High Solubility and Rapid Hydrolysis in Aqueous Nematic Lyotropic Liquid Crystalline Solvents

V. Ramesh and M. M. Labes*

Department of Chemistry, Temple University, Philadelphia, PA 19122, U.S.A.

It is demonstrated that a nematic lyotropic liquid crystalline solvent can be utilized as a reaction medium affording solubility 100-fold greater than the corresponding micellar reagent while retaining rate constants of the same order of magnitude.

The need for efficient cleavage of phosphate, phosphonate, and phosphinate esters for decontamination of exposed areas is a problem which has been approached utilizing micellar, microemulsion, or vesicular media to solubilize these substrates, accompanied by catalysts to enhance the rates of cleavage. Pioneering work has been done in this area by Bunton,[1] Moss,[2—5] Menger,[6] Mackay,[7] and their associates. Utilizing *o*-iodosylbenzoic acid (IBA) and its functionalized derivatives 5-(n-octyloxy)-2-iodosylbenzoate (FIBA-1) and 5[2-(*N*-n-hexadecyl-*N*,*N*-dimethylammonio)ethoxy]-2-iodosylbenzoate (FIBA-2)[3,4] as catalysts, remarkably rapid hydrolysis of such esters has been achieved in micellar media. For example,[3] the hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNDPP) (1×10^{-5} M) in aqueous micellar cetyltrimethylammonium chloride (2×10^{-4} M) catalysed by FIBA-1 (7.14×10^{-5} M) has a pseudo-first-order rate constant of 1.04 s^{-1}.

Recently we have reported that *concentrated* surfactant solutions form rod- or disk-like aggregates which in turn constitute lyotropic nematic phases, and that such phases show dramatic reactivity control through the phase transitions from rod- to disk- to sphere-like aggregates.[8] In the case of the *o*-iodosylbenzoic acid-catalysed hydrolysis of phosphinate esters in the lyotropic nematic phases of myristyltrimethyl-

Table 1. Observed pseudo-first-order rate constants for the cleavage of PNPIP by IBA, FIBA-1, and FIBA-2 at 24 ± 0.5 °C.[a]

	% (w/w) of components					k/s^{-1}		
Phase	MTAB	H_2O	Decan-1-ol	NH_4Br	η/poise	IBA	FIBA-1	FIBA-2
N_C	39	61	—	—	9.3	1.0×10^{-2}	1.8×10^{-2}	5.8×10^{-3}
N_L	30	60	3.8	6.2	2.7	1.0×10^{-4}	1.5×10^{-4}	5.0×10^{-5}
Micellar	0.24	99.76	—	—	0.01	4.2×10^{-3}	1.7×10^{-2}	2.6×10^{-2}

[a] Experimental conditions: pH 8.5 (0.02 M phosphate buffer); [PNPIP] = 3.4×10^{-5} M; [catalyst] = 2.0×10^{-4} M for micellar and 1.0×10^{-2} M for N_C and N_L phases. [b] Reactions were followed spectrophotometrically[8,9] by the release of *p*-nitrophenoxide ion at 400 nm. *k* Values are an average of at least three determinations. ± 10% Errors in *k*.

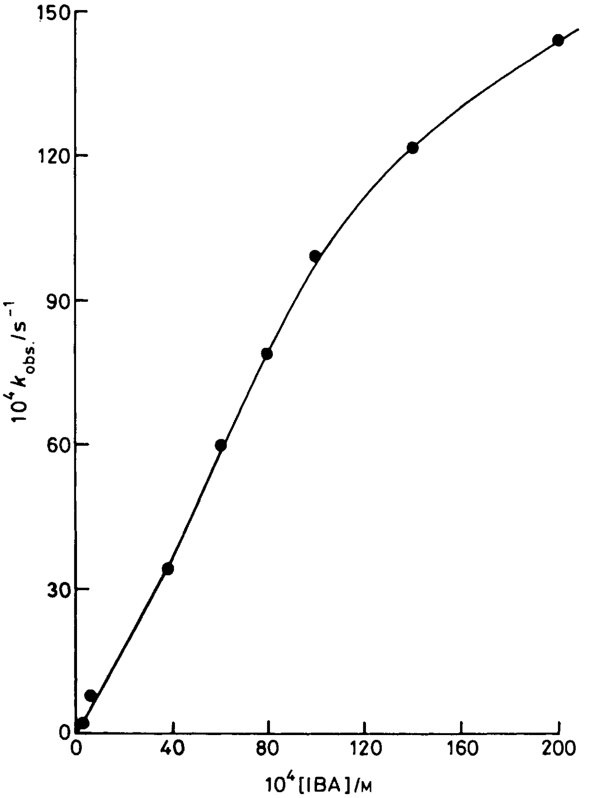


Figure 1. Pseudo-first-order rate constants for the cleavage of PNPIP by IBA as a function of catalyst concentration in N_C MTAB.

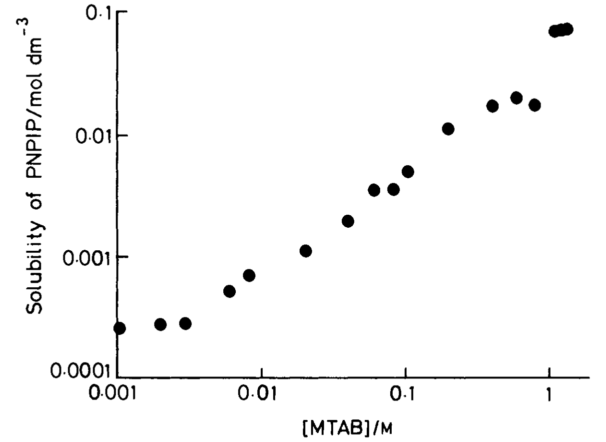
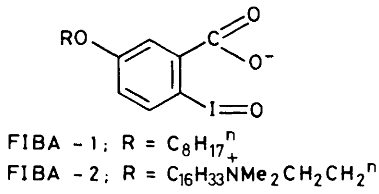


Figure 2. Solubility of PNPIP as a function of MTAB concentration.



ammonium bromide (MTAB), the rod-like N_C phase allows the reaction to proceed three orders of magnitude faster than in the disk-like N_L phase.[9] The rate constant was, however, lower by a factor of 40 in the liquid crystalline phase than in the dilute micellar phase.[9] We now report that we have found conditions in which the rates of hydrolyses in lyotropic liquid crystalline solvents are comparable with those in micellar media.

The reaction studied is the hydrolysis of *p*-nitrophenyl isopropyl(phenyl)phosphinate (PNPIP) using IBA, FIBA-1, and FIBA-2 as catalysts in MTAB/decan-1-ol/NH_4Br/H_2O. Table 1 summarizes the pseudo-first-order rate constants as well as the composition of the various phases and compares the rates with micellar phase. As has been pointed out by a number of authors and discussed by Bunton,[1] usually it is expected that the rate constant reaches a maximum at a certain surfactant concentration, and that additional surfactant simply generates more micelles which distribute substrate or catalyst to more sites and lower the observed rate of reaction. In this work we chose to have not only a high concentration of anisotropic micelles but also an appropriately high concentration of catalyst so that the catalyst/aggregate ratio is constant. As can be seen from Table 1, at a catalyst concentration of 10^{-2} M and a detergent concentration of 39% by weight (1.16 M), the rate constant is actually higher than that in micellar media at a catalyst concentration of 2×10^{-4} M and a detergent concentration of 0.24% by weight (9×10^{-3} M). These concentrations are selected so that the catalyst/aggregate ratios in the concentrated and dilute solutions are constant; in both cases there are about 20 catalyst molecules per aggregate.

Figure 1 presents the dependence of the rate constant on catalyst concentration in the N_C phase. Note that the rate constant is starting to level off with increased concentration of catalyst, and that we have reached the solubility limit of IBA in the detergent solution. The solubility of PNPIP as a function of surfactant phase is shown in Figure 2. Near the critical micelle concentration of 3.5×10^{-3} M, there is an increase in solubility; above this point solubility increases linearly with log concentration. At the isotropic-N_C phase transition (~1 M), there is an abrupt increase of solubility presumably associated with the formation of the larger rod-like aggregates.

In order to demonstrate that IBA is a turnover catalyst, the approach of Mackay *et al.*[7] was followed where repeated addition of PNPIP to the same reaction mixture was effected. Firstly, PNPIP was added to the lyomesophase solution and kinetics followed. After 10 half-lives, a second addition of PNPIP was made to the same solution and kinetics were again followed. The pseudo-first-order rate constants obtained from both segments of the reaction were identical within experimental error, indicating that IBA concentration remained unaltered. In earlier work, it has already been demonstrated that IBA functions catalytically in the N_C phase even at high substrate : catalyst ratio.[9]

In conventional micellar phases, Moss *et al.*[3,4] have shown that functionalized IBA can enhance the rate of hydrolysis of phosphate esters. For the cleavage of PNPIP by IBA and two functionalized catalysts, similar enhancements are seen in the micellar phase (Table 1), but little enhancement is seen in the liquid crystalline phases. Indeed for one functionalized catalyst (FIBA-2, Table 1), the rate actually decreases as compared to the non-functionalized catalyst. One possible explanation is that the bulk viscosity of and the microviscosity within the lyomesophase aggregate are vastly different from that of micellar aggregates. FIBA-2, with its long hydrocarbon chain, could be buried deeper in the lyomesophase aggregate and experience greater constraints on its motion than IBA.

In conclusion, we have found that the nematic lyophase of $MTAB/H_2O$ is a highly appropriate medium for conducting hydrolyses of phosphorus esters. Such a phase solubilizes 100-fold greater concentrations than conventional micellar phases. At identical catalyst : aggregate ratios, the pseudo-first-order rate constants are comparable in micellar and liquid crystalline (N_C) solvents. It is anticipated that similar utility as reaction media can be found with other surfactant liquid crystals and other substrates.

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