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The influence of sodium salicylate on the micellar rate effect and the structural behaviour of dodecylpyridinium bromide micelles

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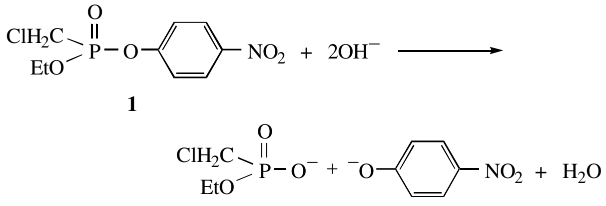
A correlation between salt-induced structural transitions of dodecylpyridinium bromide micelles and their catalytic effect on the basic hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate has been found.

Although the electrolyte effects on the micellar catalysis are widely investigated,[1–3] some urgent aspects of the problem remain hitherto unsolved. The most important problem is the influence of salt-induced micellar transitions on the micellar rate effect. It is well known[4–6] that addition of electrolytes results in a change in micellar characteristics such as a critical micellar concentration (cmc), an aggregation number, a degree of counter-ion binding, a micellar shape *etc*. At a definite counter-ion concentration, a gradual change in the above parameters with counter-ion concentration turns into a sharp change, which is revealed by a break in the 'property' *vs.* lg C_{salt} plot. In accordance with the literature,[4] these threshold electrolyte concentrations are associated with micellar sphere-to-rod transitions. It is reasonably to assume that alterations in the above micellar parameters should exert an influence on the reactivity in the micelles. In our earlier studies,[7,8] a mechanism of the electrolyte effect on nucleophilic substitution reactions and acid–base equilibria in cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB) micelles has been investigated. The aim of this work was to study the kinetics of basic hydrolysis of *O*-ethyl *O*-*p*-nitrophenyl chloromethylphosphonate **1** in dodecylpyridinium bromide (DPB) micellar solutions (Scheme 1) in a wide range of sodium salicylate (NaSal) concentrations and the structural behaviour of the micelles used as nanoreactors by surface tension measurements and NMR and EPR spectroscopy. Cationic micelles exhibit a unique behaviour in the presence of Sal-anions, which requires further investigation.



Scheme 1

Substrate **1** was prepared according to the published procedure.[9] The surfactant DPB of 'pure' grade was twice recrystallised from ethanol. The surface tension measurements were performed by the anchor-ring method.[10] The surface tension isotherms were used to determine the counter-ion binding with the ±0.01 accuracy.[11] The Fourier transform proton pulsed-gradient spin-echo (FT-PGSE) measurements were performed using a modified TESLA-BS 576A NMR spectrometer at 100 MHz to give the self-diffusion coefficients of micellar components.[12] The X-band EPR spectra were recorded on an RE 1306 spectrometer under conditions described elsewhere.[13] 5-Doxyl-stearic acid (Sigma) was used as a spin label in a concentration of 5×10^{-4} mol dm^{-3}. The reaction was monitored by observing the *p*-nitrophenolate anion absorption using a 'Specord M-400' spectrophotometer equipped with temperature-controlled cell holders. The kinetic data were treated in terms of the pseudophase model using the equation[14]

$$k'_{\text{obs}} = \frac{k_{2,\text{w}} + k_{2,\text{m}}K_{\text{S}}K_{\text{OH}}C/V}{(1 + K_{\text{S}}C)(1 + K_{\text{OH}}C)}, \tag{1}$$

where k'_{obs} (dm^3 mol^{-1} s^{-1}) is the second-order rate constant obtained by division of the observed pseudo-first-order rate constant k_{obs} by the total nucleophile concentration; $k_{2,\text{w}}$ and $k_{2,\text{m}}$ (dm^3 mol^{-1} s^{-1}) are the second-order rate constants in the aqueous and micellar phases, respectively; K_{S} and K_{OH} (dm^3 mol^{-1}) are the substrate and nucleophile binding constants, respectively; V is the molar volume of the surfactant assumed to be equal to 0.3 dm^3 mol^{-1}; C is the DPB concentration below the cmc. Problems and approximations involved in these definitions have been discussed earlier.[14]

Figures 1 and 2 represent the kinetic data, which demonstrate a decrease in the observed rate constant with addition of NaSal. According to the pseudophase model,[14] such an inhibition can result from a decrease in the micellar surface potential with counter-ion concentration, which in turn is responsible for weakening the electrostatic attraction of hydroxide ions with positively charged micelles, in which the reaction occurs. In addition, the displacement of the substrate by Sal$^-$ ions from the micellar surface is probably observed. The results of the quantitative treatment of the kinetic data in terms of equation (1) summarised in Table 1 show a reduction in the substrate binding constants and the rate constants in the micellar pseudophase as the counter-ion concentration increases. Note that in the absence of electrolytes both the concentrating factor (F_{c}) and the micellar microenvironment (F_{m}) make positive contributions to the micellar rate effect, which is unusual for the ion–molecule nucleophilic substitution reactions in cationic micelles.[2]

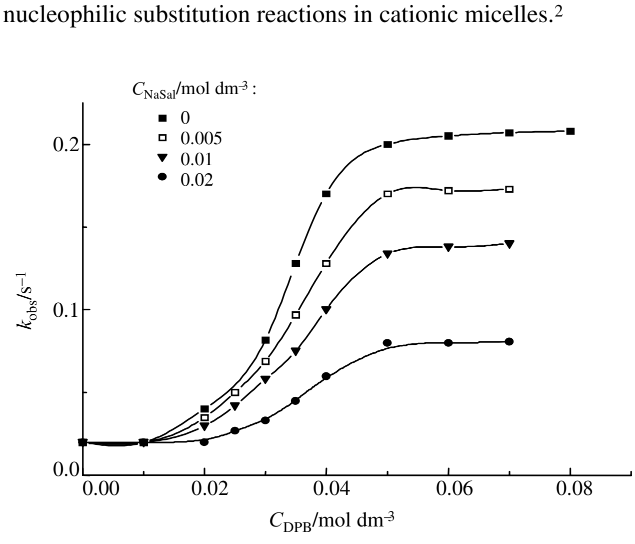


Figure 1 The observed rate constant of basic hydrolysis of **1** in micellar solutions of DPB as a function of surfactant concentration at different NaSal concentrations (0.005 mol dm^{-3} NaOH, 25 °C).

Table 1 Kinetic data for the different NaSal concentrations (Figure 1) treated in terms of the pseudophase model.

C_{NaSal}/mol dm^{-3}	$k_{2,m}$/dm^3 mol^{-1} s^{-1}	K_S/dm^3 mol^{-1}	K_{OH}/dm^3 mol^{-1}	F_c^a	F_m^a	$(k_{obs}/k_w)_{max}$	$F_cF_m^a$	β
0	11.7	233	1.4	3.9	2.9	10.4	11.5	0.71
0.005	5.0	200	3.0	7.9	1.3	8.6	9.8	0.92
0.01	4.5	83	3.0	7.0	1.1	7.0	8.0	0.94
0.02	1.1	63	11.0	19.0	0.3	4.0	5.0	0.96

[a]The F_c and F_m values were calculated using the modified equation

$$(k_{obs}/k_w)_{max} = \frac{k_{2,m}}{k_{2,w}}\,\frac{K_SK_{OH}}{V(K_S^{1/2}+K_{OH}^{1/2})^2}.$$

The left member (the ratio between the pseudo-first-order rate constants in the micellar system and water) describes the maximum acceleration of the reaction. The first multiplier is associated with the influence of the micellar microenvironment (F_m), and the second multiplier reflects concentrating the reagents in micelles (F_c).

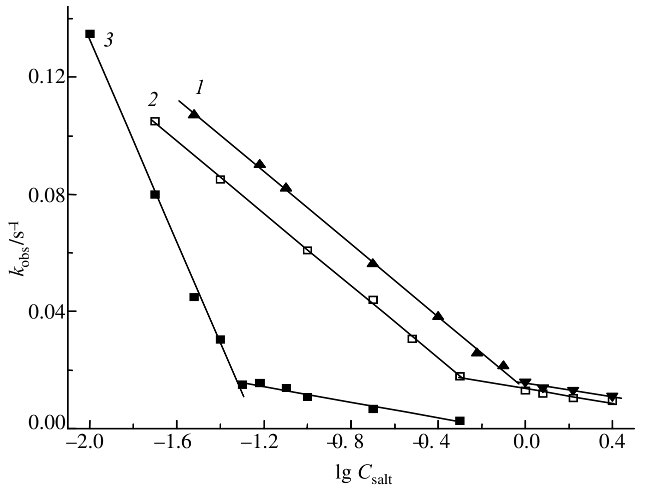


Figure 2 The observed rate constant of basic hydrolysis of **1** in micellar solutions of DPB as a function of the logarithm of salt concentration (0.005 mol dm^{-3} NaOH, 25 °C): (*1*) KCl, (*2*) KBr and (*3*) NaSal.

An analysis of the kinetic data on semilogarithmic coordinates has been carried out (Figure 2), which revealed critical NaSal concentrations (C_{cr}) corresponding to the breaks in the k_{obs} *vs.* lg C_{salt} plot. For comparison, analogous data for Br$^-$ and Cl$^-$ counter-ions were obtained. According to refs.7 and 8, C_{cr} values can be associated with the above structural transitions in the DPB micelles. The value of C_{cr} for Sal$^-$ is equal to 0.05 mol dm^{-3} (for Cl$^-$ and Br$^-$, C_{cr} values are equal to 1.1 and 0.5 mol dm^{-3}, respectively).

In order to test correlation between the micellar structure and reactivity, the structural behaviour of the DPB micelles has been studied by surface tension measurements, NMR and EPR spectroscopy. The surface tension experiments yielded the cmc values of micellar DPB solutions at various NaSal concentrations. Based on published data,[6] the empirical equation lg cmc = -0.851lg $C_{salt} - 5.32$ has been drawn. An analysis of the surface tension isotherms using the known methodology[11] enables us to calculate the degree of counter-ions binding (β) at various NaSal concentrations (Table 1). A marked increase in the β value is observed as bromide ions are replaced by Sal$^-$ ions.

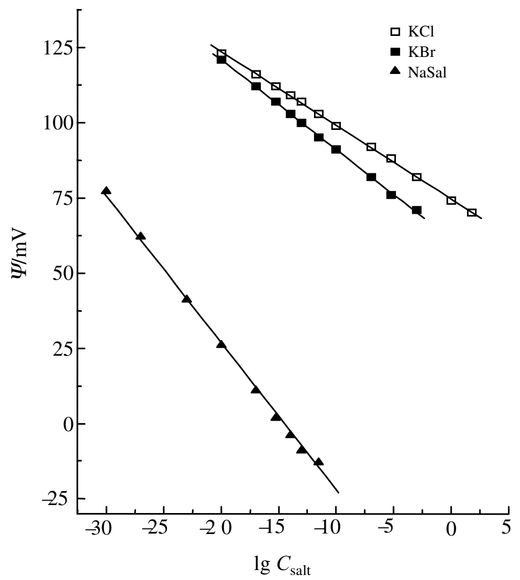


Figure 3 The surface potential of DPB micelles as a function of the logarithm of electrolyte concentration.

Using the Nernst correlation between the surface potential and cmc d|Ψ|/dlg cmc = 59.16 mV,[15] the DPB surface potential has been calculated at different NaSal concentrations. The results are shown in Figure 3 together with the data for hydrophilic counter-ions, added for comparison. Similarly to published data,[8] we found a coincidence of Ψ values corresponding to the C_{cr} values for Br and Cl, which are 74 and 71 mV, respectively. This fact indicates a prevalent role of the surface potential in the inhibition mechanism of inorganic counter-ions. The C_{cr} value for Sal$^-$ corresponds to -7 mV. This result is consistent with the published data on negative surface potentials Ψ[16] and ξ-potentials[17,18] of cationic micelles in the presence of Sal$^-$ ions. An unique effect of Sal$^-$ on CTAB, CPB and tetradecyltrimethylammonium halide micelles, which dramatically differs from that of hydrophilic inorganic counter-ions is extensively studied,[17,18] whereas the behaviour of DPB micelles in the presence of NaSal is almost unknown. We examined the influence of Sal$^-$ on the structure of DPB micelles.

The micellar size and shape were determined on the basis of the DPB self-diffusion coefficients (D) (Table 2) obtained from the diffusive decay of a line due to the $(CH_2)_n$ protons in the NMR spectra of DPB. The experimental details were published elsewhere.[12,19,20] The Stokes–Einstein equation

$$D = kT/6\ \eta R, \qquad (2)$$

where η is the solvent viscosity, gives the effective radius of DPB micelles in the absence of NaSal R = 15.4 Å, which is very close to the DPB molecule length calculated from the bond

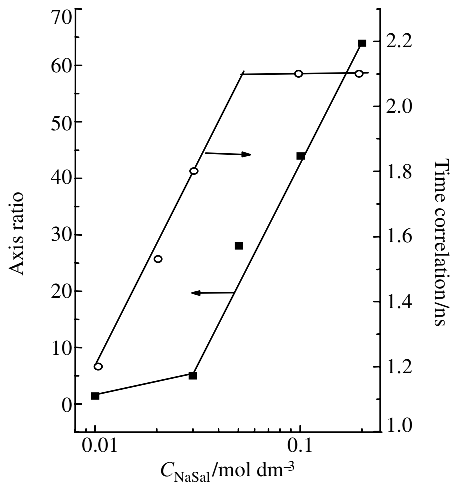


Figure 4 The spin-label correlation time (τ = 1.1 ns with no NaSal added) and the axis ratio of DPB micelles as functions of NaSal concentration.

Table 2 The self-diffusion coefficients of DPB D_{DPB} in water at different NaSal concentrations (C_{DPB} = 0.05 mol dm^{-3}).

C_{NaSal}/mol dm^{-3}	D_{DPB}/10^{-11} m^2 s^{-1}
0	14.0
0.01	11.4
0.03	6.21
0.05	2.00
0.1	1.38
0.2	1.04

parameters (15.5 Å). This fact is indicative of a spherical shape of DPB micelles with no NaSal added. In the presence of NaSal, equation (2) gives improbably high values of *R*. Because of this, we used *D* to obtain the axis ratio $P = B/2A$ (Figure 4) considering the DPB micelles as prolate ellipsoids.[21] Here, *B* is the length of an ellipsoidal micelle, and *A* is equal to the radii of a spherical micelle in the absence of NaSal. Figure 4 shows that an increase in the Sal$^-$ concentration results in changes of the micellar shape from spherical to intermediate sphere-cylindrical (P = 1–5) at the first stage and to strongly stretched at C_{NaSal} ~ 0.05 mol dm^{-3}.

The sphere-to-rod transition is reflected in the packing density of surfactant molecules in the micelle structure.[22] To characterise it, we made EPR measurements and found the correlation time of spin-label rotation $\tau = 6.65\ H_+[(I_+/I_-)^{-1/2} - 1]\times 10^{-10}$ s, where H_+ is the width of the low-field component in the EPR spectrum, I_+ and I_- are the intensities of the low- and high-field hyperfine components, respectively. The mobility of a spin label connected with the carbon atom of stearic acid at the 5-position can characterise the packing degree of DPB molecules close to polar head groups of the micelles. Figure 4 exhibits two linear regions in the NaSal concentration dependence of τ. At the first stage (below ~0.05 mol dm^{-3} NaSal), an increase in the correlation time shows that the fraction of cylindrical micelles increases as compared with spherical micelles, *i.e.*, the micelles lengthened. At the second stage when micelles become long enough, the contribution from spherical particles exerts no effect on the average correlation time.

Thus, the NMR self-diffusion and EPR data give evidence for the structural transition in DPB micelles at a 0.05 mol dm^{-3} NaSal concentration. Comparing Figures 2 and 4, it can be seen, that C_{cr} values (Figure 2) are in the NaSal concentration range corresponding to dramatic structural changes in the DPB micelles.

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