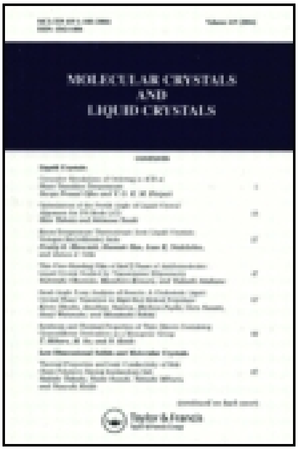

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Bimolecular Reactions in Nematic Lyotropics: A Study of Catalyzed Ester Hydrolysis in N_C, N_L, and I Phases

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Bimolecular Reactions in Nematic Lyotropics: A Study of Catalyzed Ester Hydrolysis in N_C, N_L, and I Phases

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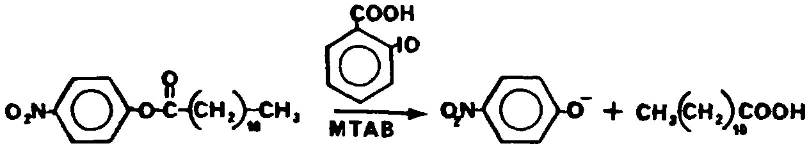
Myristyltrimethylammonium bromide forms both a nematic cylindrical and lamellar lyophase depending on the concentrations of water, ammonium bromide and 1-decanol. The rate of *o*-iodosobenzoic acid catalyzed hydrolysis of *p*-nitrophenyl laurate is significantly higher in the cylindrical phase, indicating that the size and shape of an aggregate can influence reactivity of dissolved species. Similar effects have been reported by us earlier for the bromination of trans-stilbene (a bimolecular reaction) in sodium decyl sulfate surfactant lyophase.

INTRODUCTION

Although there have been many studies of kinetic and geometric control of reaction pathways in micellar[1-3] and vesicular media,[4,5] there has been little investigation of reactions in lyotropic liquid crystals. In lyotropic nematic systems in particular, one can often observe phase transitions from rod to disc to spherical aggregates as a function of either concentration of surfactant, cosurfactant and/or electrolyte, or as a function of temperature.[6] One can orient these structures and observe the degree of ordering of the guest reactants, or their penetration into the micellar media by assessing the polarity of their environment.

In a recent study on the bromination of trans-stilbene in the nematic lyophase of an anionic surfactant—sodium decyl sulfate—we have shown that there is a significant rate change associated with the N_C-N_L (rod-disc) transition.[7] It was the purpose of this study to evaluate whether this type of control of reaction kinetics by manipulation of the size and shape of the aggregates is more general. In this report, we investigate a reaction in a cationic surfactant lyophase: the *o*-iodosobenzoic acid (*o*-IBA) catalyzed ester hydrolysis of *p*-nitrophenyl laurate (PNPL) in myristyltrimethylammonium bromide (MTAB) aggregates.



This reaction was chosen since there already exists a careful study of this reaction in aqueous cationic micelles.[8,9] We anticipated that marked changes in reaction characteristics may occur by using cationic micellar systems which are substantially larger in size and different in shape compared to the conventional micelle.

EXPERIMENTAL

A 1.5×10^{-3}M solution in the liquid crystalline solvent [MTAB/water (N_C); MTAB/water/1-decanol/NH_4Br (N_L)] was prepared by stirring together for 12 hr weighed amounts of PNPL and the components forming the lyomesophases. The N_L and N_C phases were buffered to pH = 7 using phosphate buffer. The N_L-*I* and N_C-*I* transitions were depressed by approximately 1°C in these solutions. 0.4 g of solution was placed in a 1 mm path length uv cuvette, and thermostated at 27°C for 20 min. Ester cleavage was initiated by injecting 30 μl of a 2.0×10^{-3} aqueous solution of *o*-IBA and stirring vigorously. Utilizing a Perkin-Elmer 330 spectrophotometer interfaced with a Model 3600 data station, the appearance of *p*-nitrophenolate anion was monitored at 400 nm for at least two half-lives. No significant phase separation could be detected by optical microscopy for the entire course of the reaction. The pseudo-first order rate constant (k) was evaluated from a plot of ln[PNPL] vs time. At least three independent experiments were conducted on each sample. The estimated error in the rate constants is 10%.

RESULTS AND DISCUSSION

It has been reported that MTAB forms cylindrical or rod-like (N_C) and bilayer or disc-like (N_L) aggregates upon addition of appropriate

TABLE I

Rate constants for the *o*-iodosobenzoic acid (*o*-IBA) cleavage of *p*-nitrophenyl laurate (PNPL) at 27°C in MTAB aggregates.

Phase	wt % of components MTAB	 H_2O	 1-decanol	 NH_4Br	$k \times 10^3$ (s^{-1})
N_C	42	58	—	—	1.3
N_C	41	59	—	—	1.3
N_C	39.5	60.5	—	—	1.4
I	38.4	61.6	—	—	1.8
I	37	63	—	—	1.75
I	36	64	—	—	1.8
N_L	29	61	3.8	6.2	0.24
N_L	30	60	3.8	6.2	0.30
N_L	31	59	3.8	6.2	0.44
N_L	32	58	3.8	6.2	0.49
N_L+I	33	57	3.0	7.0	0.66
I	35	60	1.9	3.1	1.8
I	36	61	1.9	3.1	1.9

amounts of water and water/1-decanol/NH_4Br respectively.[10] The experimentally determined compositions of the components required to form the N_C, N_L and I phases are given in Table I. The pseudo-first order rate constant k, determined for the hydrolysis of PNPL by *o*-IBA in each of these compositions is tabulated in Table I and pictorally depicted in Figure 1. It is observed that k is significantly larger in the N_C phase compared to the N_L phase and that the N_C-I phase transition does not affect k as drastically as does the N_L-I transition. Based on this observation we suggest that changes in the shape of the aggregate alter the solubilization sites, orientation or local motions of the micelle associated PNPL leading to substantial reactivity changes.

The rate constants for this reaction in the liquid crystal N_C phase are approximately 4 times larger than the rate constant in dilute micellar solution. The critical micelle concentration of MTAB is $3.5 \times 10^{-3}M$.[2] The rate constant for ester cleavage in $8 \times 10^{-3}M$ MTAB containing $5 \times 10^{-5}M$ PNPL is $3.6 \times 10^{-4} s^{-1}$ at pH = 7 and 27°C. Two clear advantages exist in running reactions in lyotropic liquid crystal phases: enhanced solubilization of substrate (in this case 100 fold greater than the dilute micellar phase) and rate constant. Thus it appears that the influence of liquid crystal phase transitions on the kinetics of bimolecular reactions is a more general phenomenon. In

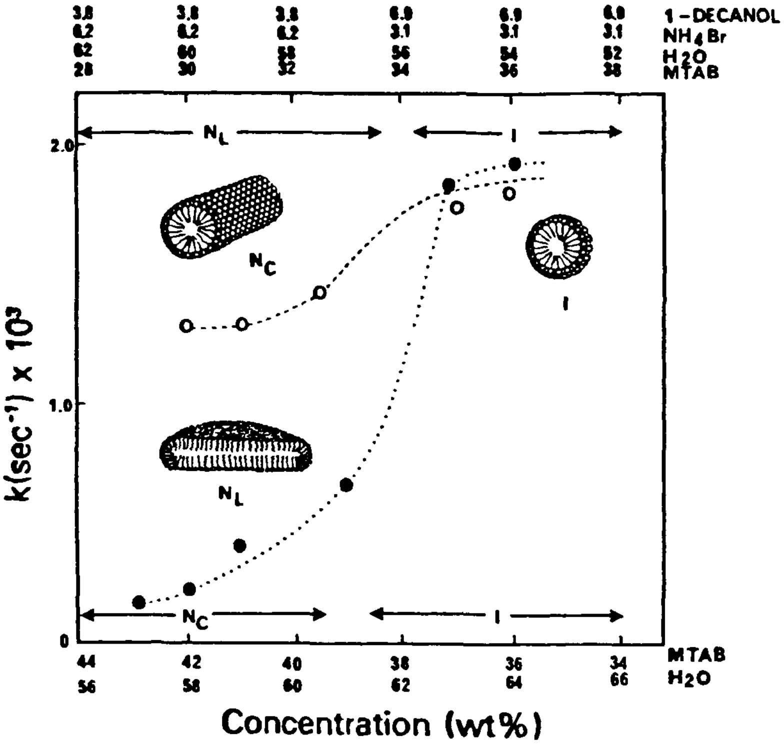


FIGURE 1 Plots of pseudo first order rate constant (k) versus concentration for the *o*-IBA catalyzed cleavage of PNPL in MTAB lyomesophase.

our ongoing work, the extent and scope of this phenomenon will be explored in detail.

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References

1. D. G. Whitten, R. C. Russell and R. H. Schmehl, *Tetrahedron*, **38**, 2455 (1982).
2. J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York (1975).
3. R. A. Moss, K. Y. Kim and S. Swarup, *J. Am. Chem. Soc.*, **108**, 788 (1986).
4. J. H. Fendler and P. Tundo, *Acc. Chem. Res.*, **17**, 3 (1984).

5. J. H. Fendler, *Acc. Chem. Res.*, **13**, 7 (1980).
6. B. J. Forrest and L. W. Reeves, *Chem. Rev.*, **81**, 1 (1981), and references therein.
7. V. Ramesh and M. M. Labes, *J. Am. Chem. Soc.*, **108**, 4643 (1986).
8. R. A. Moss, K. W. Alwis, G. W. Bizzigotti, *J. Am. Chem. Soc.*, **105**, 682 (1983).
9. R. A. Moss, K. W. Alwis and J. S. Shin, *J. Am. Chem. Soc.*, **106**, 2651 (1984).
10. N. Boden, K. Radley and M. C. Holmes, *Mol. Phys.*, **42**, 493 (1981).