Dialkylaminopyridine catalysed esterolysis of *p*-nitrophenyl alkanoates in different cationic microemulsions

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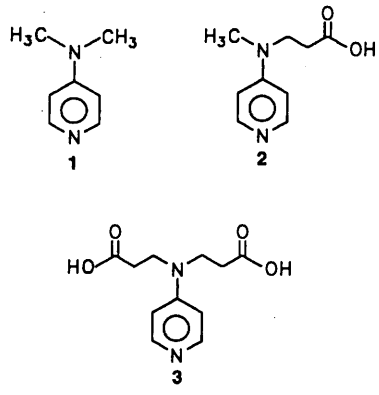
The reactions of *p*-nitrophenyl alkanoate esters with dialkylaminopyridine (DAAP) and its related mono- and di-anionic water-soluble derivatives have been studied separately in three different microemulsion (ME) media. These were (*a*) oil-in-water ME (O/W), (*b*) water-in-oil ME (W/O) and (*c*) a bicontinuous ME, where oil and water are in nearly comparable amounts. All the ME systems were stabilized by cationic surfactant, cetyltrimethylammonium bromide (CTABr) and butanol as a cosurfactant. The second-order rate constants (k_2) in the microemulsion media were also determined over a phase volume (φ) of approximately 0.13–0.46. In order to explain the contribution of effective concentration of the nucleophiles in the aqueous pseudophase, corrected rate constants $k_{2\varphi} = k_2(1 - \varphi)$ were obtained. The rate constants of the corresponding hydrolytic reactions were also examined in CTABr micelles. While the DAAP catalysts were partitioned between the micellar and aqueous pseudophases in ME, the hydrophobic substrates were found to be mainly confined to oil-rich phases. Present results indicate that the main effect of ME media on the hydrolysis reaction is due to both electrostatic reasons and substrate partitioning.

Introduction

Micellar and vesicular aggregates have been extensively employed as reaction media for different esterolysis reactions.[1] Their mode of action involves hydrophobic association of the organic substrates with reactive nucleophiles cosolubilized in the host organized assemblies.[2,3] An alternative media for partial reproduction of the effects of substrate partitioning, binding and functional catalyses involving the reacting partners are provided by self-organizing surfactant, oil, water and cosurfactant in a single pot. This type of organized medium is described as a microemulsion.[4,5] Microemulsion droplets are stabilized by combination of a short chain alcohol and surfactant and are optically stable oil-in-water or water-in-oil dispersions. Owing to their high solubilization capacities microemulsions are increasingly being used as a medium for detoxification of harmful compounds such as mustard and organophosphates.[6-8]

Over the last few years, we have examined a variety of organized assemblies,[9,10] including the reactivities of dialkylaminopyridine (DAAP) functionalized surfactants in micellar media. 4-Dialkylaminopyridines and their derivatives showed high reactivity in a number of systems and were frequently employed as 'supernucleophilic' catalysts in a variety of reactions.[11-13] However, no such studies have been reported so far which examines the esterolytic potencies of DAAPs in microemulsion aggregates. In this paper we describe the reactivities of DAAP catalysts **1–3** towards hydrolysis of *p*-nitrophenyl acetate and also compare their esterolytic capacities against a set of *p*-nitrophenyl alkanoates (n = 2–14) in different cationic microemulsion recipes that vary in terms of water and oil content.



Results and discussion

Microemulsions as reaction media

Different microemulsions (ME) were prepared by mixing definite quantities of various components necessary for the formation of ME. The recipes for different MEs were obtained from a pseudo-ternary phase diagram which will be described in detail elsewhere.[14] The three compositions of the ME chosen for each kinetic study were from three different regions of the phase diagram and the MEs used herein for the kinetic studies remained optically stable. The specific details pertaining to the compositions of different MEs employed in this work for studying the esterolysis reactions have been summarized in Table 1. As is clear from the relative amounts of water and oil, the ME1 can be described as water-rich, oil-in-water ME, whereas the ME3 represents an oil-rich, water-in-oil system. However, the ME2 is probably a bicontinuous system [15] which can neither be described as a water-in-oil or an oil-in-water formulation as both the oil and water contents are quite comparable. An idealized aggregation pattern present in one representative ME system has been exemplified schematically (Fig. 1). In this system, ME1 represents an oil-in-water ME and also contains both the catalyst and the substrate.

Table 1 Percentage composition by weight of microemulsion formulations[a]

ME	Water[b]	Oil[c]	Surfactant[d]	Cosurfactant[e]
1	87.93	1.97	5.05	5.05
2	35.32	45.84	9.42	9.42
3	2.5	87.5	5.0	5.0

[a] See Experimental section for details. [b] Phosphate buffer, pH 8.7. [c] Cyclohexane is the oil. [d] Cetyltrimethylammonium bromide. [e] Cosurfactant is butanol.

The hydrolysis reactions of *p*-nitrophenyl acetate (PNPA) in

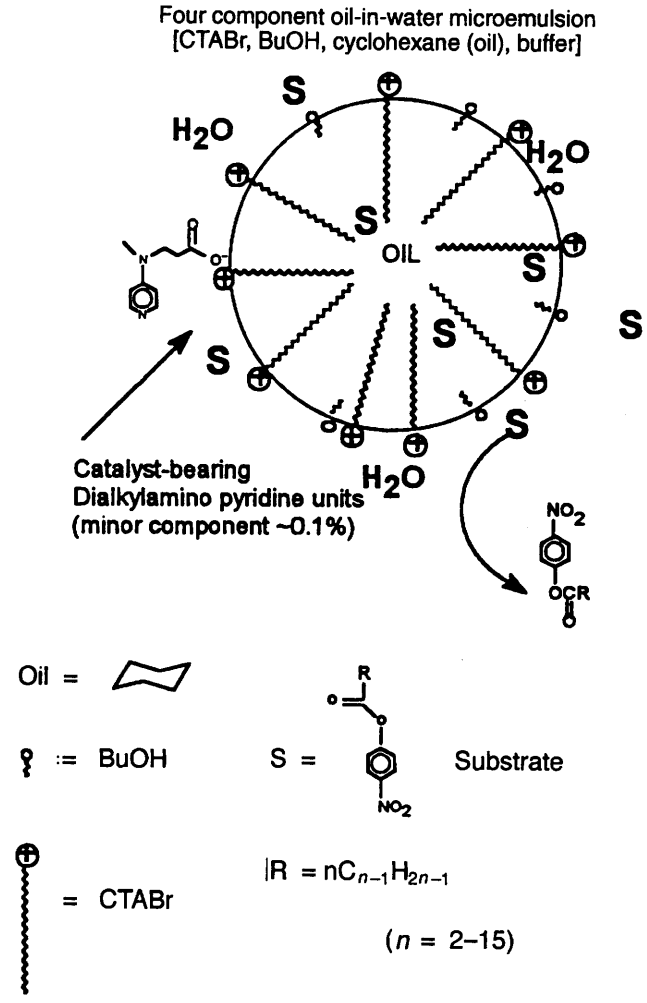


Fig. 1 Schematic representation of oil-in-water (O/W) microemulsion consisting of CTABr, butanol, cyclohexane and buffer with DAAPs and ester substrates incorporated in the system

three different MEs in the presence of DAAPs **1–3** were studied. The catalyst and substrate concentrations in different MEs were maintained uniformly at 5×10^{-4} and 2.5×10^{-5} M, respectively. Inclusion of such small quantities of DAAPs or substrates did not cause any noticeable effect on the microemulsion stability and allowed examination of the time-course studies by following the changes in optical absorbancies arising out of the reaction product formation.

pK_a determinations

The pK_a values for different DAAPs **1–3** in water are known.[13a] The corresponding values in cationic aggregates such as micellar or ME assemblies are, however, not available. Therefore, we decided to first determine the pK_a values for different DAAPs **1–3** in micellar CTABr. These were determined titrimetrically in aqueous micellar (5×10^{-3} M CTABr) solutions (Fig. 2). Plots of the pH *vs.* rate constants for *p*-nitrophenyl acetate hydrolysis in 5×10^{-3} M CTABr micellar solution at several pH values also gave pK_a values. Importantly, the systemic pK_a values for **1–3** obtained by either procedure were very similar.

In CTABr micelles, 4-(dimethylamino)pyridine, **1** showed greater reactivity toward PNPA when compared with the same as the other DAAP derivatives, *e.g.* 3-(methyl-4-pyridylamino)-propionic acid, **2** and 3,3′-(4-pyridylamino)dipropionic acid, **3** (see Table 2). The nucleophilic forms of catalysts **1**, **2** and **3** are the free unprotonated forms of the respective dialkylamino-pyridine moieties. Therefore, the pK_a values for the conversions of conjugate acid dialkylaminopyridinium moieties to the

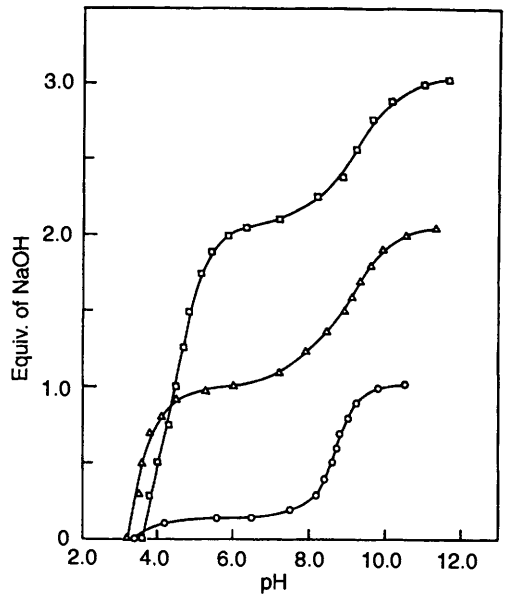


Fig. 2 Titration curves for **1**·HCl (○), **2**·HCl (△) and **3**·HCl (□) at 25 ± 0.1 °C and μ = 0.1 M (NaCl) in aqueous CTABr (5×10^{-3} M) micellar solutions

Table 2 Kinetic parameters for micellar esterolysis of *p*-nitrophenyl acetate by DAAP catalysts **1–3**[a,b]

Catalyst	pK_a[c]	$k_\psi/10^{-3}$ s^{-1}	k_2/M^{-1} s^{-1}	k_{cat}/M^{-1} s^{-1}[d]
1	8.85 [41.4%]	9.3	18.6	45
2	9.0 [33.5%]	2.5	5.0	15
3	9.1 [28.4%]	1.5	3.1	11

[a] Conditions: 0.02 M phosphate buffer, pH 8.7, μ = 0.08 M (KCl), 25 ± 0.1 °C, [catalyst] = 5×10^{-4} M, [*p*-nitrophenyl acetate] = 2.5×10^{-5} M, 1.0 vol% CH_3CN. [b] Concentration of CTABr at which k_ψ^{obs} was determined = 5×10^{-3} M. [c] See text for discussion of pK_a values. Values in brackets are % ionizations at pH 8.7. [d] $k_{cat} = k_\psi^{obs}$/[DAAP catalyst], corrected for 100% ionization of catalytic systems.

corresponding unprotonated dialkylaminopyridine forms are important data in all the cases. The reported pK_a of DAAP catalysts (**1**, **2** and **3**) in water are 9.71, 9.78 and 9.76, respectively.[13a] However, when solubilized in CTABr micelles, the corresponding pK_a values for these catalysts decrease to 8.85, 9.0 and 9.1 for **1**, **2** and **3**, respectively (Fig. 2). The extents of decrease of the pK_a values are also functions of [CTABr].[9] The decrease in the pK_a values for **1**, **2** and **3** could be attributed to the binding of these catalysts to net cationic micellar surfaces. The ionizations of the carboxyl groups of micellar or ME bound reagents **2** and **3** however, also suppress the extent of deprotonation of their protonated dialkylaminopyridinium forms into unprotonated nucleophilic dialkylaminopyridine forms. This also leads to partial neutralization of the positively charged cetyltrimethylammonium head groups. Both factors mitigate the catalytic potential for **2** and **3** in mildly basic media at pH 8.7. This factor is absent with **1** and thus the pK_a of **1** has been found to be a little lower when compared with that of **2** and **3**. From the pK_a values, it is possible to determine percentages of the nucleophilic forms of **1–3** in micellar and ME media (see below).

Kinetic studies with 1–3 in micellar or ME aggregates

Esterolysis reactions using **1–3** with PNPA were performed under the following conditions: 25 ± 0.1 °C, pH = 8.7, 0.02 M phosphate buffer, μ = 0.08 M (KCl), [PNPA] = 2.5×10^{-5} M. Solubilization of 5×10^{-4} M **1**, **2** or **3** required a few minutes of initial stirring in the buffered CTABr ME media. Reactions

Table 3 Rate constants for the reaction of *p*-nitrophenyl acetate with DAAP catalysts **1**–**3** in different CTABr microemulsions

ME	Phase volume (φ)[a]	Catalyst	$k_\psi^{obs}/10^{-3}$ s^{-1} [b]	k_2/M^{-1} s^{-1} [c]	$k_2(1-\varphi)/M^{-1}$ s^{-1} [d]
1	0.13	**1**	2.0	4.0	3.5
1	0.13	**2**	1.9	3.7	3.3
1	0.13	**3**	1.5	3.0	2.6
2	0.46	**1**	0.4	0.8	0.5
2	0.46	**2**	0.4	0.8	0.5
2	0.46	**3**	0.3	0.5	0.3
3	0.33	**1**	0.6	1.1	0.8
3	0.33	**2**	0.2	0.5	0.3
3	0.33	**3**	0.2	0.4	0.3

[a] Phase volume (φ) is given by $1 - wg$, where w = the weight fraction of the major component, water or oil and g is the specific gravity of a given microemulsion. [b] k_ψ^{obs} = pseudo-first-order rate constant. [c] Second-order rate constant k_2 (M^{-1} s^{-1}) where, $k_2 = k_\psi^{obs}/$[DAAP catalyst]. [d] Corrected for effective concentration of reagent, $k_{2,\varphi} = k_2(1-\varphi)$. Data tabulated as $k_2(1-\varphi)$ M^{-1} s^{-1}.

were followed beyond 90% completion and showed good pseudo-first-order kinetics. The reproducibilities of k_ψ with all the kinetic runs were generally better than 3% with micellar systems. With reactions in the MEs, the reproducibility of k_ψ remained within 5% for all the catalytic systems. From the respective pseudo-first-order rate constants for the cleavage reactions of PNPA in the micellar or in either of the three different MEs, different catalytic rate constants (k_2) were calculated from the ratios of k_ψ^{obs}/[catalyst]. The relevant data with reactions in micellar media and with reactions in different MEs have been included in Tables 2 and 3, respectively.

Among the three catalysts included in ME1, the neutral **1**, showed a marginally higher rate of hydrolysis (Table 3) of PNPA compared with its charged counterparts, **2** and **3**, under similar kinetic conditions. This could be due to a greater extent of deprotonation of **1** (favourable pK_a) if we assume that the corresponding pK_a values for **1** when included in CTABr stabilized cationic MEs remain comparable to that in CTABr micelles. It should be mentioned here that the rate of DMAP promoted cleavage is *ca.* 43-fold greater than the background rate of hydrolysis of *p*-nitrophenyl acetate in ME1 microemulsion assemblies at pH 8.7. The origin of such a rate acceleration lies in the hydrophobic binding of the catalyst and the substrate at the aggregate interfaces and *ca.* 0.9 unit reduction in pK_a of DMAP relative to that in aqueous buffer.

Several features of Table 3 are noteworthy. The DAAPs, irrespective of their structures, showed greater esterolytic reactivities in water-rich ME1 than in either oil-rich ME3 or bicontinuous ME2. In ME1, the DAAPs may be present at the interfaces, whereas in ME2 and ME3, the DAAPs may be confined within the 'water-pool' region. The order of reactivities in ME1, ME2 and ME3 systems, is also similar to their order of solubilities in water, *i.e.* **3** > **2** > **1**. Compound **3** is highly soluble in water. Hence it might tend to stay in the water-pool, which may render it inaccessible to substrate molecules which should be primarily located in the oil-rich microdomains or at the interfaces (for substrates with a shorter chain) (Table 4).

Table 3 also shows the effect of phase volume φ (the volume occupied by micro-droplets) on the hydrolysis rate. Since the effective concentration of reagents is altered due to the differences in location of water-soluble DAAP catalysts and oil-soluble ester substrates, the values of k_2 are corrected,[8] and are represented as $k_2(1-\varphi)$ in Table 3. The intrinsic rate constant (the rate constant for the reaction at the interface) should be directly proportional to $k_2(1-\varphi)$ values. The $k_2(1-\varphi)$ values decrease with increasing φ. In the ME1 system, which has a low φ value, the reagents are concentrated mostly at the interface and hence the reaction is fast. In the cases of ME2 and ME3 which have greater phase volume, the substrate is located mostly in the oil phase and hence may not conveniently be available for hydrolysis. This also leads to slower esterolysis in ME2 and ME3. The relatively higher rate for **1** in the ME3 system suggests that DMAP is present mostly at the interfacial region because it is sparingly soluble in water. The ME2 system has the maximum phase volume, but the rate constants for PNPA esterolysis with **2** and **3** are larger when compared with that in ME3 system. This could possibly be due to the differences in the internal structure of different ME aggregates.

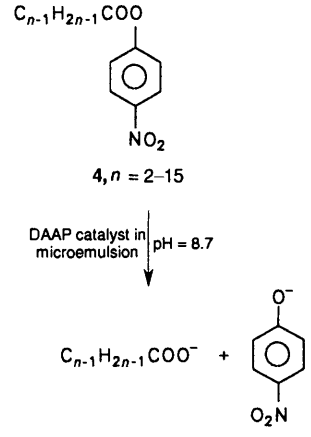
Table 4 Partition coefficient (K_D) values for *p*-nitrophenyl alkanoates in cyclohexane and water[a]

Entry	Substrate	K_D[b]	R_f[c]
1	**4** (n = 2)	10.8	0.2
2	**4** (n = 8)	95.9	0.5
3	**4** (n = 12)	205.4	0.6

[a] See text for experimental conditions. [b] K_D = [*p*]cyclohexane/[*p*]-water, where [*p*] = concentration of substrate in either cyclohexane phase or water phase. [c] R_f values are determined by thin layer chromatography, using an eluent composed of 7% ethyl acetate in light petroleum (bp 60–80 °C).

Influence of substrate chain length

Hydrophobic association of a nucleophile with a substrate, leading to rate enhancements, is well documented in the literature.[16] The migration of hydrophobic substrates to lipophilic domains in aqueous media has been shown.[17] Examination of alkaline hydrolysis reactions of substrates such as *p*-nitrophenyl stearate, laurate, caprylate and acetate in a detergentless water-in-oil (hexane) (W/O) microemulsion stabilized by propan-2-ol[18] revealed that the rate increased with increasing hydrophilic character of the esters.[18] However, a systematic examination of the dependence of ester hydrolysis rates as a function of substrate chain length in a cationic surfactant stabilized microemulsion formulation has not been examined. In view of this, DAAP-mediated hydrolysis of a series of *p*-nitrophenyl alkanoates **4** ranging from the acetate to the



tetradecanoate (n = 2–15) were examined. This study allows estimation of the hydrophobic effects in the hydrolysis catalysed by the reagents **1**, **2** and **3** solubilized in CTABr ME. The reactions were carried out under pseudo-first-order conditions in a phosphate buffer at pH 8.7 with [substrate] = 2.5×10^{-5} M and [catalyst] = 5×10^{-4} M. Since the alkanoate esters differed only by the number of CH_2 groups in the alkanoate chain, the results of these studies provide indications of the preferences of different ME-bound DAAPs towards substrates of specific chain length.

Fig. 3 shows a plot of second-order 'catalytic' rate constants ($k_{cat.} = k_\psi^{obs}$/[catalyst]) as a function of the chain length of

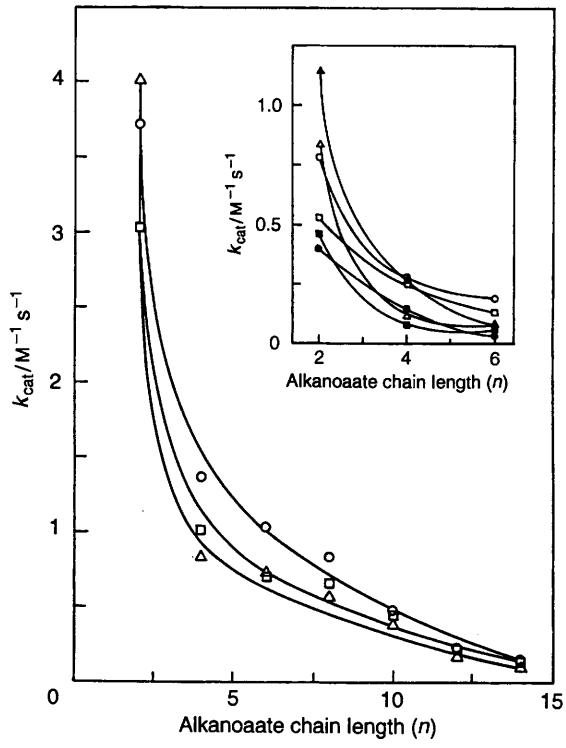


Fig. 3 Dependence of the catalytic rate constants (k_{cat} M^{-1} s^{-1}) for esterolysis as a function of alkanoate chain length of **4** in oil-in-water microemulsion (ME1) at 25 ± 0.1 °C. The aqueous phase is 0.02 M $H_2PO_4^{2-}$–HPO_4^{2-}, pH = 8.7, μ = 0.08 M KCl, [**4**] = 2.5 × 10^{-5} M, [cat] = 5 × 10^{-4} M. **1** (△), **2** (○), **3** (□). See Table 1 for ME1 composition. Inset. The plots of variation of catalytic rate constants ($k_{cat}/M^{-1}\,s^{-1}$) for DAAP catalysts **1**, **2** and **3**, in ME2 and ME3. **1** (△), **2** (○), **3** (□) for ME2 and **1** (▲), **2** (●) and **3** (■) for ME3.

the alkanoyl portion of the substrate. To understand clearly the effects of substrate chain length on esterolytic rates, we determined the k_2/k_6 ratios for the pseudo-first-order rate constants of the hydrolyses of **4** (n = 2) to that of **4** (n = 6) in different microemulsions. We found that the esterolyses rate of **4** (n = 2) was *ca.* 5.4-fold greater than that of **4** (n = 6) with **1**, *ca.* 3.6 times greater with **2** and *ca.* 4.3-fold greater with **3** in ME1. The k_2/k_{14} ratio for the pseudo-first-order rate constants for hydrolyses of **4** (n = 2) to that of **4** (n = 14) with **1** in ME1 was found to be even higher (*ca.* 13.9) indicating a preference of esterolysis towards shorter chain substrates in water-rich MEs. In the more oil-rich ME2 and ME3 microemulsions, the corresponding ratios for the rates of esterolysis against **4** (n = 2) and **4** (n = 6) are considerably greater than the same in the ME1 microemulsion. Thus, we found the k_2/k_6 ratios to be 9.3, 4.1 and 4.1 for **1**, **2** and **3**, respectively, in the ME2 and 14.3, 13.3 and 7.5 for **1**, **2** and **3**, respectively, in the ME3 system. Remarkably however, when the corresponding rate constant ratio was determined for the hydrolyses of **4** (n = 2) to that with **4** (n = 6) by **1** in micellar CTABr assemblies, the same was only *ca.* 2.9-fold greater and *ca.* 1.5 and *ca.* 1.1 times higher, respectively, for **2** and **3** in CTABr micelles under comparable kinetic conditions. Note however, in the CTABr micellar media alone at pH 8.7 in the absence of DAAPs, the rate constants increased first with an increase in chain length (up to n ~ 8), then gradually decreased with a further increase in the chain length beyond n > 10. In CTABr ME alone at pH 8.7, in the absence of DAAPs, the rate constants increased monotonously with the decrease in the chain length irrespective of the water-content of the microemulsion (Fig. 3). Thus, all the presently described ME systems prefer reactions toward esters with diminishing hydrophobicity and appear to protect the substrates with longer chain length. The protection of the hydrophobic substrates was more pronounced with oil-rich MEs and with more water soluble DAAPs. With increasing hydrophobicity of the substrates, greater substrate partitioning into the oil phase takes place. In this situation, substrates become unavailable to the water soluble DAAPs that are likely to be located at the interface or in the water-pool. The experimentally determined partition coefficient values of the substrates also support this notion (Table 4). Interestingly, when DAAPs are covalently attached to amphiphilic headgroups, under comicellar CTABr conditions however, the hydrolysis rate constants were found to be maximal with medium chain (n ~ 6–10) substrates.[9] Therefore, the substrate hydrophobicities and reagent locations in different loci of ME play an important role in such reactions.

In summary, we found that the esterolytic reactions were faster in micelles than that in MEs even when both the aggregates are cationic. The reactivities in terms of substrate hydrophobicities also differ in the two organized media. Such variations could originate from differences in core structures and also due to differential substrate partitioning effects.

Experimental

General methods

Melting points were taken on a uni-melt apparatus using open capillary tubes and are uncorrected. ^{1}H NMR spectra were obtained on a JEOL FX-90 NMR spectrometer (90 MHz). Chemical shifts (δ) are reported in ppm downfield from the internal standard. Steam distilled water was used for all kinetic studies and pH measurements were made using Schott pH-meter CG-825 under inert atmosphere.

Materials

The commercially available DMAP was recrystallized from ethanol, CTABr was recrystallized and used for making the microemulsion. Silica gel (60–120 mesh) (Merck) used for chromatography. Butanol and cyclohexane were freshly distilled before use.

4-(Methylamino)pyridine. 4-Chloropyridine hydrochloride (Aldrich) (2.4 g, 0.016 mol) was placed in a 700 Paar steel reactor. Aqueous 40% CH_3NH_2 solution (Merck) (140 ml) was cooled to 0 °C and poured directly into the reactor and the mixture was heated at 175 °C under 25 atm pressure for 8 h. The reaction mixture was then allowed to cool and the contents were extracted with 400 ml of $CHCl_3$. The solvent from the organic layer was removed *in vacuo* leaving a yellow material which was further purified by sublimation, 4-(methylamino)pyridine; yield 92%, mp 122–124 °C, lit.,[19] 124.5–126 °C. δ_H(90 MHz, D_2O), 3.0 (s, 3 H), 6.7 (apparent d, 2 H) and 8.2 (apparent d, 2 H).

Methyl 3-(methyl-4-pyridylamino)propionate. A solution of 4-(methylamino)pyridine (1.74 g, 0.016 mol) and 16 ml of methyl acrylate (Merck) was refluxed for 20 h. Excess methyl acrylate was removed under vacuum and the oily residue thus obtained was purified by column chromatography over silica gel by elution with 5% MeOH in $CHCl_3$ to yield 42% of the title compound. δ_H(90 MHz, $CDCl_3$) 2.6 (t, 2 H), 3.0 (s, 3 H), 3.7 (s, 3 H), 3.75 (t, 2 H), 6.0 (apparent d, 2 H) and 8.2 (apparent d, 2 H). In the freezer, it was recrystallized from EtOH in the presence of 1 equiv. of HCl, mp 116–118 °C, lit.,[13a] 115–117 °C.

3-(Methyl-4-pyridylamino)propionic acid (2). To a solution of 3.2 g (0.02 mol) of methyl 3-(methyl-4-pyridylamino)propionate in 1:1 MeOH and water, 1.6 g (0.04 mol) of NaOH was added. The resulting mixture was refluxed for approximately 0.5 h. This gave a yellow solution which was cooled and carefully neutralized with HCl which was concentrated and the residue was purified by column chromatography over silica gel by elution with 1:1 MeOH–$CHCl_3$ to yield 50% of **2**; mp 194–196 °C, lit.,[13a] 195–197 °C. δ_H(90 MHz, D_2O) 2.6

(t, 2 H), 3.2 (s, 3 H), 3.9 (t, 2 H), 6.9 (apparent d, 2 H) and 8.0 (apparent d, 2 H).

Dimethyl 3,3′-(4-pyridylamino)dipropionate. A mixture of 1 g (0.01 mol) 4-aminopyridine (Aldrich) and methyl acrylate (15 ml) was refluxed for 24 h. Excess methyl acrylate was removed leaving a gummy residue which was purified by column chromatography using 1:9 MeOH–$CHCl_3$ to yield 40% of the title compound; mp 60 °C, lit.,[13a] 59–60 °C. δ_H(90 MHz, $CDCl_3$) 2.6 (t, 4 H), 3.7 (t, 4 H), 3.7 (s, 6 H), 6.5 (apparent d, 2 H) and 8.2 (apparent d, 2 H).

3,3′-(4-Pyridylamino)dipropionic acid (3). Dimethyl 3,3′-(4-pyridylamino)dipropionate (1.0 g, 0.0037 mol) was dissolved in 1:1 MeOH–water containing 0.29 g (0.007 mol) of NaOH. The mixture was refluxed for 1 h, allowed to cool and neutralized with HCl at 0 °C and concentrated. The crude product was purified by column chromatography over silica gel using 1:1 MeOH–$CHCl_3$ to yield 60% of **3**; mp 200–202 °C, lit.,[13a] 198–200 °C. δ_H(90 MHz, D_2O) 2.5 (t, 4 H), 3.7 (t, 4 H), 6.9 (app. d, 2 H) and 8.0 (app. d, 2 H).

Potentiometric pH titration

Solutions of protonated DAAP catalysts (1×10^{-3} M) in aqueous micellar 5×10^{-3} M CTABr (μ = 0.1 M NaCl) were titrated with aqueous carbonate free 0.1 M NaOH solution under nitrogen. The temperature was maintained at 25 ± 0.1 °C. After addition of each aliquot of NaOH solution, the pH values were recorded with a Schott pH-meter CG 825.

Partition coefficients

The partition coefficients of the substrates in water and cyclohexane (oil) at 25 °C were determined. The substrate concentration in the water-phase was determined spectrophotometrically, by hydrolysing the ester with excess NaOH and monitoring the absorbance of the *p*-nitrophenoxide ion (PNPO) (λ = 400 nm, $\varepsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}) formed. The hydrolysis produces a stoichiometric amount of PNPO in a 1:1 ratio with the ester. The ester concentration in the cyclohexane phase was obtained by mass balance knowing the volume of the cyclohexane phase. The partition coefficient K_D was calculated by the following equation, $K_D = [p]_{cyclohexane}/[p]_{water}$.

Phase volume determinations

The phase volumes (φ) were determined from the equation $\varphi = 1 - wg$, where w = weight fraction of water or oil depending on the nature of the ME and g is the specific gravity of the microemulsion.

Kinetic studies

The appearance of *p*-nitrophenoxide was monitored at 400 nm. The kinetic run was initiated by injecting a 5 μl portion of PNPA in CH_3CN into a cuvette containing 2.97 ml of micellar or ME solution containing 5×10^{-4} M of either **1**, **2** or **3** at pH 8.7, [0.02 M phosphate buffer, μ = 0.08 M (KCl)]. Each reaction was carried out in a thermostatted compartment (TCC-260) at 25 ± 0.1 °C of a Shimadzu model UV 2100 spectrophotometer. Pseudo-first-order rate constants were obtained from computer generated correlations of log ($A_\infty - A_t$) with time for the appearance of *p*-nitrophenoxide. All reactions showed good pseudo-first-order kinetics. Duplicate runs generally showed a measurement discrepancy of less than ± 5%.

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