

Effect of microemulsion-like polysoap on the catalysed esterolysis of hydrophobic *p*-nitrophenyl esters

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Received 22 April 1998; accepted 8 July 1998

Abstract

The esterolytic activity of metal ion complexes of *n*-alkyl-2-hydroxymethylbenzimidazoles/ Zn^{2+} towards *p*-nitrophenyl esters (picolinates and alkanooates) was investigated in the presence of an amphiphilic polymer, poly(1-hexadecyl-3-vinylpyridinium bromide), as a macromolecular matrix. The reaction rate constants obtained for the polymer hydrophobic microdomains were compared with those observed for the new conventional surfactant, 3-ethyl-1-hexadecylpyridinium bromide, chosen as the model of the repeat unit of the homopolymer. In both cases, the kinetic analysis indicated that the esterolysis reaction proceeds through the formation of an initial binary complex Ligand- Zn^{2+} , the stoichiometry of which is 2/1 type. © 1999 Elsevier Science B.V. All rights reserved.

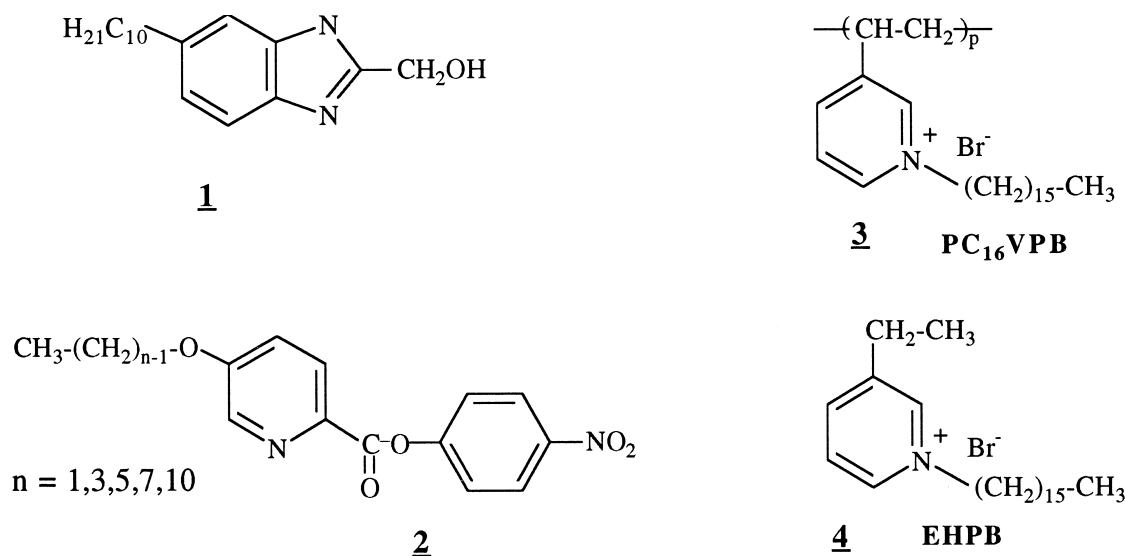
Keywords: Hydrophobic *p*-nitrophenyl esters; Alkyl-chain benzimidazole ligands; Esterolysis activity; Amphiphilic polymer microdomains; Microenvironment effects

1. Introduction

The interest to create original catalytic processes by effects favouring the reactivity, has initiated many researches at the end of the sixties. The main idea has been the search of such a spatial disposition where the catalytic site and the reactants should be confined in a reduced space. In that perspective, the authors have used different systems like micelles, vesicles, macrocycles or dedicated polymers [1–4]. These systems constituting places of solubilization for outside molecules, and create a desol-

vated environment for a favourable entropy putting together of the reactants. They are also of particular interest because they exhibit many features observed in enzyme reactions. When dealing with such macromolecular systems, we are confronted with two alternatives: either polymers bearing reactive sites [5–11] or polymers lacking in catalytic groups, but the main property of which is, through appropriate coilings in aqueous medium, to form hydrophobic microdomains so as to concentrate the reactants in their vicinity [12–15]. In the present work, we report our preliminary results on the microdomain influence of an homopolymer belonging to the second class, the poly(1-hexadecyl-3-vinylpyridinium bromide) (PC₁₆VPB) **3** on

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Scheme 1.

the esterolysis kinetics of picolinic esters **2** catalyzed by linear alkyl-chain substituted hydroxymethylbenzimidazoles **1** either alone or associated with Zn^{2+} ions. In parallel and in order to better evaluate the efficiency of the polymer microdomains on the esterolysis, the reaction rate constants are compared to those obtained in the presence of the new conventional surfactant 3-ethyl-1-hexadecylpyridinium bromide **4**, model of the homopolymer repeating unit (Scheme 1).

2. Experimental

2.1. Materials

5(6)-Decyl-2-hydroxymethylbenzimidazole (noted $\text{C}_{10}\text{BimOH}$) was prepared by cyclization of 4-decyl-1,2-diamino benzene with glycolic acid according to the Phillips' method [16]. 5-alkoxy-4'-nitrophenylpicolinate (noted C_mE with $m = 1, 3, 5, 7, 10$) have already been described elsewhere [17].

3-Vinylpyridine was prepared from 3-pyridinecarboxaldehyde via a Wittig reaction [18] using sodium hydride as the base. 1-hexadecyl-

3-vinylpyridinium bromide (C_{16}VPB) was prepared by quaternization of 3-vinylpyridine with hexadecylbromide in the solvent mixture acetonitrile/chloroform (50/50 v/v) [18].

Poly(1-hexadecyl-3-vinylpyridinium bromide) (PC_{16}VPB) was prepared by homopolymerization of 1-hexadecyl-3-vinylpyridinium bromide in distilled benzene using 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN from Polysciences) as the free radical initiator ($[\text{ADVN}] = 1\% \text{ mol/monomer}$, $T = 60^\circ\text{C}$, 24 h).

3-Ethyl-1-hexadecylpyridinium bromide (EHPB) was prepared by quaternization of 3-ethylpyridine with hexadecylbromide [18].

2.2. Techniques

The occurrence of EHPB micelles and hydrophobic microdomains for the polymer PC_{16}VPB was evidenced by fluorescence spectroscopy through the emission shift (λ_{fmax}) of a fluorescent molecular rotor (e.g., 1,1-dicyano-(4'-dimethylaminophenyl)-1,3-butadiene) as a function of the polymer or the surfactant concentration. Indeed, the use of a conventional probe such as pyrene was not here possible

because of the quenching processes, due to the presence of long alkyl chain quaternized pyridine rings in both the polymer and the model [19]. Fluorescence emission spectra of the rotor (4.3×10^{-6} M stock solution in ethanol at 1.3×10^{-3} M) were recorded at 500–600 nm on a SPEX Fluorolog-2 spectrofluorometer (slit width: 1.5 mm; bandpass = 5.64 nm), equipped with a thermostated cell compartment ($T = 30.0 \pm 0.1^\circ\text{C}$). The excitation wavelength λ_{ex} was 490 nm. From the plots $\lambda_{\text{fmax}} = f(\text{surfactant or polymer concentration})$, the beginning of the polymer aggregation C_m and cmc of EHPB were determined: $C_m = 2.3 \times 10^{-5}$ M and cmc (EHPB) = 3.9×10^{-4} M. For EHPB, the cmc value was also determined by surface-tension measurements at $30.0 \pm 0.1^\circ\text{C}$ (cmc = 3.7×10^{-4} M) with a Wilhelmy type surface tensiometer (Krüss K8). For this new surfactant, the Krafft's point was found to be: $T_{\text{krafft}} = 9.8^\circ\text{C}$ by solubility measurements in neat water.

The observation of homopolymer (PC₁₆VPB) aqueous solutions by Cryo-Transmission Electron Microscopy (Philips CM 20 microscope) has revealed an entangled structure in 'strings of beads' for a polymer concentration equals to 0.5 mg/ml (succession of hydrophobic microdomains connected to each other) or steadily arranged superstructures looking like fingerprints (polymer concentration = 1.5 mg/ml) [20].

2.3. Kinetics

The kinetics of the reactions were studied by following the appearance of the *p*-nitrophenolate anion at $\lambda_{\text{max}} = 400$ nm using a SHIMADZU UV-2101 PC spectrophotometer (coupled with a Victor V 386 DSX microcomputer). The reactions were run at $(30.0 \pm 0.1)^\circ\text{C}$ in 0.015 M HEPES buffer containing NaNO₃ ($I = 6 \times 10^{-3}$ M) at pH = 7.1. Typically the stock solutions were prepared by dissolution of the polymer (PC₁₆VPB) or the surfactant (EHPB) in a small amount of 1-propanol and then by addition, under stirring, of a ligand solution in ethanol followed by the buffer solution to give the final concentrations: 3% (vol.) 1-propanol, 1% (vol.) ethanol, [polymer units] or [surfactant] = 6×10^{-4} M and [ligand] = 1×10^{-4} M. The usual procedure was as follows: 10 μl of ester in acetonitrile were injected into a cuvette containing 3 ml of the buffered stock solution at the desired concentration and the reaction was followed up to completion. In all cases, good pseudo-first-order kinetics were observed.

3. Results and discussion

The data given in Table 1 indicate that in comparison with the ester spontaneous hydroly-

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 C₁₀BimOH

n^{a} (ester)	PC ₁₆ VPB:C = 6×10^{-4} M ^d					EHPB:C = 6×10^{-4} M ^d				
	1	3	5	7	10	1	3	5	7	10
k_0 (10^{-4} s ⁻¹)	0.16	0.14	0.25	0.22	0.29	0.23	0.29	0.61	0.73	0.79
k_{obs} (10^{-4} s ⁻¹) ^b (Zn ²⁺)	0.48	0.36	0.63	0.81	0.96	1.0	1.20	1.54	2.12	2.5
k_{M} (M ⁻¹ s ⁻¹)	0.16	0.11	0.19	0.29	0.33	0.39	0.45	0.46	0.69	0.86
k_{obs} (10^{-4} s ⁻¹) ^c (C ₁₀ BimOH)	1.05	6.50	20.2	36.6	38.4	1.5	10.3	45.2	47.0	41.4
k_{L} (M ⁻¹ s ⁻¹)	0.9	6.4	19.95	36.4	38.1	1.26	10	44.6	46.3	40.55
k_{obs} (10^{-4} s ⁻¹) ^c C ₁₀ BimOH/Zn ²⁺	2.8	11.7	34.9	82.5	73.5	16.9	28.6	66.2	73.9	96.75
$k_{\text{c}}[\text{C}]$ (10^{-4} s ⁻¹)	1.4	5.0	14.3	45.3	34.4	14.6	17.4	20.0	25.5	53.7

^aNumber of carbon atoms in the alkyl chain (ester).

^b[Zn²⁺] = 2×10^{-4} M.

^c[C₁₀BimOH] = 1×10^{-4} M.

^dHEPES buffer = 0.015 M; $I = 6 \times 10^{-3}$ M; pH = 7.1; $T = 30^\circ\text{C}$.

sis, the addition of Zn^{2+} ions results in a 3- to 4-fold acceleration of the reaction in the presence of the homopolymer or its model EHPB. When the esterolysis reaction is carried out in the presence of the ligand $\text{C}_{10}\text{BimOH}$ only and the polymer, the overall rate constant k_{obsd} is strongly increased by factors going from 7 to 170 according to the ester alkyl chain length. The same evolution is observed in the presence of EHPB micelles. The $\text{C}_{10}\text{BimOH}/\text{Zn}^{2+}$ association leads to a strong enhancement for the esterolytic activity which is 20 to 300-fold higher than in the case of the spontaneous hydrolysis of the different esters. On the other hand, this activity increase is only 2-fold higher relative to that in the absence of metal ions. However, the activity of the ligand in the presence of Zn^{2+} is higher than the sum of the effects of the ligand and the metal ions considered separately. This observation allows us to assume the formation of a reactive complex responsible of the esterolytic activity as for in the presence of EHPB micelles or of the polymer as well.

3.1. Determination of the reactive complex stoichiometry PC_{16}VPB polymer

The stoichiometry of the reactive complex was determined by means of a kinetic version of a Job plot for the system $\text{C}_{10}\text{BimOH}/\text{Zn}^{2+}/\text{C}_7\text{Ester}$. Indeed, the variations of the corrected overall rate constant $k_{\text{obsd}} - k'_0$ were observed as a function of the molar fraction of one of the constituent of the complex (in this case the ligand). The total concentration of ligand and metal was maintained constant at 1×10^{-4} M. As shown in Fig. 1 and for the homopolymer PC_{16}VPB , the Job curve profiles $k_{\text{obsd}} - k'_0 = f([\text{C}_{10}\text{BimOH}])$ exhibit a maximum at around 0.67, which corresponds to a stoichiometry of $\text{C}_{10}\text{BimOH}/\text{Zn}^{2+} = 2/1$. It should be observed that the maximum position is independent of the polymer concentration up to 6×10^{-4} M. Around this value, we observed a gradual

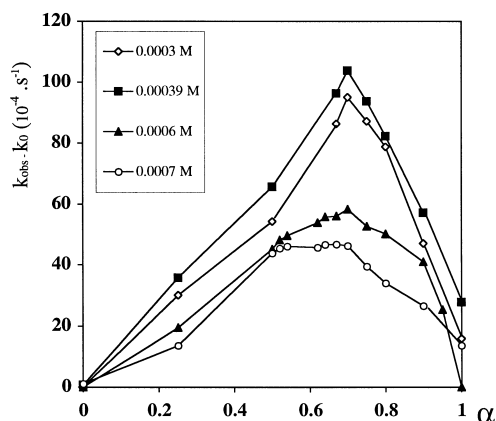


Fig. 1. Job plot for the hydrolysis of C_7E by $\text{C}_{10}\text{BimOH}$ in the presence of PC_{16}VPB . $T = 30^\circ\text{C}$; HEPES buffer = 0.015 M (containing ethanol 1% / *n*-propanol 3% vol.); $I = 6.10^{-3}$ M; $\text{pH} = 7.1$. $[\text{PC}_{16}\text{VPB}]$ varied from 3×10^{-4} M to 7×10^{-4} M. The sum of the zinc ion and $\text{C}_{10}\text{BimOH}$ concentrations was kept constant at 1×10^{-4} M; $[\text{C}_7\text{E}] = 2.5 \times 10^{-5}$ M.

spreading of the curves with the concomitant appearance ($C = 7 \times 10^{-4}$ M) of a second maximum at $\alpha = 0.5$, which is typical of a reactive 1:1 complex. The coexistence of these two complexes in the presence of the polymer is also exemplified by the increase of the 1:1 complex contribution to the detriment of the 2:1 one; indeed, when the polymer concentration is increased, the greater distribution of the ligand within the hydrophobic microdomains is unfavourable to the formation of a 2:1 complex. The maximum efficiency was obtained when the polymer concentration equaled 3.9×10^{-4} M.

3.1.1. EHPB micelles

Fig. 2 shows the variations of $k_{\text{obsd}} - k'_0$ as a function of the ligand molar fraction for various EHPB concentrations superior to the cmc (3.6×10^{-5} M). The general curve profile is very comparable to that of the polymer. Indeed, the corrected overall rate constant goes through a maximum at $\alpha = 0.67$, which corresponds to a 2:1 complex. This activity decreases when the surfactant concentration increases and the reactivity maximum was obtained, as for the polymer, at a concentration equal to 4×10^{-4} M.

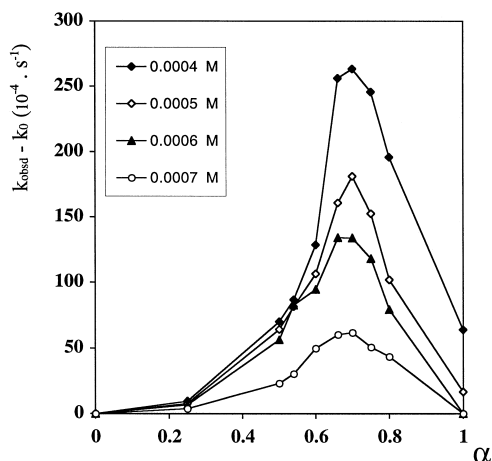


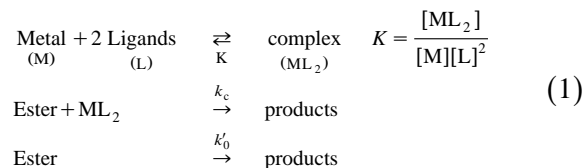
Fig. 2. Job plot for the hydrolysis of C_7E by $C_{10}BimOH$ in the presence of EHPB. $T = 30^\circ C$; HEPES buffer = 0.015 M (containing ethanol 1% / *n*-propanol 3% vol.); $I = 6x c$; pH = 7.1. $[PC_{16}VPB]$ varied from 4×10^{-4} M to 7×10^{-4} M. The sum of the zinc ion and $C_{10}BimOH$ concentrations was kept constant at 1×10^{-4} M; $[C_7E] = 2.5 \times 10^{-5}$ M.

Some differences may be observed between the two Job curves (polymer and EHPB). The peak profile is sharper and the values at the maximum reactivity are higher in the case of EHPB micelles. At high EHPB surfactant concentrations ($6-7 \times 10^{-4}$ M), the curves are less spread than that for the polymer and exhibit a single maximum at $\alpha = 0.67$.

3.2. Determination of the specific constant k_c and K for the complexes (polymer and model)

As shown by the saturation curves in Fig. 3, the overall rate constant k_{obsd} is depending both on the ligand and the metal ion concentration. These curves may be analyzed by considering the generally admitted reaction process. A metal ion and one or more ligands form an active complex with a complexation constant K . At the working concentration of polymer or surfactant ($C = 6 \times 10^{-4}$ M), the stoichiometry of the complex is 2:1 (ML_2). Thus, the reaction is represented by Eq. (2). The products are obtained from two simultaneous pathways: the catalyzed reactions by the metal ions

only ($k_M[M]$, the ligand only ($k_L[L]$) and the complex ($k_C[C]$) and the uncatalyzed reaction (spontaneous hydrolysis of the ester (k_0)).



$$\text{Rate} = k_{obsd}[\text{Ester}] = (k'_0 + k_c[ML_2])[\text{Ester}] \quad (2)$$

with $k'_0 = k_0 + k_M[M] + k_L[L]$

For the determination of the second-order rate constant and the complexation constant, the

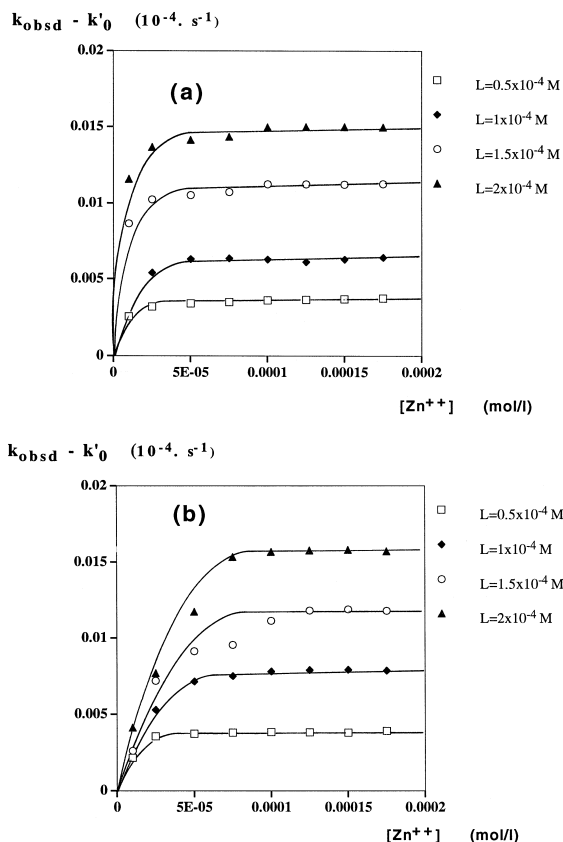


Fig. 3. Plots of $k_{obsd} - k_0$ for the hydrolysis of C_7E as a function of zinc ion concentration. $T = 30^\circ C$; $[C_{10}BimOH] = 0.5, 1, 1.5, 2 \times 10^{-4}$ M; $[C_7E] = 2.5 \times 10^{-5}$ M. (a) In the presence of $PC_{16}VIB$; (b) in the presence of EHPB. $[PC_{16}VIB] = [EHPB] = 6 \times 10^{-4}$ M, see Table 1 for other conditions.

kinetic curves were considered at the saturation plateau value in order to leave the parameter [Ligand] out of account. Indeed, the characteristic constants of the complex are not directly accessible by calculation. For that, it is necessary to be acquainted with the complex concentration. Thus, the kinetic runs are performed at a fixed ligand concentration and by checking the variations of $k_{\text{obsd}} - k'_0$ as a function of the metal ion concentration. Fig. 3 represents the plots of $k_{\text{obsd}} - k'_0 = f([\text{Zn}^{2+}])$ for various ligand concentrations in the presence of the polymer (a) and the model (b). The profile of these curves exhibits a rapid increase at low metal concentrations and reaches soon a plateau at 5×10^{-5} M which should evidence very high complexation constants.

At saturation,

$$(k_{\text{obsd}} - k'_0)_{\text{sat}} = k_c \frac{[\text{L}]_0}{2} \quad (3)$$

The overall corrected rate constant $k_{\text{obsd}} - k'_0$ is directly estimated from the graph. Based on Eq. (2), the plots of $(k_{\text{obsd}} - k'_0)_{\text{sat}}$ vs. $[\text{L}]_0/2$, give a straight line (Fig. 4), the slope of which is k_c . k_c values were found to be equal to 157 and $147 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of EHPB micelles and the homopolymer, respectively.

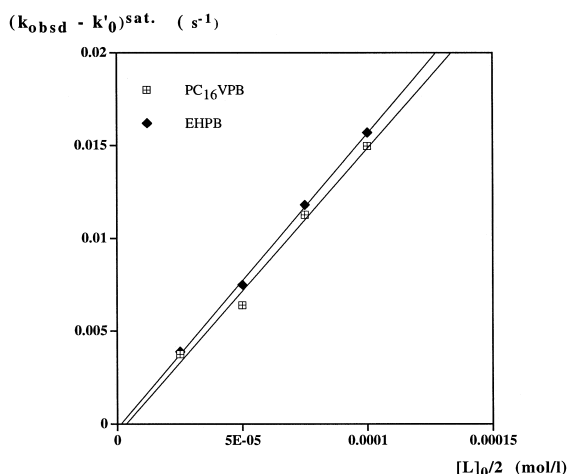


Fig. 4. Plots of $k_{\text{obsd}} - k'_0$ at saturation as a function of $[\text{L}]_0/2$ for the pair ($\text{C}_{10}\text{BimOH}$, C_7E).

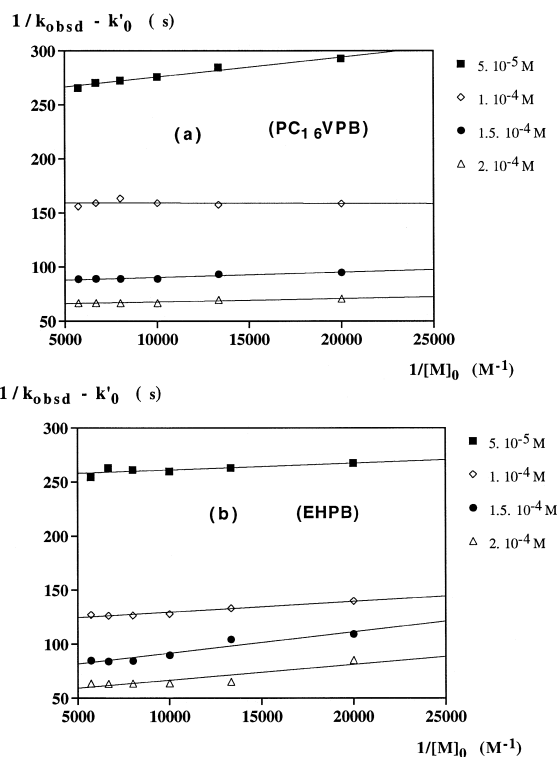


Fig. 5. Plots of $1/k_{\text{obsd}} - k'_0$ vs. $1/[\text{M}]_0$ for the pair ($\text{C}_{10}\text{BimOH}$, C_7E). $T = 30^\circ\text{C}$; $[\text{C}_{10}\text{BimOH}] = 0.5, 1, 1.5, 2 \times 10^{-4} \text{ M}$; $[\text{C}_7\text{E}] = 2.5 \times 10^{-5} \text{ M}$. (a) In the presence of PC_{16}VIB ; (b) in the presence of EHPB. $[\text{PC}_{16}\text{VIB}] = [\text{EHPB}] = 6 \times 10^{-4} \text{ M}$.

The activity of the complexes are very similar in both cases with a slight improvement for the micellar system.

Another point of this work consists of the determination of the association complex constant between the ligand $\text{C}_{10}\text{BimOH}$ and the metal in the presence of EHPB micelles or PC_{16}VPB . From Eq. (1) and 2, the concentration terms $[\text{ML}_2]^2$ and $[\text{ML}_2]^3$ in comparison with $[\text{M}]_0$ and $[\text{L}]_0$ become negligible. Indeed, from the previous k_c values and by likening the concentrations $[\text{M}]$ and $[\text{L}]$ to $[\text{M}]_0 = 1.75 \times 10^{-4} \text{ M}$ and $[\text{L}]_0 = 2 \times 10^{-4} \text{ M}$, the K value for the pair $\text{C}_{10}\text{BimOH}/\text{C}_7\text{E}$ is at least equal to $1.4 \times 10^7 \text{ M}^{-2}$. Consequently

$$[\text{C}] = \frac{K[\text{M}]_0[\text{L}]_0^2}{1 + 4K[\text{M}]_0[\text{L}]_0 + K[\text{L}]_0^2} \quad (4)$$

and the overall observed rate constant may be approximated by:

$$k_{\text{obsd}} - k'_0 = \frac{K[M]_0[L]_0^2}{1 + 4K[M]_0[L]_0 + K[L]_0^2} \quad (5)$$

or

$$\frac{1}{k_{\text{obsd}} - k'_0} = \frac{1 + K[L]_0^2}{k_c K [L]_0^2} \times \frac{1}{[M]_0} + \frac{4}{K [L]_0^2} \quad (6)$$

At various ligand concentrations, the plots of $1/k_{\text{obsd}} - k'_0$ vs. $1/[M]_0$ exhibit linear relationships for Zn^{2+} concentrations as shown in Fig. 5. From the straight lines, the plot of the slopes vs. $1/[L]_0^2$ allows the calculation of the product $k_c K$ and consequently the complexation constant K by using the k_c values obtained from saturation curves. K could be evaluated at $3.3 \times 10^9 \text{ M}^{-2}$ and $1.1 \times 10^{10} \text{ M}^{-2}$ for the homopolymer and the model, respectively. In both cases, it must be noted that the very high values of the complexation constants corroborate the intervention of the complex at low Zn^{2+} concentrations which is evidenced by a rapid increase of $k_{\text{obsd}} - k'_0$ at the same concentrations.

3.3. Influence of the hydrophobicity of the esters 5-alkoxy-4'-nitrophenyl picolinate

Fig. 6 illustrates the dependence of k_{obsd} on the hydrophobicity degree of the esters in the presence of the polymer and its micellar analogous EHPB. We observe an increase of the esterolysis rate constant with an the lengthening of the alkyl chain ester for the two systems. In the presence of amphiphilic polymer PVPB, the activity passes through a maximum for C_7 ester and then k_{obsd} decreases because of a lower incorporation of esters in the organized system. Taken as a whole, the esterolytic activity in the presence of EHPB micelles remains slightly higher than that observed with the polymer microdomains.

3.4. Esterolysis of *p*-nitrophenyl alkanooates

In parallel and by comparison with the picolinate, a series of *p*-nitrophenyl alkanooates (noted C_nONP with $n = 2, 6, 10, 12$) was tested in order to observe the incidence of the co-complexing character of the esters on the formation of a possible ternary complex. The kinetic runs

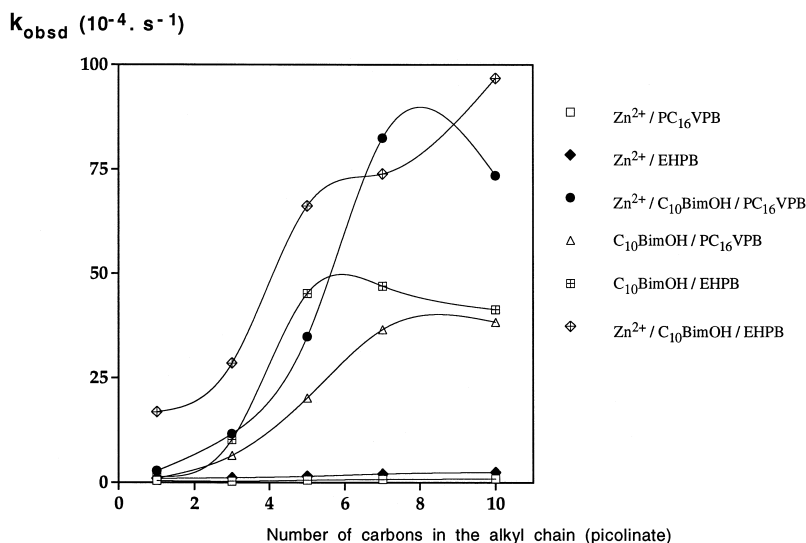


Fig. 6. Dependence of k_{obsd} on the chain length of the esters (picolinate) for the ligand $\text{C}_{10}\text{BimOH}$. $T = 30^\circ\text{C}$; $\text{pH} = 7.1$; HEPES buffer = 0.015 M (ethanol 1%/n-propanol 3%) M ; $I = 6 \times 10^{-3} \text{ M}$; $[\text{PC}_{16}\text{VPB}] = [\text{EHPB}] = 6 \times 10^{-4} \text{ M}$, $[\text{Ligand}] = 1 \times 10^{-4} \text{ M}$, $[\text{Zn}^{2+}] = 2 \times 10^{-4} \text{ M}$, $[\text{C}_7\text{E}] = 2.5 \times 10^{-5} \text{ M}$.

Table 2
Pseudo-first-order rate constants for the esterolysis of the *p*-nitrophenyl alkanooates

Esters	k_0 (10^{-4} s^{-1})	k_{obsd} (10^{-4} s^{-1}) Zn^{2+}	k_{obsd} (10^{-4} s^{-1}) $\text{C}_{10}\text{BimOH}$	k_{obsd} (10^{-4} s^{-1}) $\text{C}_{10}\text{BimOH}-\text{Zn}^{2+}$
C_2ONP	0.06	0.084	0.88	1.49
C_6ONP	0.14	0.16	6.64	17.93
C_{10}ONP	0.15	0.17	17.05	48.65
C_{12}ONP	0.16	0.17	16.51	44.72

$T = 30^\circ\text{C}$; HEPES buffer = 0.015 M (containing ethanol 1% / *n*-propanol 3% vol.); $I = 6 \times 10^{-3}$ M; pH = 7.1; $[\text{PC}_{16}\text{VPB}] = 6 \times 10^{-4}$ M; $[\text{C}_{10}\text{BimOH}] = 1 \times 10^{-4}$ M; $[\text{Zn}^{2+}] = 2.5 \cdot 10^{-5}$ M.

were performed under the same conditions than for picolinates (Table 2). As shown in Fig. 7, an increase of the hydrophobicity of the esters leads to an increase of the overall rate constant of esterolysis. The decrease observed for C_{12}ONP in the presence of the ligand alone or the complex $\text{C}_{10}\text{BimOH}-\text{Zn}^{2+}$ is also due to a lower micellisation of this ester. As for the picolinates, besides the influence of the hydrophobic character of the esters, we examined the effect obtained on the hydrolysis of *p*-nitrophenyl alkanooates by addition of Zn^{2+} ions. The addition of Zn^{2+} ions did not modify k_{obsd} when compared with k_0 (spontaneous hydroly-

sis rate constant). However, a increase in rate magnitude (10-fold) was observed in the presence of the ligand alone. When Zn^{2+} ions are combined with $\text{C}_{10}\text{BimOH}$, k_{obsd} is 3-fold higher than that for the ligand alone and the acceleration is 16 to 300-fold according to the nature of the ester and compared with Zn^{2+} ions alone. This effect is due to the formation of a previous binary complex (2/1 type) as soon observed in the case of the picolinates. However, the overall esterolysis rate constants for the alkanooates are 2-fold lower than that for their picolinate homologues. This result can be explained by a participation of the picolinate pyridin ring nitrogen atom to the stabilization of the active binary complex.

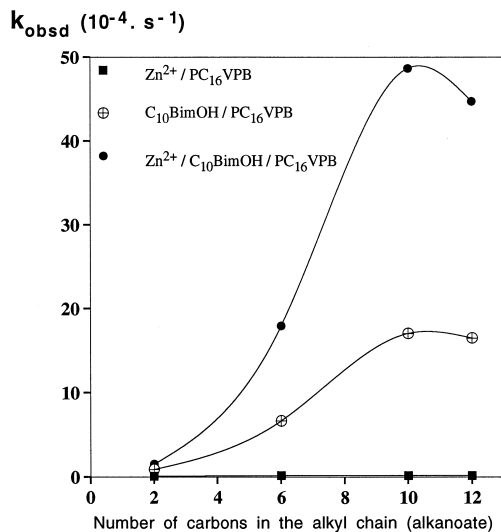


Fig. 7. Dependence of k_{obsd} on the chain length of the esters (alkanoates) for the ligand C_{10}Bim . $T = 30^\circ\text{C}$; pH = 7.1; HEPES buffer = 0.015 M (ethanol 1% / *n*-propanol 3%) M; $I = 6 \times 10^{-3}$ M; $[\text{PC}_{16}\text{VPB}] = [\text{EHPB}] = 6 \times 10^{-4}$ M, $[\text{Ligand}] = 1 \times 10^{-4}$ M, $[\text{Zn}^{2+}] = 2 \times 10^{-4}$ M, $[\text{C}_n\text{ONP}] = 2.5 \times 10^{-5}$ M.

4. Conclusion

The homopolymer poly(1-hexadecyl-3-vinylpyridinium bromide) (PC_{16}VPB) generates in aqueous medium hydrophobic microdomains, the influence of which on catalytic reactions is very comparable to that of conventional surfactants (EHPB model or CTAB). Unlike poly(3-hexadecyl-1-vinylimidazolium bromide) (PC_{16}VIB) and its model 3-hexadecyl-1-methylimidazolium bromide (HMIB) where the addition of Zn^{2+} ions leads to either a lack of $\text{C}_{10}\text{BimOH}$ ligand effect in the presence of HMIB, or an inhibition of the reaction for PC_{16}VIB [15], in the case of PC_{16}VPB and the model EHPB, the esterolytic activity is due to the formation of a 2/1 active complex.

The reactivity of *p*-nitrophenyl alkanoates is lower than that of their picolinate homologues. This effect is linked to the co-complexing character of the picolinic esters which contributes to speed up the process by intramolecular catalysis and by activation of the carbonyl group due to a polarization induced by the Zn^{2+} ion charge.

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