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Effect of polymer microdomains on the catalysed esterolysis of hydrophobic picolinic esters

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Abstract

Hydrophobic microdomains are generated in aqueous solutions by intramolecular coiling of poly(3-hexadecyl-1-vinylimidazolium bromide) ($PC_{16}VIB$). The influence of the so produced microenvironments on the chemical reactivity of water non-soluble reactants was studied by the following kinetics of the hydrolysis of hydrophobic picolinic esters, catalysed by hydrophobic benzimidazoles in the presence of Zn^{2+} ions or not. The results are compared with the rate constants obtained for cationic micellar systems prepared either from 3-hexadecyl-1-methylimidazolium bromide (HMIB), a model of polymer repeat unit, or from the conventional CTAB surfactant. The esterolytic activity of benzimidazoles, when alone, was similar in the presence of $PC_{16}VIB$ and HMIB, and it increases with the alkyl chain length of the reactants. Compared with the CTAB medium, their strong esterolytic power is the highest ever reported for a benzimidazole ring. In the presence of Zn^{2+} ions, the observed difference between the reactivities was also striking due to either the lack of an additional catalytic effect (in the case of HMIB) or an inhibition phenomenon in the case of the polymer whereas it had been shown that a CTAB medium favoured the formation of a 2/1 active complex.

Keywords: Hydrophobic esters; *p*-Nitrophenyl esters; Alkyl-chain benzimidazole ligands; Benzimidazole ligands; Esterolysis; Amphiphilic polymer microdomains; Microenvironment effects

1. Introduction

For the last three decades there has been an increasing interest in the development of chemical reactions in different types of microenvironments in order to study the catalytic or inhibitory effects in the presence of organized assemblies such as macrocycles, micelles, surfactant vesicles or macromolecules. For these systems the aim was to mimick the contributions which are responsible of the activity of some enzymes, and which essentially come from electrostatic interactions and hydrophobic effects [1–5].

In the case of amphiphilic polymers, the property of such macromolecules to form self-assemblies and/or aggregates in the presence of water, can open interesting possibilities. However, little information is available on their behaviour in comparison with micellar media, especially their solubilizing power towards hydrophobic reactants and their ability at favouring reaction rates.

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In a previous paper we reported the esterolytic activity of lipophilic substituted Zn^{2+} complexes towards a series of hydrophobic esters in the presence of CTAB micelles [6]. Our purpose, in this paper, is to examine the reactivity change of such a system when a classical cationic surfactant such as CTAB is replaced by a cationic amphiphilic polymer with a related structure (e.g. poly(3-hexadecyl-1-vinylimidazolium bromide): $PC_{16}VIB$) [7].

We here report the kinetic study of the hydrolysis of picolinic esters **2** with a series of linear alkyl-chain substituted hydroxymethylbenzimidazoles **1** alone or associated with Zn^{2+} ions in the presence of polymer ($PC_{16}VIB$) microdomains. In order to highly emphasize the efficiency of these microdomains, the reaction rates will be compared to those measured in the presence of micelles of a new conventional surfactant (3-hexadecyl-1-methylimidazolium bromide (HMIB) **3**) which is the analogue of the polymer repeat unit (Scheme 1).

2. Experimental

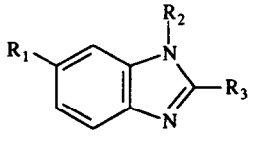
2.1. Materials

5(6)-Alkyl-2-hydroxymethylbenzimidazoles and 5(6)-alkyl-benzimidazoles (noted C_nBi-mOH and C_nBim, respectively, with $n = 0$, 7, 10) were prepared by cyclization of the corresponding *o*-phenylenediamine with glycolic or formic acid according to the Phillips method [8]. N-decyl-2-hydroxymethylbenzimidazole was synthesized in 3 steps: condensation of *o*-nitrofluorobenzene with decylamine in N,N-dimethylformamide to give N-decyl-2-nitroaniline, then reduction of the nitro group by H_2 under pressure in the presence of Pd/C catalyst and at least cyclisation of N-decyl-*o*-phenylenediamine by glycolic acid. 5-alkoxy-4′-nitrophenylpicolinates (noted C_mE with $m = 1$, 3, 5, 7, 10) have already been described elsewhere [9].

Poly(3-hexadecyl-1-vinylimidazolium bromide) ($PC_{16}VIB$) was prepared by homopolymerization of 3-hexadecyl-1-vinylimidazolium bromide in aqueous solution using 4,4′-azobiscyanovaleric acid (ACVA) as free radical initiator ([ACVA] = 1% mol./monomer, $T = 60°C$, 20 h). 3-hexadecyl-1-methylimidazolium bromide (HMIB) was prepared by quaternization of N-methylimidazole with hexadecylbromide [7].

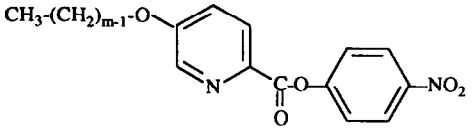
2.2. Techniques

Fluorescence emission spectra of pyrene (1.1×10^{-6} M) were recorded on a Spex Fluorolog 2 spectrometer for various concentrations in



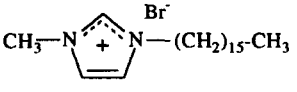
1

$R_1 = C_{10}H_{21}$, $R_2 = H$, $R_3 = CH_2OH$
$R_1 = C_7H_{15}$, $R_2 = H$, $R_3 = CH_2OH$
$R_1 = H$, $R_2 = H$, $R_3 = CH_2OH$
$R_1 = H$, $R_2 = C_{10}H_{21}$, $R_3 = CH_2OH$
$R_1 = C_{10}H_{21}$, $R_2 = H$, $R_3 = H$
$R_1 = H$, $R_2 = H$, $R_3 = H$



m = 1, 3, 5, 7, 10

2



3

Scheme 1.

polymer $PC_{16}VIB$ and model. All the measurements were carried out at $T = (30.0 \pm 0.1)°C$, pH 7.1 in a HEPES buffer (0.015 M) containing $NaNO_3$ (6×10^{-3} M), n-propanol 3% and ethanol 1% in volume. The excitation wavelength was 332 nm and the vibronic peaks were at $\lambda_1 = 372$ nm (I_1) and $\lambda_3 = 382$ nm (I_3). The change in the ratio of the intensities I_1/I_3 as a function of the polymer or model concentration gives information on the microenvironment polarity of the probe [10]. From these results, the onset of the self-aggregation of the polymer C_m and the cmc of the model were determined : $C_m = 3.2 \times 10^{-6}$ M and cmc (HMIB) = 1.9×10^{-4} M. For HMIB, the cmc value was also corroborated by surface-tension measurements with a Wilhelmy type surface-tensiometer Krüss K8. For this new surfactant, the Krafft's point ($T = 28.6°C$) was determined by solubility measurements in distilled water and the aggregation number was found to be equal to 50 (at 30°C) by the fluorescence time-decay technique with a single-photon counting apparatus.

2.3. Kinetics

The kinetics of the reactions were studied by following the appearance of the *p*-nitrophenolate anion at $\lambda_{max} = 400$ nm using a Shimadzu UV-2101 PC spectrophotometer (coupled with a Victor V 386 DSX microcomputer). The reactions were run at $(30.0 \pm 0.1)°C$ in 0.015 M HEPES buffer containing $NaNO_3$ ($I = 6 \times 10^{-3}$ M) at pH 7.1. Typically the stock solutions were prepared by dissolution of the polymer ($PC_{16}VIB$) or the surfactant (CTAB or HMIB) in a small amount of 1-propanol and addition under stirring of a solution of the ligand in ethanol and the buffer solution to give the final following concentrations: 3% (vol.) 1-propanol, 1% (vol.) ethanol, [polymer units] or [surfactant] $= 6 \times 10^{-4}$ M and [ligand] $= 1 \times 10^{-4}$ M. The usual procedure was as follows: 10 μl of ester in acetonitrile was injected into a cuvette containing 3 ml of the buffered stock solution at the desired concentrations and the reaction was followed to completion. In all cases, good pseudo-first-order kinetics were observed.

2.4. Determination of distribution constants between the water and micellar phases

A waterproof flask of $C_{10}BimOH$ saturated solution (in the presence or not of $PC_{16}VIB$ or surfactant) was immersed in a thermostated bath at $(50.0 \pm 0.2)°C$ overnight and then at $(30 \pm 0.2)°C$ for one week under agitation. After decantation, 3 ml of the floating was filtered through Whatman paper (1 qualitative) and then introduced in the cell of the UV spectropho-

Table 1
Pseudo-first-order rate constants and second-order rate constants for the *p*-nitrophenolate ion release of the picolinic esters in the presence of $C_{10}BimOH$. $[Zn^{2+}] = 2 \times 10^{-4}$ M, $[C_{10}BimOH] = 1 \times 10^{-4}$ M

	CTAB [a] ($C = 10^{-3}$ M)				HMIB [b] ($C = 6 \times 10^{-4}$ M)				$PC_{16}VIB$ ($C = 6 \times 10^{-4}$ M)			
$m_{(ester)}$ [d]	3	5	7	10	3	5	7	10	3	5	7	10
k_0 (10^{-4} s^{-1})	0.012	0.012	0.012	0.012	0.56	1.3	3.1	2.6	0.27	0.51	0.52	0.61
k_{obs} (10^{-4} s^{-1}) Zn^{2+}	0.58 [c]	0.5 [c]	0.3 [c]	0.58		2.3			0.64	1.1	1.2	1.46
k_M (M^{-1} s^{-1})	0.1	0.08	0.05	0.28		0.5			0.18	0.29	0.34	0.43
k_{obs} (10^{-4} s^{-1}) $C_{10}BimOH$	2	3.8	4	4	19.3	54.7	120	72	14.9	58.5	100	47.7
k_L (M^{-1} s^{-1})	2	3.8	4	4	18.7	53.4	117	69.4	14.6	58	99.5	47.1
k_{obs} (10^{-4} s^{-1}) $C_{10}BimOH/Zn^{2+}$	23 [c]	37 [c]	38 [c]	31.8 [c]		59			9	38	53	33

[a] HEPES buffer = 0.05 M, $I = 0.1$ M, pH = 7.1, $T = 30°C$ (results from [6]).
[b] HEPES buffer = 0.015 M, $I = 6.10^{-3}$ M, pH = 7.1, $T = 30°C$.
[c] $[Zn^{2+}] = 6 \times 10^{-4}$ M.
[d] Number of carbon atoms in the alkyl chain (ester).

tometer. Optical densities were measured at 280 and 287 nm (concentrations in surfactant or in polymer units ranging from 0 to 2×10^{-3} M).

3. Results and discussion

As previously shown in the study on the catalysed hydrolysis of long-chain picolinic esters **2** in the presence of CTAB micellar solutions [6], a high esterolytic activity was exhibited by the $C_{10}BimOH/Zn^{2+}$ association, in comparison with either the ligand or the Zn^{2+} ions alone, owing to the formation of a 2/1 active complex [11]. When occurring in the presence of the polymer ($PC_{16}VIB$) (see Table 1) in place of CTAB, preliminary investigations pointed out the high esterolytic activity of the ligand alone whereas the addition of Zn^{2+} ions, at the opposite, led to a decrease of the ester hydrolysis rate. For the micellar system involving HMIB, no significant change in the activity of $C_{10}BimOH$ was observed in the presence of Zn^{2+} ions. Either for the polymer or for the HMIB system, the esterolytic activity of the ligand alone was 7 to 25-fold higher than in the CTAB system, in relation with the ester hydrophobicity.

However, in the presence of Zn^{2+} ions, this activity was found to be of the same magnitude (except for the C_3 ester) in the three different systems. In order to explain such a change in behaviour, the medium effects could first be considered. Indeed experimental conditions, differing from those of the two other systems, have been used for the determination of the hydrolysis rate constants in the case of the CTAB system [6] ([CTAB] = 1×10^{-3} M above the cmc of the comicellar system $C_{10}BimOH/CTAB/Zn^{2+}$ (cmc = 1×10^{-4} M); HEPES buffer = 0.05 M, I = 0.1 M ($NaNO_3$)) i.e. higher concentrations in surfactant, buffer and ionic strength. Polymer solutions at lower concentrations were needed in

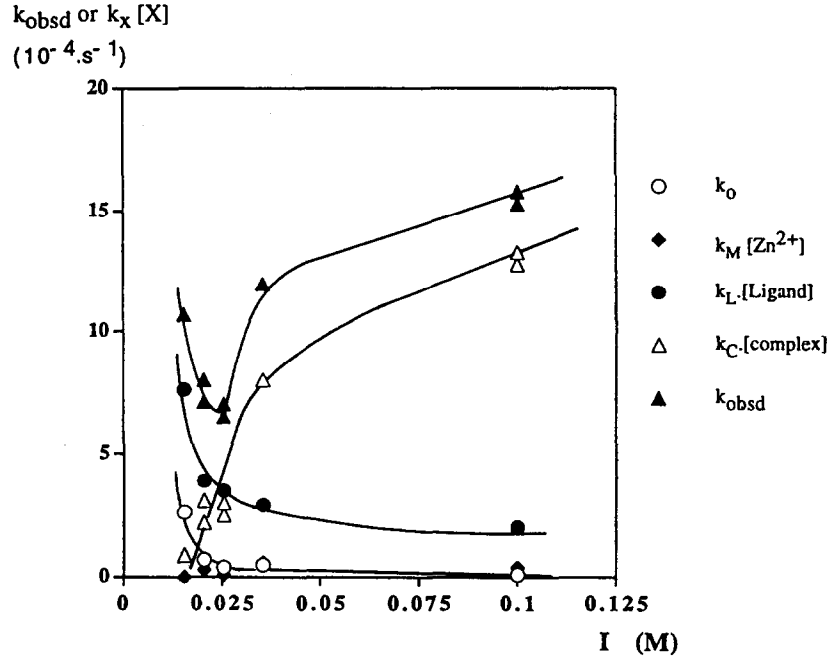


Fig. 1. Variation of k_{obsd}, k_0 and $k_X[X]$ as a function of the ionic strength. T = 30°C, pH 7.1; HEPES buffer = 0.05 M (ethanol 1%/n-propanol 3% vol.); [CTAB] = 5×10^{-3} M, [$C_{10}BimOH$] = 1×10^{-4} M, [Zn^{2+}] = 2×10^{-4} M, [$C_{10}E$] = 2.5×10^{-5} M.

order to avoid any precipitation of the amphiphilic macromolecules. The same lowering was also made on HMIB solutions in order to allow a comparison.

However, the precedent investigations [6] have already shown a weak dependence of the activity of the ligand which adopts the same tendency in the presence of Zn^{2+} or not, on CTAB concentration. Therefore the CTAB solutions differing essentially in their ionic strength, the investigations were performed in order to study the influence of this parameter on the reactivity of the ligand in the CTAB micellar system by varying the nitrate concentration, HEPES concentration being kept at 0.05 M.

3.1. Influence of the ionic strength in the CTAB system

This effect was studied on the hydrolysis of C_{10} picolinic ester catalysed by the C_{10}BimOH/Zn^{2+}/CTAB system; the reactivity of the C_{10}BimOH/C_{10} ester pair being weakly dependent on CTAB concentration [6]. As shown in Fig. 1 the overall rate constant k_{obsd} measured as a function of the ionic strength exhibits a minimum for $I = 0.025$ M, getting a two-fold increase with an increasing ionic strength. This variation is the result of two opposite effects: indeed, the plots of the specific activities of the ligand alone (k_L[L]), the free metal ions (k_M[M]) and the Zn^{2+}/ligand complex (k_C[C]) corrected for the spontaneous ester hydrolysis (k_0) point out a weak decrease of the ligand activity (half of the initial value) and simultaneously a strong increase (10-fold) of the contribution of the complex as the ionic strength is increased. High ionic strengths are thus enhancing the catalytic activity of such complexes. Concerning the dependence of the ligand activity on the ionic strength, a similar result has already been reported by Martinek [12] for the esterolysis of *p*-nitrophenyl heptanoate catalysed by benzimidazole in CTAB micellar medium. The inhibiting effect, consecutive to added salts, was attributed to the increase in counterions concentration close to the micelles, that leads to a decrease in the sorption ability of these cationic micelles towards an anionic reagent (e.g. the benzimidazolide anion described hereafter).

With regard to the increase of the complex contribution, since the hydrophobic tail of the ligand is incorporated into the micelles while its hydrophilic end is located in the surrounding of the micelle, the following assumption can be done: by increasing I, the higher screening effect of NO_3^- ions unleads to lower electrostatic repulsions between micelles cationic sites and Zn^{2+} ions, thus favouring the formation of an active complex.

Nevertheless, whatever the ionic strength value for the CTAB system, the activity of the ligand in the presence of Zn^{2+} was higher than the sum of the activities of the ligand and the metal ions considered separately, thus involving the occurrence of a complex.

In the case of HMIB micellar system (see Table 1, e.g. C_5 ester) an additive effect of the reactants alone was observed (i.e. $k_{obsd} = k_L$[L] + k_M[M] with k_C[C] $\neq 0$) showing that the formation of a complex was prevented.

In contrast with the two micellar systems (CTAB and HMIB), the presence of Zn^{2+}, in the case of the polymer, leads to an inhibition of the ligand activity. This effect can be attributed to the particular character of the polymer hydrophobic coiling (microdomains) which appeared to have more a compact structure compared to that of the model micelles as determined by polarity measurements in fluorescence spectroscopy [7]. This feature could either make the formation of active complexes difficult or, at the contrary, favour that of inactive ones, or also hinder the approach of the ester and thus explain the lack of activity of eventually formed complexes. Another distinctive feature of the polymer system and its model HMIB compared to CTAB was the strong enhancement of the activity of the ligand alone. To define the origin of this phenomenon better, further investigations on the influence of the pH on the esterolysis rate were necessary.

3.2. Effect of pH on C_{10}BimOH activity

A similar behaviour and the same level of reactivity were observed for the ligand in the amphiphilic polymer system and its micellar model, in the absence of Zn^{2+} ions. The influence of the pH was thus examined only for the polymer system on the esterolysis of the C_5 picolinic ester, buffer concentration and total ionic strength being kept constant (experimental part). Some experiments, carried out in the absence of ligand, showed the expected linear enhancement of k_0 (spontaneous ester hydrolysis rate constant) with increasing pH i.e. the effects of the catalysis by OH^- (Fig. 2).

When occurring in the presence of the ligand only, a linear increase of the second-order-rate constant k'_2 with increasing pH values was observed, which is characteristic of a reaction involving anionic esterolytic species at pH rather far from their pK_a. In the present case, the ionisation of the imidazole ring N–H can be considered owing to previously reported results on reactivity of benzimidazoles in CTAB micellar medium [12], the pK_a being reduced by the cationic surrounding of the micelles. However, a so high esterolytic activity has never been observed for a benzimidazole ring and the question was whether its nucleophilicity was increased or its pK_a was much more lowered than in the presence of CTAB micelles.

The aqueous solutions of polymer PC_{16}VIB generate hydrophobic microdomains which can behave as classical micelles and, thus, kinetic processes in these systems can be described by the pseudophase model [13]. On this basis, we can assume that the overall esterolysis reaction rate R, related to the total volume of the system, is the sum of the individual rates R_μ and R_b in the hydrophobic pseudophase (subscript μ) and in the aqueous bulk pseudophase (subscript b) by involving the neutral AH and the anionic form A^- forms of the ligand as nucleophilic species.

However, the modelling requires the knowledge of the concentrations of the reactants in each of the two pseudophases and, therefore, the capacity of the microdomains to incorporate the

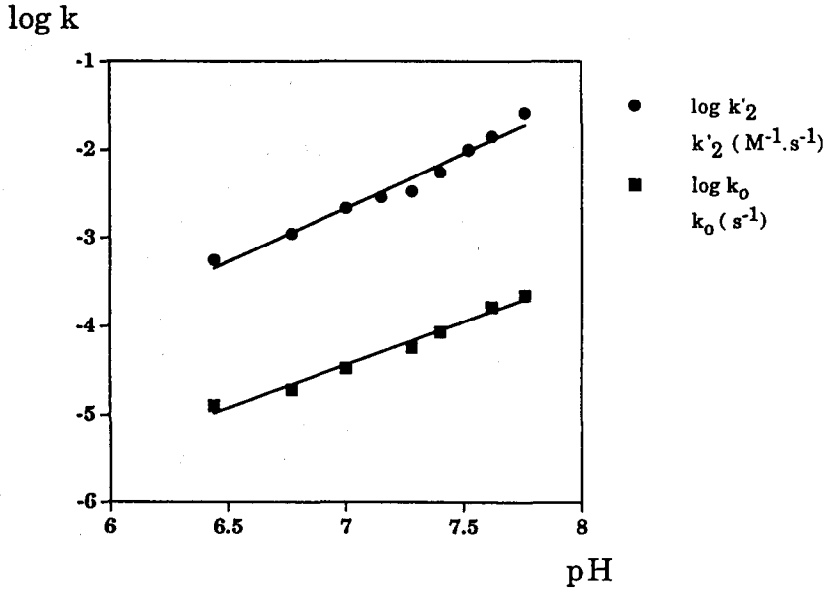


Fig. 2. pH–rate profile for the C_{10}BimOH-catalysed hydrolysis of C_5E. $T = 30°C$; HEPES buffer $= 7.5 \times 10^{-3}$ M, (ethanol 1%/n-propanol 3% vol.), $I = 6.10^{-3}$ M; $[PC_{16}VIB] = 6 \times 10^{-4}$ M, $[C_{10}BimOH] = 1 \times 10^{-4}$ M, $[C_5E] = 2.5 \times 10^{-5}$ M. k_0 = spontaneous hydrolysis rate constant for C_5E, k'_2 (second-order rate constant) $= k_{obsd} - k_0/[\text{ligand}]$.

ligands and the esters. The solubilizing ability of the polymer solutions was determined only in the case of the ligand C_{10}BimOH. Unfortunately, for the esters no reproducible measurement was obtained because of the very slow dissolution rate (> 1 week), thus producing an extensive spontaneous hydrolysis.

The solubilizing power with respect to the ligand is defined as [14]:

$$p = \frac{[\text{ligand}] - [\text{ligand}]_b}{[D] - C_m}$$

where [ligand] is the total apparent concentration of the solubilized ligand in the presence of the polysoap, $[\text{ligand}]_b$ the concentration in the absence of polysoap, [D] the concentration of amphiphilic units in the solubilizing system and C_m the concentration of these units corresponding to the onset of the aggregation phenomenon as determined by fluorescence spectroscopy. But, C_m being generally low (for PC_{16}VIB, $C_m = 3.2 \times 10^{-6}$ M), can be neglected in comparison with [D]. The association constant K is given by $K = p/[\text{ligand}]_b$ and the partitioning coefficient, which involves the true concentrations in the two pseudophases by $P = K + \bar{V}/\bar{V}$.

As shown in Fig. 3, p as obtained from the slope of the straight line [ligand] vs. [D] and was found to be equal to 0.145 and $K = 1.45 \times 10^{-4}$ M^{-1}(for HMIB model and C_7BimOH: $p = 0.2$, $K = 2 \times 10^{-4}$ M^{-1}). In the micellar systems, the values of the volume of a surfactant mole $\bar{V} \approx 0.2$–0.4 M^{-1} [15], taken for the calculation of P are related to the volume of the micelle limited to the Stern layer. Owing to the p and K close values found for the polymer system and its micellar model, the molar volume of a cationic surfactant ($\bar{V} = 0.37$ M^{-1}) was taken as an approximate $\bar{V}$ value for the polymer.

The high value $P = 40000$ indicates that the ligand is mainly located in the microdomains; the reaction does thus occur essentially in this phase and the esterolysis rate in the bulk phase can be neglected. For the C_5 ester, a distribution between the two pseudophases has to be sup-

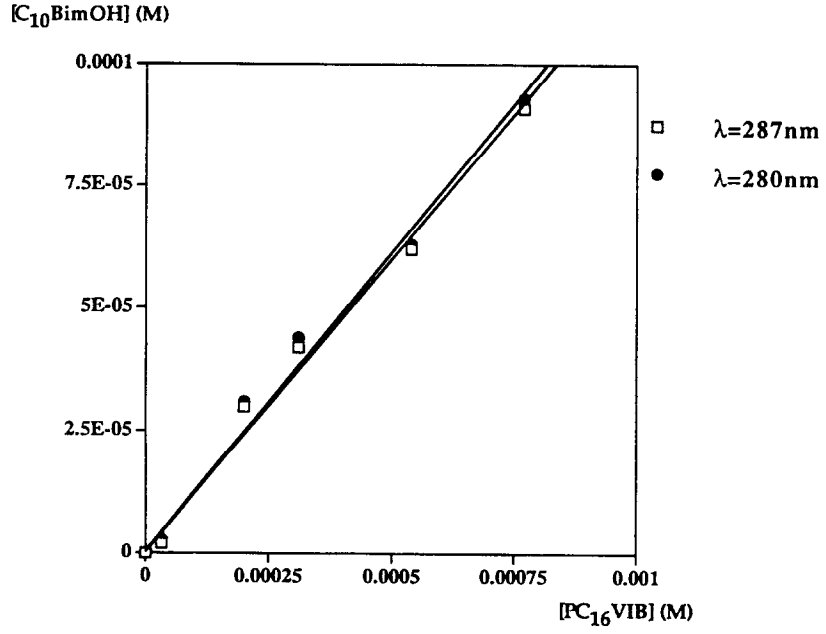


Fig. 3. Solubilization of C_{10}BimOH in aqueous solutions of PC_{16}VIB (containing ethanol 1%/n-propanol 3%); $T = 30$°C.

posed, in comparison with its P_E value measured for CTAB solutions ($P_E \approx 7500$) [6].

Under the above conditions :

$$R = k'_2[\text{ligand}]_{\text{total}}[\text{ester}]_{\text{total}}$$

with

$$[\text{ligand}]_{\text{total}} = ([\text{AH}]_\mu + [\text{A}^-]_\mu)[D]\bar{V}$$

and

$$[\text{ester}]_{\text{total}} = [\text{ester}]_\mu[D]\bar{V} + [\text{ester}]_b(1 - [D]\bar{V})$$

then

$$R = k'_2([\text{AH}]_\mu + [\text{A}^-]_\mu)[D]\bar{V}\left[[\text{ester}]_\mu[D]\bar{V} + [\text{ester}]_b(1 - [D]\bar{V})\right]$$

$$= \left[k^\mu_{\text{A}^-}[\text{A}^-]_\mu + k^\mu_{\text{AH}}[\text{AH}]_\mu\right][\text{ester}]_\mu[D]\bar{V}$$

where $k^\mu_{\text{A}^-}$ and k^μ_{AH} are the second-order rate constants, corresponding respectively to the benzimidazolide anion and the neutral form in the hydrophobic pseudophase. $[\text{AH}]_\mu$ and $[\text{A}^-]_\mu$ are linked together by the overall dissociation constant $K^\mu_a = [\text{H}^+][\text{A}^-]\mu/[\text{AH}]\mu$ [16]. Since $[\text{D}]\bar{V} \ll 1$, k'_2 can thus be expressed as:

$$k'_2 = \frac{(k^\mu_{\text{AH}}[\text{H}^+] + k^\mu_{\text{A}^-} \cdot K^\mu_a)}{[\text{H}^+] + K^\mu_a} \times \frac{P_E}{1 + P_E D\bar{V}} \quad (1)$$

$$P_E = \frac{[\text{ester}]_\mu}{[\text{ester}]_b}$$

with four adjustable parameters k^μ_{AH}, $k^\mu_{\text{A}^-}$, K^μ_a and P_E.

From the results of the adjustment (Fig. 4), it is clear that the calculated curve is in good agreement with the experimental results ($r^2 = 0.945$). Owing to the values obtained for $k^\mu_{\text{AH}} = 1.6 \times 10^{-9}\ \text{M}^{-1} \cdot \text{s}^{-1}$ and $k^\mu_{\text{A}^-} = 0.95\ \text{M}^{-1} \cdot \text{s}^{-1}$, i.e. $\frac{k^\mu_{\text{A}^-}}{k^\mu_{\text{AH}}} = 6 \times 10^8$: the benzimidazolide anion was the unique species responsible for the overall esterolytic activity. The value, $P_E = 8400$, for the ester partitioning coefficient, considered as an adjustable parameter, is in good agreement with those determined experimentally for the homologous esters series in CTAB solutions

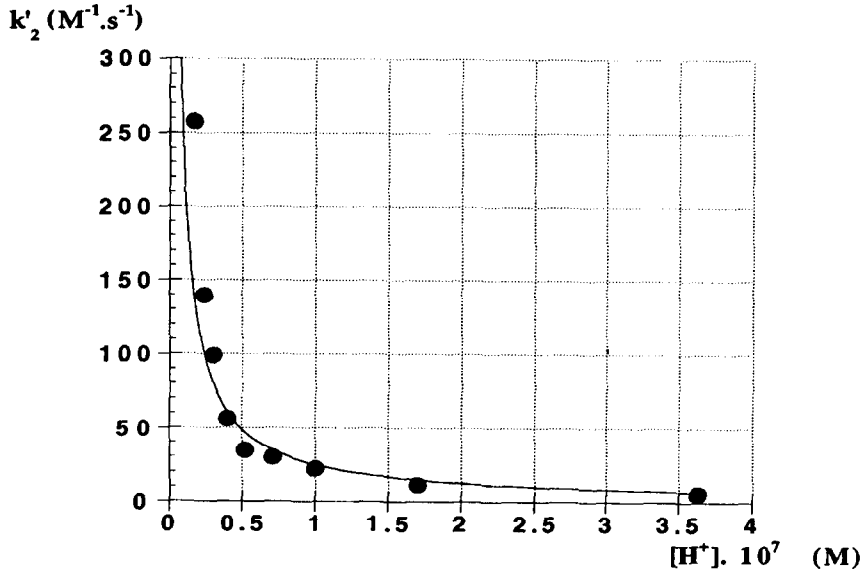


Fig. 4. Plot of k'_2 vs. $[\text{H}^+]$ for the C_{10}BimOH-catalysed hydrolysis of C_5E in the presence of PC_{16}VIB. $T = 30$°C; pH 7.1; HEPES buffer = 7.5×10^{-3} M, (ethanol 1%/n-propanol 3%), $I = 6 \times 10^{-3}$ M; $[PC_{16}VIB] = 6 \times 10^{-4}$ M, $[C_{10}BimOH] = 1 \times 10^{-4}$ M, $[C_5E] = 2 \times 5.10^{-5}$ M. ●, Experimental data; — theoretical simulation according to Eq. 1.

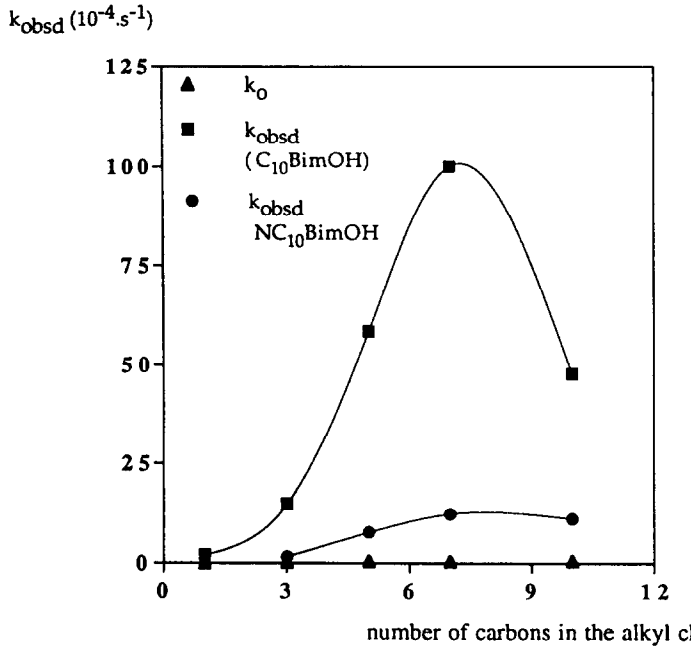


Fig. 5. Dependence of k_{obsd} on the chain length of the esters for the ligands C_{10}BimOH and NC_{10}BimOH. $T = 30°C$, pH 7.1; HEPES buffer = 0.015 M (ethanol 1%/n-propanol 3%) M; $I = 6 \times 10^{-3}$ M; [PC_{16}VIB] = 6×10^{-4} M, [C_{10}BimOH] = [NC_{10}BimOH] = 1×10^{-4} M, [Zn^{2+}] = 2×10^{-4} M, [C_mE] = 2.5×10^{-5} M.

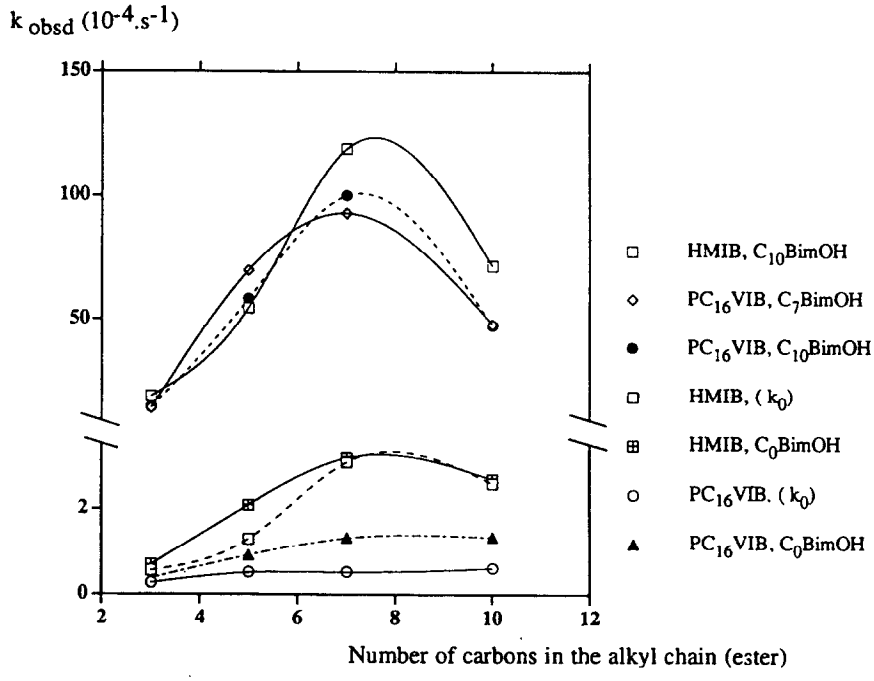


Fig. 6. Dependence of k_{obsd} on the chain length of the esters for the ligands C_0BimOH, C_7BimOH and C_{10}BimOH. $T = 30°C$, pH 7.1; HEPES buffer = 0.015 M (ethanol 1%/n-propanol 3%) M; $I = 6 \times 10^{-3}$ M; [PC_{16}VIB] = [HMIB] = 6×10^{-4} M, [ligand] = 1×10^{-4} M, [Zn^{2+}] = 2×10^{-4} M, [C_mE] = 2.5×10^{-5} M.

[6]. However, the pK_a^{μ} found to be equal to 9 shows a difference of up to 2 units in comparison with the values given by Martinek for the benzimidazole ($pK_a = 11.45$) [12] or Krati in the case of a C_{10} benzimidazole ($pK_a = 11.3$) in CTAB micellar medium [17]. The pK_a drop causes a strong increase in the anion concentration and thus the unusual increase of the benzimidazole ring activity.

The existence of such an active anion was also corroborated by investigations on the esterolytic activity of the ligand NC_{10}BimOH which has a similar structure to C_{10}BimOH but whose the decyl chain, substituting the NH group, prevents the formation of an anion. Fig. 5 represents the variation of the global rate constant k_{obsd} for these two ligands as a function of the carbon atoms number in the n-alkyl chain of the esters. A decrease in rate magnitude (4- to 9-fold) according to the ester chain-length, was observed for NC_{10}BimOH.

3.3. Influence of the hydrophobicity of the reactants

The esterolysis rates of the different picolinic esters **1** in the presence of the polymer system PC_{16}VIB and its micellar analogous HMIB were compared in relation with the structure and the hydrophobicity of the esterolytic benzimidazoles **2** and **3**.

As shown in Figs. 6 and 7, C_nBim ligands are more nucleophilic than the hydroxy derivatives C_nBimOH: both for the higher activities ($n = 7$, 10) and still more for the weaker esterolytic rates (e.g. $n = 0$). The assumption of the benzimidazolide anion occurrence was thus supported by excluding the potential activity of the alcohol functional group, even without Zn^{2+} ions.

In the presence of the polymer or the surfactant model, in all cases, the overall rate constant k_{obsd} strongly increases with the chain-length of

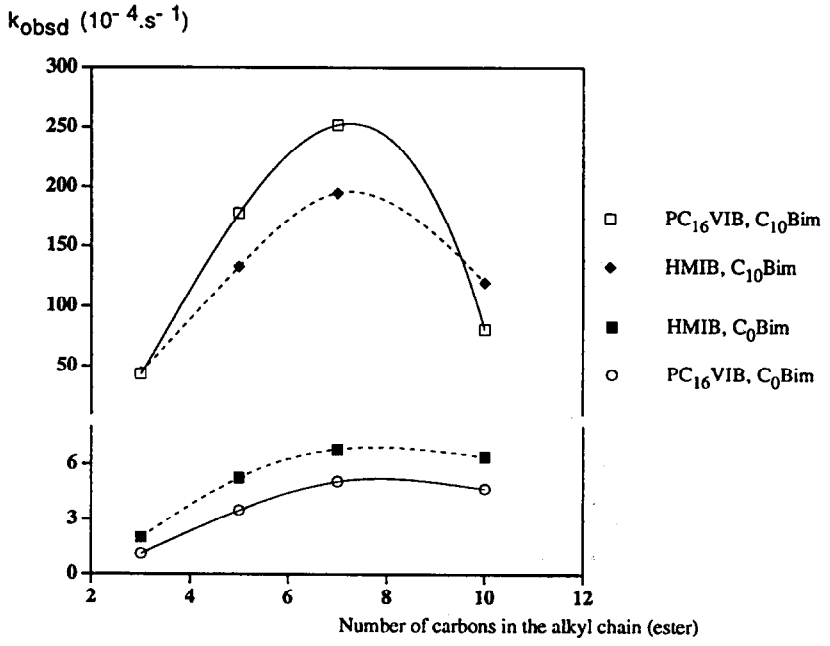


Fig. 7. Dependence of k_{obsd} on the chain length of the esters for the ligands C_0Bim and C_{10}Bim. $T = 30°C$, pH 7.1; HEPES buffer = 0.015 M (ethanol 1%/n-propanol 3%) M; $I = 6 \times 10^{-3}$ M; $[PC_{16}VIB] = [HMIB] = 6 \times 10^{-4}$ M, [ligand] = 1×10^{-4} M, $[Zn^{2+}] = 2 \times 10^{-4}$ M, $[C_mE] = 2.5 \times 10^{-5}$ M.

the ligand (Fig. 6; Table 1), 7- to 35-fold according to the ester chain size, the maximum value being reached already for the C_7 chain. The same behaviour is observed for the esters from C_3E to C_7E. For $C_{10}E$, whatever the polymer or the surfactant model, the rate constant k_{obsd} decreases as a result of the slower incorporation of this ester in microdomains or micelles.

On the other hand, no significant difference of reactivity was observed between the two solubilizing media, the polymer system being a little more active with the more hydrophobic C_nBim.

4. Conclusion

The homopolymer of 3-hexadecyl-1-vinylimidazolium bromide generates, in aqueous solution, hydrophobic microdomains, the properties of which are very close to those of the surfactant model (3-hexadecyl-1-methylimidazolium bromide) micelles: a similar solubilization capability of hydrophobic reactants and an accelerating effect on the esters hydrolysis catalyzed by long-chain substituted benzimidazoles. However, the microenvironment of these microdomains appears noticeably different from that of the conventional cationic surfactant micelles, such as CTAB, with the following consequences:

(i) a strong decrease of the pK_a of the benzimidazole ring NH group responsible for an increase of the conjugated anion concentration at pHs close to neutrality.The result is a high enhancement of the esterolytic activity of a benzimidazole which has never been described for this species up to now;

(ii) for hydroxymethyl substituted benzimidazoles, the absence of any effect on this activity (for the model) or the appearance of an inhibition (for the polymer) induced by the addition of Zn^{2+} ions. On the contrary, in the case of the CTAB micellar system, the main esterolytic activity is due to the presence of these Zn^{2+} ions which are responsible for the formation of a 2/1 active complex. These singularities can be attributed to the strong polarity of the cationic part (imidazolium head) and to the more compact structure of the generated microdomains. Concerning the model micelles, the aggregation number is only half that of CTAB. This more compact structure could hinder the formation of an active complex or the approach of the substrate to form a second complex (ternary complex) before the formation of the determining transition state. All these characteristics are in agreement with each other and further studies are now in progress in order to examine the influence of the constraint removal in the vicinity of the cationic sites.

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