I) micellar solvents were first prepared by stirring together for 10 h weighed amounts of the components. A weighed amount of PNPEP was then added to the solvent and stirred for ~20 min to solubilize the phosphinate ester in the aggregate; 25 × 2 mm circular barium fluoride cells (Wilmad Glass Co.) and a 0.006-mm Teflon spacer were used to contain the samples for spectral examination. All spectra were recorded at room temperature, 24 ± 0.5 °C.

Results and Discussion

pK_a Determination. A pH–rate constant profile was determined for the cleavage of PNPEP by IBA in the N_C phase of MTAB. For reactions of 3.4×10^{-5} M PNPEP with 2.0×10^{-4} M *o*-IBA (0.02 M phosphate buffer), a plot of log k vs. pH (Figure 1) gave a sharp break at pH 7.75. pH 7.75 was taken as the systematic pK_a of the I–OH function of IBA under our lyotropic liquid crystalline conditions, implying that IBA is >85% converted to its catalytically active I–O^- tautomeric form at pH 8.5.

Kinetic Studies. The cleavage of PNPEP and PNPIP by IBA was conducted in the lamellar (N_L), cylindrical (N_C), and isotropic (I) phases of MTAB, and for comparison in the corresponding dilute micellar solution under identical conditions: 0.02 M pH 8.5 phosphate buffer, [substrate] = 3.4×10^{-5} M, [IBA] = 2.0×10^{-4} M at 24 ± 0.5 °C. The weight percent of the components required for the specific phase formation is indicated in Table I. The two entries for the isotropic phase refer to those phases obtained from N_C and N_L, respectively. Table I gives the observed pseudo-first-order rate constant k for the phosphinate ester cleavage in dilute micellar and concentrated surfactant aggregates along with the viscosity of each phase. It is observed that k is an order of magnitude lower in the N_C and I phases as compared to the dilute micellar solution. This could be attributed to the higher viscosity of the liquid crystalline phases. The most significant feature of the cleavage reaction is that k is about three orders of magnitude lower in the N_L phase than in the N_C phase. Dilution of N_C to I causes a moderate increase in k, but a phase transition from N_L to I causes a three-order of magnitude enhancement of k. The observed trend in reactivity of PNPEP and PNPIP in the N_L, N_C, and I phases does not correlate with the viscosity differences among the various phases. The viscosity changes can be quite large; note particularly the effect of 1-decanol and NH_4Br on the isotropic phase viscosity. It is evident from these observations that the lamellar morphology of the disk-like N_L phase is in some manner protecting the solubilized phosphinate ester from attack by IBA, whereas in the cylindrical and spherical aggregates the phosphinate ester IBA attack is less hindered.

Previously, we examined several model reactions of both a bimolecular and unimolecular nature such as: IBA-catalyzed cleavage of *p*-nitrophenyl laurate in MTAB[2], bromination of *trans*-stilbene in SDS,[1] and unimolecular photoisomerization of a merocyanine to a spiropyran in SDS and KL lyomesophase aggregates.[3] Significant discontinuities in reaction rates were observed at the phase transitions from lamellar (N_L) to cylindrical (N_C) to spherical (I) micellar structures. The present observation on PNPEP and PNPIP cleavage by IBA is of a similar nature, but the magnitude of the effect is the largest encountered thus far.

Turnover Experiments. In order to examine the catalytic efficiency of IBA toward the cleavage of phosphinate esters in the nematic lyotropic phase (N_C), kinetic runs were carried out varying the [substrate]/[catalyst] ratio. The data in Table II show that the value of k for liberation of *p*-nitrophenoxide ion from PNPEP and PNPIP decreases by ~60% as the [substrate]/[catalyst] ratio is decreased 100-fold. In dilute micellar solutions it has been observed[6-9] that k is highest when [catalyst] > [substrate]. Even if there is efficient turnover, k has been observed to decrease ~10% when substrate is in excess due to saturation of catalyst.[6-10] On the contrary, in the case of IBA cleavage of PNPEP and

Table II. Cleavage of Excess Substrate by IBA in the N_C Phase of MTAB at 24 ± 0.5 °C[a]

run	substrate	[substrate], M	[substrate]: [catalyst]	$k \times 10^4$, s^{-1}
1	PNPEP	3.4×10^{-3}	17:1	4.2
2	PNPEP	3.4×10^{-4}	1.7:1	2.4
3	PNPEP	3.4×10^{-5}	0.17:1	1.5
4	PNPIP	3.4×10^{-3}	17:1	4.7
5	PNPIP	3.4×10^{-4}	1.7:1	2.9
6	PNPIP	3.4×10^{-5}	0.17:1	1.9

[a] Experimental conditions: pH 8.5 (0.02 M phosphate buffer); [IBA] = 2.0×10^{-4} M; ±10% errors in rate constants.

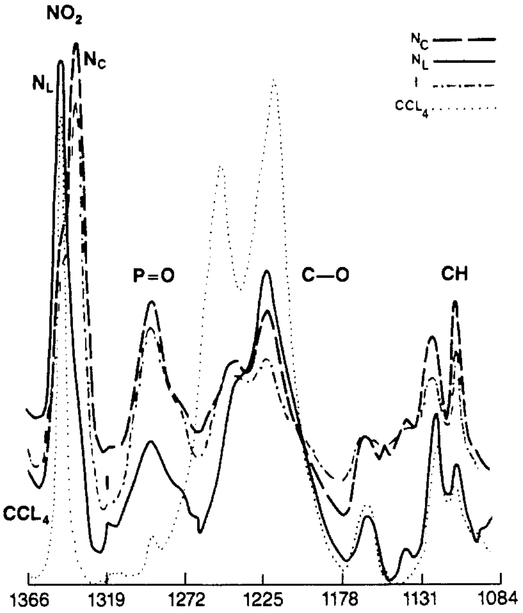

Figure 2. FT-IR spectra of PNPEP in the N_L, N_C, and I phases of MTAB and CCl_4.

PNPIP in lyomesophase aggregates it is observed that *k increases* as [substrate]/[catalyst] increases in the range of concentrations studied. One possible explanation for this observation is that in the concentration range 3.4×10^{-5} to 3.4×10^{-3} M the mean occupancy number of PNPEP and PNPIP in the large lyomesophase aggregate increases with increasing substrate concentration; within each aggregate then the probability of its encounter with the catalyst is increased and a rate enhancement is observed.

FTIR Studies. Spectroscopic investigations on micelle solubilized substrates yield information on the microenvironment of the probe.[5] 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.

Figure 2 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 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}) (Figure 3); (2) the relative intensities of the in-plane aromatic C–H rocking bands at ~1122 and 1100 cm^{-1} are different in the three phases (Figure 4); (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 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 ~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.

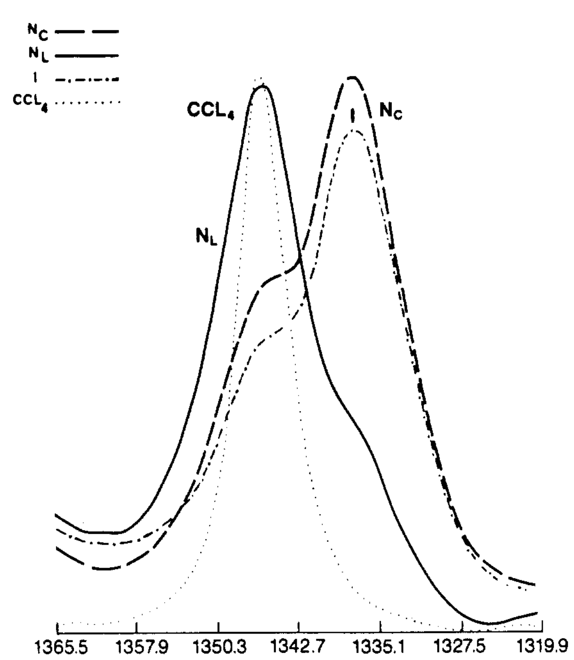

Figure 3. FT-IR spectra of PNPEP in the N_L, N_C, and I phases of MTAB and in CCl_4 depicting the nitro group symmetric stretching band.

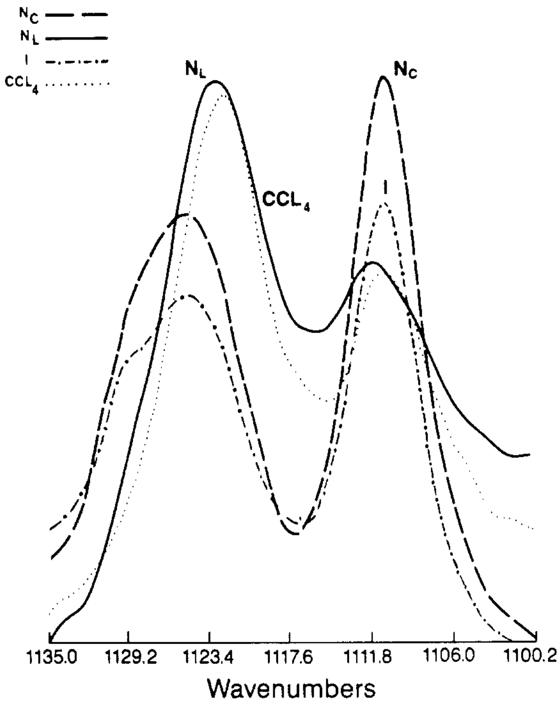

Figure 4. FT-IR spectra of PNPEP in the N_L, N_C, and I phases of MTAB and in CCl_4 depicting the aromatic C–H in-plane rocking band.

According to the above model, there exist two sites for solubilization of PNPEP: the polar interface and the hydrocarbon interior. If this is indeed the case, then, at higher substrate concentrations one would expect to observe a distribution of PNPEP between these two sites. Figure 5 depicts the FTIR spectra for 3.4×10^{-3} and 2.0×10^{-2} M solutions of PNPEP in the N_L and N_C phases. At higher substrate concentration, the distribution of PNPEP among the two sites is clearly evident from

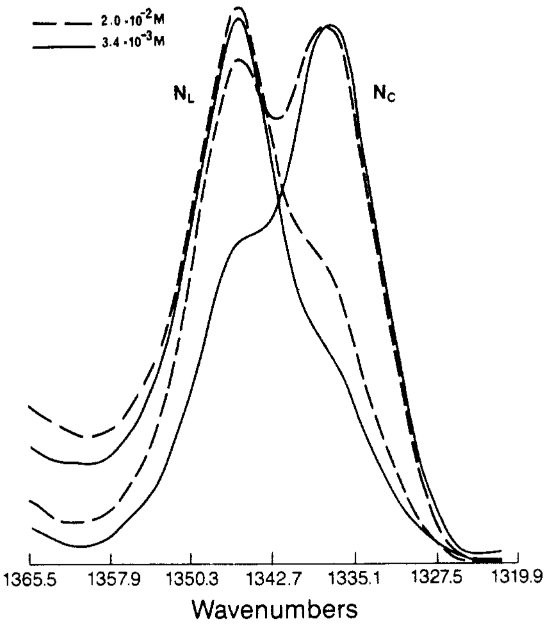

Figure 5. FT-IR spectra of PNPEP in the N_L and N_C phases of MTAB at two concentrations of PNPEP: (a) 3.4×10^{-3} M and (b) 2.0×10^{-2} M.

the appearance of the 1336.7-cm^{-1} peak for the N_L and 1345.3-cm^{-1} peak for the N_C phase.

The role of electrolytes in inhibiting anion–molecule reactions in micellar medium has been investigated.[14] 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: phosphinate esters, PNPEP and PNPIP, are solubilized in the hydrocarbon regions of the lamellar aggregates and are effectively screened from the aqueous regions by the electrolyte. In the cylindrical and spherical aggregates PNPEP and PNPIP are located nearer to the interface region. As a consequence, IBA-nucleophilic attack on PNPEP and PNPIP 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.

Conclusion

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 this work 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,[1-3] the rod–sphere transition is considerably less dramatic in its effect on reactivity. In the case of catalytic processes, the environment of the catalyst itself can also be influenced by changing its structure. Moss et al.[7-9] have shown the remarkable effects of placing a fatty group or an ionic amphiphile on the catalyst molecule. Such studies in lyotropic media might be expected to also give rise to dramatic effects.

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