The kinetics of solvolysis of *p*-nitrophenyl bis(chloromethyl)phosphinate in a micellar solution of sodium dodecyl sulfate in ethylene glycol: catalysis by metal ions

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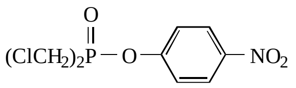
A 30-fold acceleration of the title reaction due to an increase in the activation entropy and activation enthalpy in the micellar pseudophase compared to ethylene glycol was found; Mg^{2+}, Zn^{2+} and La^{3+} ions accelerate the solvolysis by factors of 5, 8 and 20, respectively.

The kinetics of nucleophilic substitution reactions in aqueous micellar solutions is intensively studied.[1–3] These kinetic studies are based on both experimental data on micellization and solubilization in aqueous micellar solutions and a progress in the theory of micelles.[4–6] The solvophobic effects and the formation of direct micelles and solubilization in nonaqueous polar solutions are much less studied.[7–9]

Catalysis of nucleophilic substitution reactions in metallomicelles, considered as the simplest analogues of metalloenzymes, is also insufficiently studied. Data on the acceleration of hydrolysis of carbon and phosphorus acid esters by transition metal, lanthanide and actinide metal ions, including those in micelles and microemulsions, were published.[10,11]

In this study, we examined the solvolysis of *p*-nitrophenyl bis(chloromethyl)phosphinate in the direct micelles of sodium dodecyl sulfate (SDS) in ethylene glycol. The effect of metal ions on the kinetics was also investigated. The mechanism of nucleophilic substitution reactions of bis(chloromethyl)phosphinic acid esters in the absence of surfactants was studied earlier.[12] The only direction of the process *via* splitting the P–OAr bond was found, while a reaction with the CH_2Cl group occurred at extremely severe conditions if any. The solvolysis was performed at pH 6.5, which is spontaneously maintained in the solution. We did not use buffer solutions because, first, the buffer component can be involved in the reaction, which results in a complication of the process. Second, buffered solutions cannot provide a required value of pH because ion-exchange processes at the interface result in concentrating positively charged particles in anionic micelles, while the concentration of negatively charged ions is lower in anionic micelles than in the bulk phase. Thus, an apparent pH value was used in the experiment. The problem of pH in micellar solutions was discussed earlier.[13]



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Substrate **1** was prepared according to the published procedure.[14] Commercial SDS from Sigma was used. Ethylene glycol of ‘pure’ grade was carefully dried and twice distilled. $La(NO_3)_3 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl and KCl were of analytical grade. The reaction was controlled by monitoring the *p*-nitrophenol absorption on a ‘Specord M-400’ spectrophotometer. The initial substrate concentration was 5×10^{-5} mol dm^{-3}. The observed rate constants (k_{obs}) were determined to within 4% using the function: $\ln (A_\infty - A) = -k_{obs}t + {}$ $+ \text{const}$, where A and A_∞ are the absorbance of the micellar solutions at the moment t and after completion of the reaction, respectively. The kinetic data were treated in terms of the equation[3]

$$k'_{obs} = \frac{k_{2,0} + k_{2,m}K_sK_{Nu}C/V}{(1 + K_sC)(1 + K_{Nu}C)}, \quad (1)$$

where k'_{obs} (dm^3 mol^{-1} s^{-1}) is the second-order rate constant obtained by dividing the apparent pseudo-first-order rate constant by the total nucleophile concentration; $k_{2,0}$ and $k_{2,m}$ (dm^3 mol^{-1} s^{-1}) are the second order rate constants in the bulk and micellar phases, respectively; K_s and K_{Nu} (dm^3 mol^{-1}) are the substrate and nucleophile binding constants; V is the molar volume of the surfactant assumed equal to 0.3 dm^3 mol^{-1}; C is the surfactant concentration below the critical micelle concentration (cmc).

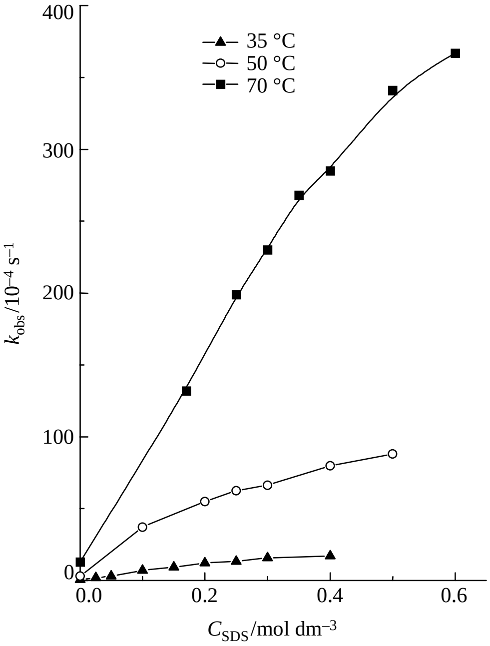

Figure 1 The observed rate constants of solvolysis of **1** as a function of the SDS concentration in ethylene glycol at different temperatures, pH 6.5.

In micellar solutions, the reactions of hydrophobic substrates mainly proceed in micelles. The microenvironments of reagents are different in the polar bulk pseudo-phase and the micellar phase. In particular, dielectric constant becomes lower on going from the bulk phase to the micellar surface and core (the microenvironment factor F_m). The local concentrations increase because the volume fraction of the micellar pseudo-phase is much lower than that of the solvent (the concentrating factor F_c). These factors change the reaction rate in micellar solutions as compared to that in ethylene glycol and can be evaluated by the equation:

$$(k_{obs}/k_0)_{max} = \frac{k_{2,m}}{k_{2,0}} \frac{K_sK_{Nu}}{V(K_s^{1/2} + K_{Nu}^{1/2})^2}, \quad (2)$$

where k_0 is the rate constant in the absence of the surfactant. The first term on the right-hand side is associated with the influence of the micellar microenvironment on the reactivity (F_m). The second term reflects concentrating the reagents in micelles (F_c).

The shape of the kinetic curves (Figure 1) is typical of micelle catalysed reactions, which can be considered as a kinetic argument in favour of SDS micellization in ethylene glycol. The ‘kinetic’ cmc value computed by equations (1) and (2) is equal to 0.16 mol dm^{-3}.

Table 1 Kinetic data treated in terms of equations (1) and (2); ΔH_0 = 76.8 kJ mol^{-1}, ΔS_0 = –66.6 J mol^{-1} K^{-1}, ΔH_m = 95.8 kJ mol^{-1}, ΔS_m = –20.1 J mol^{-1} K^{-1}.

T/°C	$k_{2,0}/10^{-3}$ dm^3 mol^{-1} s^{-1}	$(k_{obs}/k_0)_{max}$	K_s/dm^3 mol^{-1}	k_{Nu}/dm^3 mol^{-1}	$k_{2,m}/10^{-3}$ dm^3 mol^{-1} s^{-1}	F_c	F_m	$F_c \times F_m$
35	0.003	31.5	6.7	2.3	0.031	3.1	10.4	32
50	0.017	29.3	8.8	1.2	0.23	2.1	14.4	30.5
70	0.072	28.4	5.5	0.7	1.58	1.3	22.1	28.4

According to the thermodynamic approach developed in ref. 7, the aggregation in ethylene glycol occurs only at very high surfactant concentrations in contrast to the behaviour of surfactants in water, and the aggregation numbers are low.

In the micellar SDS solutions, the reaction was accelerated by a factor of 30. Table 1 indicates that the reagent microenvironment in the micelles is mainly responsible for the catalysis (F_m is 10.4–22.1 depending on the temperature), while a contribution of the concentrating factor is much lower.

We evaluated the activation parameters of the reaction (activation enthalpy and activation entropy) in different pseudophases (Table 1) using the known formalism.[15] Figure 2 shows the activation parameters ΔH_{obs} and ΔS_{obs} calculated using the observed rate constants k'_{obs}. Although these parameters are effective and reflect the contributions of both the chemical reaction and the interactions of surfactant and solvent molecules, they give an idea of the alteration in the activation parameters of the reaction systems with surfactant concentration.

Figure 2 indicates that an almost parallel compensatory change in the activation parameters occurs when the surfactant is added: unfavorable changes in the entropy ΔS_{obs} are accompanied by a decrease in ΔH_{obs}. Such a tendency is preserved nearly up to the cmc. Apparently, the above alterations in the observed activation parameters are mainly governed by the energetics of SDS monomers and by the solubilization behaviour of reagents.[6] Compensatory changes in the activation parameters ΔH_{obs} and ΔS_{obs} continued above the cmc, but the tendency was inverted (Figure 2). A comparison between the ΔH_0, ΔS_0 and ΔH_m, ΔS_m demonstrates that above the cmc the chemical reaction mostly contributes to the effective activation parameters.

Transferring the reaction from the bulk pseudophase to the micelles results in a slight increase in the activation enthalpy (by 19 kJ mol^{-1}) and a marked increase in the activation entropy (from –67.2 to –21 *J* mol^{-1} K^{-1}, Table 1). It is known that solvolysis often proceeds *via* a hybrid S$_N$1–S$_N$2 mechanism.[16] The unimolecular S$_N$1 process is assumed to proceed *via* charge generation in the transition state and can be characterised by higher activation enthalpies and higher activation entropies as compared to the S$_N$2 mechanism. The latter is treated as a synchronous single-stage break of the phosphorus–leaving group bond and the formation of the phosphorus–nucleophile bond. The values of ΔH_0 and ΔS_0 are typical of bimolecular reactions.[16,17] This fact evidences for the predominance of the S$_N$2 mechanism with no added surfactant. The favourable alterations in the activation entropy in the micellar pseudophase can be an argument in favour of the hypothesis that the S$_N$1 mechanism is prevalent over the S$_N$2 process in the micellar pseudophase.

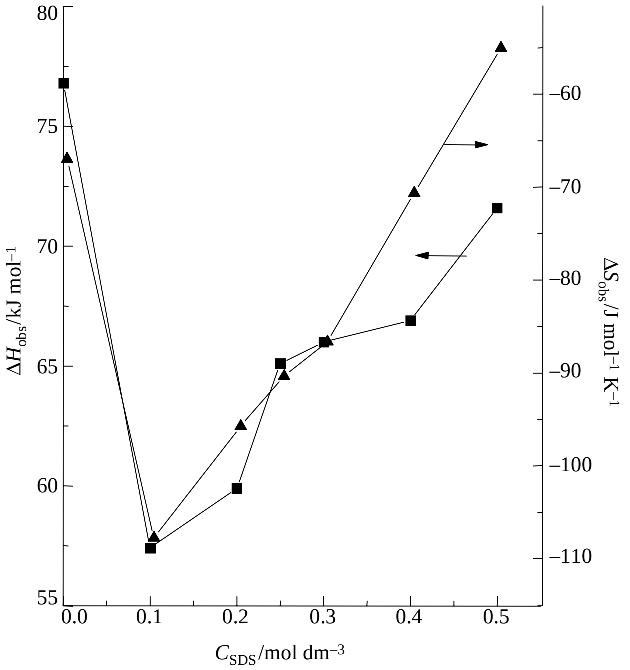

Figure 2 The effective activation entropy and activation enthalpy of solvolysis of **1** as a function of the SDS concentration in ethylene glycol, pH 6.5.

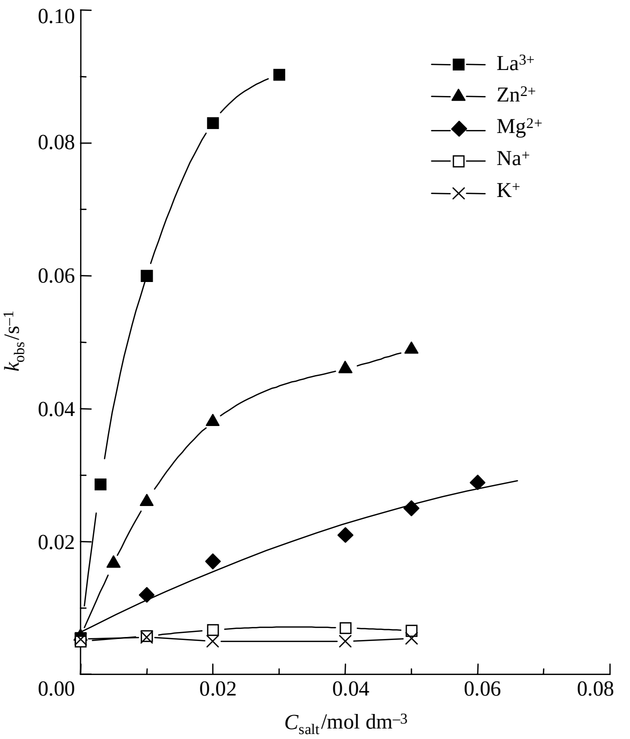

Figure 3 The observed rate constants of solvolysis of **1** as a function of the metal ion concentration (0.2 mol dm^{-3} SDS, 50 °C, pH 6.5).

Figure 3 shows the observed rate constants of the solvolysis of **1** in SDS micelles (0.2 mol dm^{-3} SDS) as functions of the concentrations of Na$^+$, K$^+$, Mg^{2+}, Zn^{2+} and La^{3+} ions. It is known[18,19] that the counter-ions of micelles can influence the reactivity, changing aggregate properties such as surface potential, cmc and aggregation number. Metal ions can also accelerate nucleophilic substitution reactions at carbon and phosphorus atoms by an electrophilic assistance and/or coordination of reagents.[20] Figure 3 indicates that Na$^+$ and K$^+$ do not affect the solvolysis of **1**, while Mg^{2+}, Zn^{2+} and La^{3+} accelerate the reaction by factors of 5, 8 and 20, respectively. We can draw some conclusions on the effects of metal ions. The catalytic properties are exhibited by ions capable of forming coordination compounds. The fact that the solvolysis of **1** is unaffected by Na$^+$ and K$^+$ ions suggests that the catalytic effect cannot be explained by only the salt effect.

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References

1 C. A. Bunton and G. Savelli, *Adv. Phys. Chem.*, 1986, **22**, 213.
2 N. Ouarti, A. Marques, I. Blagoeva and M.-F. Ruasse, *Langmuir*, 2000, **16**, 2157.

3 K. Martinek, A. K. Yatsimirsky, A. V. Levashov and I. V. Beresin, in *Micellization, solubilization, and microemulsions*, ed. K. L. Mittal, Plenum Press, New York, 1977, **2**, 489.

4 K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, *Colloidal Surfactants*, Academic Press, New York, 1963.

5 R. Zana, *J. Phys. Chem.*, 1999, **103**, 9117.

6 A. I. Rusanov, *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (*Micellization in the solutions of the surface-active substances*), Khimiya, St. Petersburg, 1992.

7 R. Nagarajan and C.-C. Wang, *J. Colloid Interface Sci.*, 1996, **178**, 471.

8 W. Binana-Limbele and R. Zana, *Colloid Polym. Sci.*, 1989, **267**, 440.

9 P. Eychenne, I. Rico, E. Perez and A. Lattes, *New J. Chem.*, 1995, **19**, 193.

10 R. A. Moss and K. G. Ragunathan, *Langmuir*, 1999, **15**, 107.

11 C. A. Bunton, P. Serimin and P. Tecilla, *J. Chem. Soc., Perkin Trans. 2*, 1975, 419.

12 V. E. Bel'skii, M. V. Efremova and I. M. Shermergorn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 923 (*Bull. Akad. Sci. USSR, Div. Chem. Sci.*, 1967, **16**, 891).

13 C. A. Bunton and B. Wolfe, *J. Am. Chem. Soc.*, 1973, **95**, 3742.

14 V. E. Bel'skii, L. A. Kudryavtseva, O. M. Il'ina and B. E. Ivanov, *Zh. Obshch. Khim.*, 1970, **49**, 2470 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1970, **49**, 2180].

15 R. W. Hoffmann, *Aufklarung von Reactionsmechanismen*, Georg Thieme Verlag, Stuttgart, 1976 (in German).

16 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca–London, 1969.

17 N. A. Loshadkin, in *Toksichnye efiry kislot fosfora* (*Toxic Esters of Phosphorus Acids*), ed. P. O'Brain, Mir, Moscow, 1964 (in Russian).

18 C. A. Bunton, in *Reaction Kinetics in Micelles*, ed. E. N. Cordes, Plenum Press, New York, 1973, p. 73.

19 L. Ya. Zakharova, F. G. Valeeva, D. B. Kudryavtsev, L. A. Kudryavtseva, A. I. Konovalov, Yu. F. Zuev, N. L. Zakharchenko, N. N. Vylegzhanina and Z. Sh. Idiatullin, *Mendeleev Commun.*, 1999, 245.

20 W. Jencks, *Catalysis in Chemistry and Enzymology*, McGraw–Hill, New York, 1969.

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