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Cetylpyridinium bromide-based microemulsions as media for the hydrolysis of phosphorus acids esters in the presence of primary amines

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The relationships between the structure of microemulsions and the kinetics of hydrolysis of phosphorus acids esters catalysed by amines in oil-in-water microemulsions have been examined.

Microemulsions are transparent isotropic thermodynamically stable oil–water dispersion systems stabilised by surfactants and co-surfactants. The high solubilising ability of microemulsions and very high areas of the oil–water interface provide effective contact between reactants differently soluble in water and oil. Such systems can be successfully used as media for various chemical reactions.[1–4]

In this work, we studied the hydrolysis of phosphorus acid esters in the presence of primary *n*-alkylamines depending on the structure of the reaction medium, namely, an oil-in-water microemulsion (ME-1) based on cetylpyridinium bromide (CPB) of the following composition:[4] CPB, 9.5; *n*-butanol, 9.1; *n*-hexane, 2.0; and water, 79.4 wt.%. Water containing 98% D_2O (Ferak) was used in the NMR measurements.

Previously,[5] we examined the kinetics of aminolysis of esters in CPB-based oil-in-water microemulsions. Here, we consider the hydrolysis of *O*,*O*-(bis-*p*-nitrophenyl)methylphosphonate **1** in analogous microemulsions with the participation of *n*-alkylamines. The catalytic effect of amines is proportional to the basicity of the nucleophile.[6,7]

$$\underset{\mathbf{1}}{MeP(O)(OC_6H_4NO_2\text{-}p)_2} + H_2O{\cdot}H_2NR + 3H_2O \longrightarrow$$

$$MeP(O)(OC_6H_4NO_2\text{-}p)O^- + {}^-OC_6H_4NO_2\text{-}p + 2H_3O^+ + H_2O{\cdot}H_2NR$$

The observed rate constants (k_{obs}) linearly depend on the concentration of amines that are unable to self-associate. If the amines participate in the micelle formation or occur in micellar solutions of surfactants, the micellar catalytic effect leads to deviations from the Brönsted relation.[7,8]

The kinetics of hydrolysis of **1** in ME-1 in the presence of primary amines was monitored spectroscopically under conditions of the pseudo-first-order reaction by measuring an increase in the absorbance due to the liberation of *p*-nitrophenolate (λ = = 400 nm).

Unlike micellar solutions,[8] the $k_{obs} = f(c_{am})$ functions in CPB-based microemulsions are linear over a wide concentration range (up to 0.2 mol dm^{-3}) for amines of various hydrophobicity (Figure 1). The second-order rate constants (k_2) averaged by volume are presented in Table 1. Note that, in contrast to the micellar solutions of CPB, all of the amines in ME-1 exhibited no significant difference in the reactivity. Butylamine and octylamine were found to be more powerful general-base catalysts in ME-1 than their hydrophobic homologues.

In the hydrolysis of **1** in the micellar CPB solutions, the ratio between the contributions from alkaline hydrolysis and hydrolysis catalysed by amines *via* the general-base mechanism, as well as the resulting micellar catalytic effect, depends on the hydrophobicity of the amines.[8] For the reaction in ME-1, the contribution from the general-base mechanism increases and becomes predominant with increasing amine concentration and decreasing pH (Figure 1); the influence of the hydrophobicity of the nucleophile is insignificant. Moreover, the high solubilising ability of ME-1 makes it possible to obtain systems with high amine concentrations. This leads to a significant catalytic effect, which is difficult to achieve in molecular and micellar solutions.

The structure of microemulsions was studied by Fourier transform pulsed-gradient spin-echo ^{1}H NMR spectroscopy[8–10] using a modified TESLA BS-587 A NMR spectrometer at 80 MHz.

The most intense ^{1}H NMR signals were used for the self-diffusion measurements in ME-1 (Table 1). The self-diffusion coefficients of water and butanol were determined from the signals of water protons (4.80 ppm with reference to tetramethyl-

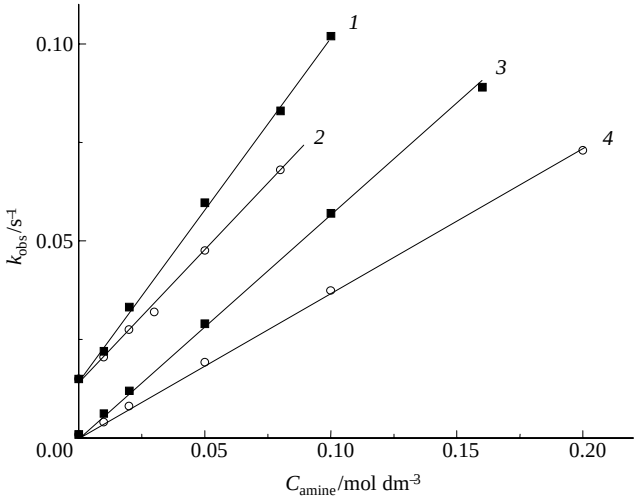

Figure 1 The observed rate constant of hydrolysis for **1** (25 °C) as a function of *n*-alkylamine concentration: octylamine, (*1*) α = 1.0 (pH 10.3), (*2*) α = 0.7 (pH 9.4); cetylamine, (*3*) α = 1.0 (pH 10.3), (*4*) α = 0.69 (pH 9.4).

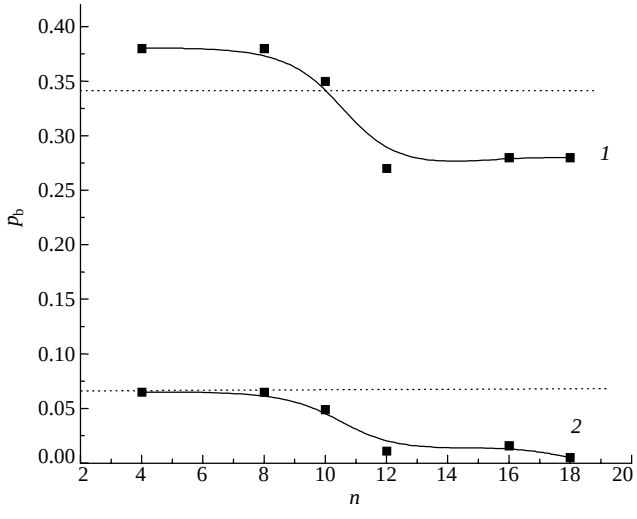

Figure 2 The weight fraction of (*1*) butanol or (*2*) water included in the drops of ME-1 as a function of carbon-chain length (*n*) in the amine hydrocarbon residue. Dotted lines show the corresponding values for amine-free ME-1.

Table 1 Self-diffusion coefficients of ME-1 components (30±0.5 °C) and the second-order rate constants of the hydrolysis of **1** in the presence of primary amines.[a]

Amine	D_{CPB}/ 10^{-11} m^2 s^{-1}	D_{Bu}/ 10^{-9} m^2 s^{-1}	D_w/ 10^{-9} m^2 s^{-1}	k_2/ dm^3 mol^{-1} s^{-1}
—	3.6	0.46	1.74	
Butylamine	4.2	0.44	1.74	1.3
Octylamine	4.1	0.44	1.74	0.85
Decylamine	4.0	0.46	1.77	0.55
Dodecylamine	3.2	0.51	1.84	0.56
Cetylamine	2.9	0.50	1.83	0.55
Octadecylamine	3.0	0.50	1.85	0.58

[a]As determined in ME-1 at 25±0.5 °C and pH 9.0–10.3, the amine concentration was up to 0.2 mol dm^{-3}. $k_2 = (k_{obs} - k_0)/\alpha C_{am}$, where k_{obs} and k_0 are the observed rate constants in the presence and absence of the amine, respectively, C_{am} is the amine concentration, and α is the fraction of the neutral (reactive) form of the amine.

silane) and α-CH_2 protons (3.63 ppm), respectively. In addition to CPB, hexane and butanol also contribute to the signal (1.3 ppm) of the $(CH)_n$ protons. The diffusion decay of this signal showed that CPB and hexane molecules are characterised by the same translational mobility.

If the total surfactant concentration in microemulsions is much higher than the critical micelle concentration, the surfactant diffusion is close to the drop diffusion, $D_{surf} \approx D_{drop}$.[11,12] Thus, the effective drop radius R_{drop} can be estimated by the Stokes–Einstein equation

$$D_{drop} = kT/6\pi\eta R_{drop} \quad (1)$$

where η is the viscosity of the dispersion medium (deuterium oxide in our case). We found $R^0_{drop} \approx 30$ Å in the absence of amines by extrapolation of the concentration dependence of CPB self-diffusion coefficients in amine-free ME-1 to the infinite dilution.

In oil-in-water microemulsions, a co-surfactant and a hydrocarbon take part in the formation of drops along with the surfactant. Our self-diffusion data suggest that this is true for hexane: the diffusion decay of the $(CH)_n$ proton signals from hexane and CPB cannot be divided. Thus, CPB and hexane form joint structural aggregates. Nevertheless, the self-diffusion coefficients of butanol in ME-1 are higher than D_{drop}. This may result from the partial presence of butanol in the bulk phase. According to the two-site model (fast exchange between two states on the NMR time scale), the observed self-diffusion coefficient for butanol D_{Bu} is

$$D_{Bu} = p_b D_{drop} + (1 - p_b) D^{fr}_{Bu} \quad (2)$$

where p_b is the weight fraction of butanol included in microemulsion drops and D^{fr}_{Bu} is the self-diffusion coefficient of butanol present in the bulk water medium. We found $D^{fr}_{Bu} = 0.69 \times 10^{-9}$ m^2 s^{-1} from independent measurements in water–butanol mixtures taking into account the obstruction effect from drops[13,14] in ME-1. Thus, it follows that disperse phase includes only 34% of butanol presented in amine-free ME-1. An analysis of the self-diffusion coefficients of water in ME-1 ($D^{fr}_w = 1.86 \times 10^{-9}$ m^2 s^{-1}) shows that 6.5% of total water is included in the drops.

The introduction of organic additives, in particular, alkylamines, can influence the structure of microemulsions. Amines may act as co-surfactants[15,16] and compete with butanol at the interface of drops. According to the self-diffusion data (Table 1, Figure 2), the amines examined can be divided into two groups according to their influence on the structure of ME-1. An increase in the self-diffusion coefficients of CPB (by approximately 15%), *i.e.*, a decrease in the drop size, and an increase in the weight fraction of butanol included in disperse phase are the characteristics of the first group (butylamine and octylamine). Starting from decylamine, the changes in the size and composition of ME-1 drops take place: the radius of drops increases, and butanol and water are forced out from the disperse phase into the bulk one. Evidently, the more hydrophilic amines can be solvated in the bulk phase. The hydrophobic amines tend to incorporate with the droplets and to increase their size. The weakening of the drop hydration may result from a decrease in the drop surface charge density because of the incorporation of neutral amine molecules between charged CPB species. Probably, the surface dehydration of micelles by hydrophobic amines leads to the separation of a nucleophile (water activated by amines) and an oil-soluble substrate and hence results in a decrease in the rate constant of hydrolysis for **1**.

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