Effect of sodium dodecyl sulfate on the reactivity of 2-dimethylaminomethylphenol with 4-nitrophenylbis(chloromethyl)phosphinate

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The reactivity of 2-dimethylaminomethylphenol (**1**) toward 4-nitrophenylbis(chloromethyl)phosphinate (**2**) was studied in micellar solutions and in the lyotropic liquid-crystalline mesophase of the sodium dodecyl sulfate (SDS)—water system. The reaction between **1** and **2** is inhibited in the presence of SDS, which is explained by the shift of the acid-base equilibrium of **1** toward the formation of a nonreactive protonated form.

Key words: micelles, liquid crystals, rate constant; sodium dodecyl sulfate, 2-dimethylaminomethylphenol, 4-nitrophenylbis(chloromethyl)phosphinate.

Anionic micelles of sodium dodecyl sulfate (SDS) efficiently inhibit the effect of anionic nucleophiles, such as OH^-, Br^-, and CN^-, in reactions of nucleophilic substitution of carbonyl and phosphoryl type esters.[1,2]

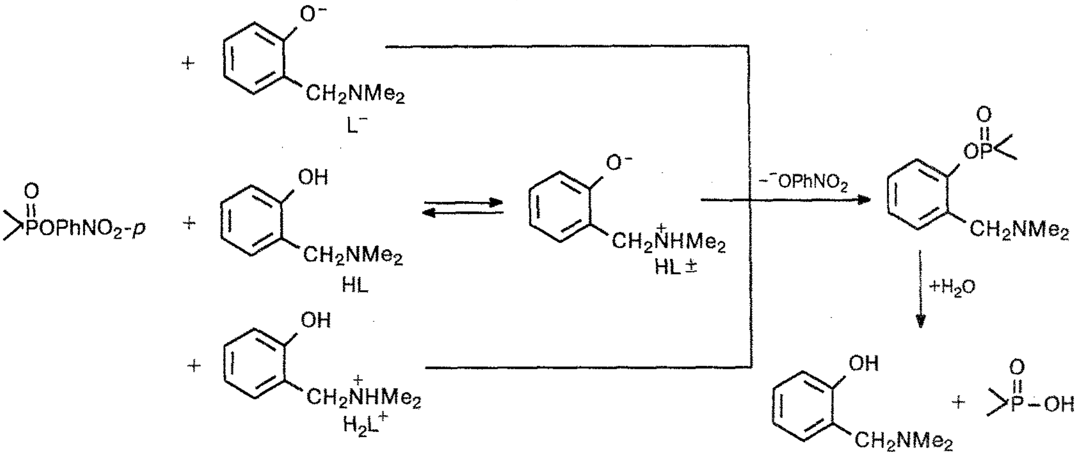
Effects of anionic surfactants on these polyfunctional nucleophiles in these reactions are almost unknown. It has been shown previously[3,4] that 2-dialkylaminomethylphenols and their copper(II) complexes in aqueous-alcohol media are bifunctional nucleophilic catalysts of hydrolysis of *p*-nitrophenyl phosphates. In particular, depending on the pH of the medium and the content of ethanol, the reactivity of 2-dimethylaminomethylphenol (**1**) is determined by its forms: phenolate L^- (pH > 9), zwitterionic $HL^{\pm}$, neutral HL (pH 7—9), and protonated H_2L^+ (pH < 7) forms, whose rate constants differ drastically. For example, in the reaction with 4-nitrophenylbis(chloromethyl)phosphinate (**2**) in 40 vol.% aqueous ethanol, the values of the rate constants are 449, 57, and 0.24 M^{-1} s^{-1} for phenolate, zwitterionic, and protonated forms, respectively (Scheme 1).

In this work, the effect of anionic SDS on the reactivity of **1** with **2** is studied.

Experimental

SDS was purified according to the known procedure,[5] compounds **1** and **2** were prepared according to the previously published procedure,[6,7] and the liquid-crystalline mesophase was prepared according to the known procedure.[8] Liquid-crystalline properties and a type of mesophase were deter-

Scheme 1



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mined by polarization microscopy on a small Boetius type heating table with a Vebanalitic PHMK 05 visual instrument. The reaction kinetics were studied spectrophotometrically on a Specord UV-VIS instrument from the increase in optical density due to the formation of *p*-nitrophenolate (λ 400 nm) under the conditions of the pseudomolecular reaction at 25±0.1 °C.

Fractions of protonated and zwitterionic forms of **1**, observed rate constants (k_{ob}), binding constants with a substrate (K_b), rate constants in the micellar phase (k_m), and critical concentrations of micelle formation (CMC) were calculated according to standard and ingenious programs on an Elektronika D3-28 microcomputer.

Results and Discussion

Analysis of the dependence of the observed rate constants on SDS concentration at pH 7—9 shows that SDS inhibits the reaction between compounds **1** and **2** (Table 1).

According to our data, SDS inhibits alkaline hydrolysis of **2** (k_{ob}/k_m = 50, K_b = 1000 mol^{-1} L) much more efficiently than its reaction with **1**. Therefore, the contribution of alkaline hydrolysis to k_{ob} is negligible, especially at pH 7—9 and [SDS] ≥ [CMC]. The run of the $k_{ob} = f(C_{SDS})$ function (reaching a plateau) allows one to interpret the data obtained in terms of the pseudophase model of micellar catalysis, which takes into account the substrate distribution between aqueous and micellar phases, and to calculate parameters of the micelle-inhibited reaction (K_b, CMC, and k_m (Table 2)) by the known equation.[9]

It has been shown previously[11] that the dissociation constant (K_1) of the H_2L^+ form of compound **1**, which is weakly protonated at the nitrogen atom, decreases considerably, and the dissociation constant (K_2) of the neutral HL form decreases slightly in aqueous solutions of SDS. For example, when C_{SDS} increases to 0.05 mol L^{-1}, the pK_1 value increases from 8.45 to 10.0, pK_2 increases from 10.9 to 11.1, and the constant of tautomeric equilibrium K_t = [zwitterion]/[neutral form] decreases from 2.5 to 1.0. In other words, the content of the almost nonreactive form HL^+ increases considerably, and the concentration of the zwitterionic form $HL^{\pm}$ decreases in the presence of SDS (Table 3). The latter is a bifunctional nucleophile, which determines the reactivity of compound **1** in the reaction studied. No reactive phenolate form L^- is observed in the presence of SDS in the 7—9 range studied (see Table 3).

Table 1. Observed rate constants of the reaction between **1** and **2** at various SDS concentrations

pH 7.0		pH 8.0		pH 9.0	
C_{SDS} /mol L^{-1}	$k_{ob} \cdot 10^3$ /s^{-1}	C_{SDS} /mol L^{-1}	$k_{ob} \cdot 10^2$ /s^{-1}	C_{SDS} /mol L^{-1}	$k_{ob} \cdot 10^2$ /s^{-1}
0.01	1.6	0.01	1.71	0.01	8.00
0.025	0.6	0.025	0.91	0.025	6.70
0.05	0.44	0.05	0.45	0.05	5.00
0.075	0.16	0.08	0.41	0.075	4.00
0.10	0.10	0.10	0.39	0.10	2.90
0.20	0.08	0.25	0.36	0.20	2.50
0.30	0.08	0.50	0.345	0.50	2.23

Note. Conditions: pH 7—9, C_1= 5 · 10^{-3} mol L^{-1}, 25 °C.

Table 2. Parameters of the SDS-inhibited micellar reaction between **1** and **2**

pH	T/°C	CMC /mol L^{-1}	K_b /mol L^{-1}	k_m/s^{-1}	$k_w{}^a$/s^{-1}
7.0	25	0.207 · 10^{-1}	583	0.69 · 10^{-4}	0.23 · 10^{-2}
8.0	25	0.125 · 10^{-1}	207	0.33 · 10^{-2}	0.21 · 10^{-1}
9.0	25	0.180 · 10^{-1}	65	0.19 · 10^{-1}	0.92 · 10^{-1}
9.25^b	45	0.210 · 10^{-2}	5	0.52 · 10^{-4}	0.45 · 10^{-3}
9.25^b	60	0.840 · 10^{-2}	14	0.32 · 10^{-3}	0.19 · 10^{-2}

Note. Conditions: pH 7—9, C_1 = 5 · 10^{-3} mol L^{-1}.
[a] k_w are the observed rate constants of the reaction between **1** and **2** in water. [b] Data on the reaction between **1** and 4-nitrophenyldiphenylphosphate in the presence of SDS.[10]

Thus, unlike reactions with anionic nucleophiles, in which Coulombic repulsion between a nucleophile and micelles with a solubilized substrate, *i.e.*, separation of reagents, is the reason for inhibition by SDS micelles, in the reaction studied the inhibition is primarily performed, in our opinion, due to suppression of the formation of nucleophilic zwitterions. The linear character of the $k_{ob} = f(C_{HL^{\pm}})$ dependence at various pH values in the whole range of SDS concentrations (C_1 = 5 · 10^{-3} mol L^{-1}) favors the assumption that zwitterions are main reagents in the studied reaction with **2** in the 7—9 range. Table 3 presents fractions of protonated ($\alpha_{H_2L^+}$) and zwitter ionic ($\alpha_{HL^{\pm}}$) forms of compound **1** and the values of effective bimolecular rate constants of the reaction of zwitterions of **1** found by the formula $k_{HL^{\pm}} = k_{ob}/C_{HL^{\pm}}$, where $C_{HL^{\pm}} = C_1 \cdot \alpha_{HL^{\pm}}$. As follows from the data presented, the reactivity of the zwitterionic form in the micellar phase is higher than that in

Table 3. Contents of protonated and zwitterionic forms of **1** and rate constants of the reaction between the zwitter ionic form of **1** and **2** at various SDS concentrations

C_{SDS} /mol L^{-1}	pH	$\alpha_{H_2L^+}$	$\alpha_{HL^{\pm}}$	$C_{HL^{\pm}}$ /mol L^{-1}	$k_{HL^{\pm}}$ /M^{-1} s^{-1}
0.01	7.0	0.989	0.68 · 10^{-2}	3.4 · 10^{-5}	47
	8.0	0.900	0.62 · 10^{-1}	3.1 · 10^{-4}	55
	9.0	0.450	0.33	1.5 · 10^{-3}	53
0.05	7.0	0.999	0.52 · 10^{-3}	2.6 · 10^{-6}	169
	8.0	0.990	0.52 · 10^{-2}	2.6 · 10^{-5}	173
	9.0	0.910	0.47 · 10^{-1}	2.4 · 10^{-4}	200
0.20	8.0	0.990	0.50 · 10^{-2}	2.5 · 10^{-5}	144
	9.0	0.910	0.40 · 10^{-1}	2.0 · 10^{-4}	115

Note. Conditions: pH 7—9, C_1 = 5 · 10^{-3} mol L^{-1}.

the aqueous phase ($k_{HL^{\pm}}$ is equal to 30 M^{-1} s^{-1} in water in the absence of a surfactant, see Table 1). The $k_{HL^{\pm}}$ value is 54 M^{-1} s^{-1} below the CMC, which is equal to 0.02 mol L^{-1} in the system studied (see Table 2), and it is 3.5 times higher when the CMC is reached. This agrees with the fact that the nonpolar medium formed in the nucleus of a micelle favors the bifunctional mechanism of action of zwitterions.[12] Some decrease of $k_{HL^{\pm}}$ when C_{SDS} = 0.2 mol L^{-1} could be related to the phenomenon of polymorphism[13] of micelles in concentrated solutions of SDS.

Compound **1** is grouped with aromatic organic electrolytes, which can substantially affect the process of micelle formation. It is mentioned in the literature[14,15] that additives of organic electrolytes result in a change in parameters of micelles, such as the aggregation number, molecular mass, and CMC. These changes are complicated and depend on the nature and concentration of additives. In the system studied, CMC slightly increases from $8.1 \cdot 10^{-3}$ mol L^{-1} (see Ref. 9) (SDS—H_2O, 25 °C) to $2.1 \cdot 10^{-3}$ mol L^{-1} (see Table 2). The change in the amount of the positively charged electrolyte **1** as pH is varied results most probably in the change in properties of anionic SDS micelles and exerts an effect on K_b of a substrate with micelles. In our opinion, this explains the increase in K_b values as pH of the medium decreases (see Table 2).

We studied the effect of the concentration of **1** on k_{ob} when the concentration of SDS is constant and equal to 0.2 mol L^{-1} and the pH is 7—8 (Table 4).

An increase in the concentration of **1** results in an increase in k_{ob}, which reaches a plateau. This is probably caused by the capability for saturation of the micellar Stern layer. The data obtained at pH 8 were analyzed in the semilogarithmic coordinates $k_{ob} = f(\log C_1)$ and are presented as an example in Fig. 1. The dependence (see Fig. 1) has linear regions with inflection points that characterize changes in the structure of micelles, which in turn result in change in the reactivity of **1**. For example, the values of the effective bimolecular rate constants $k_{HL^{\pm}}$ of the zwitter ionic form of **1** (see Table 4) calculated as described above remain constant within linear regions of the $k_{ob} = f(\log C_1)$ dependence, being equal to 123 M^{-1} s^{-1} (C_1 = 0.005 to 0.02 mol L^{-1}), 192 M^{-1} s^{-1} (C_1 = 0.025 to 0.05 mol L^{-1}), and 281 M^{-1} s^{-1} (C_1 = 0.06 to 0.085 mol L^{-1}), *i.e.*, increasing after each inflection point as C_1 increases.

Table 4. Observed second-order rate constants for the reaction between the zwitter ionic form of **1** and **2** at various concentrations of **1**

C_1 /mol L^{-1}	k_{ob}/s^{-1}	$C_{HL^{\pm}}$ /mol L^{-1}	$k_{HL^{\pm}}$ /M^{-1} s^{-1}
0.005	$0.33 \cdot 10^{-2}$	$0.25 \cdot 10^{-4}$	132
0.010	$0.60 \cdot 10^{-2}$	$0.50 \cdot 10^{-4}$	120
0.015	$0.85 \cdot 10^{-2}$	$0.75 \cdot 10^{-4}$	113
0.025	$0.20 \cdot 10^{-1}$	$0.125 \cdot 10^{-3}$	160
0.025*	$0.24 \cdot 10^{-2}$	$0.12 \cdot 10^{-4}$	192
0.040	$0.41 \cdot 10^{-1}$	$0.20 \cdot 10^{-3}$	205
0.050	$0.49 \cdot 10^{-1}$	$0.24 \cdot 10^{-3}$	200
0.060	$0.76 \cdot 10^{-1}$	$0.30 \cdot 10^{-3}$	253
0.060*	$0.89 \cdot 10^{-1}$	$0.30 \cdot 10^{-4}$	296
0.067	$0.96 \cdot 10^{-1}$	$0.34 \cdot 10^{-3}$	286
0.075	$1.07 \cdot 10^{-1}$	$0.37 \cdot 10^{-3}$	285
0.075*	$0.11 \cdot 10^{-1}$	$0.37 \cdot 10^{-4}$	296
0.885	$1.16 \cdot 10^{-1}$	$0.42 \cdot 10^{-3}$	273

Note. Conditions: pH = 8.0, C_{SDS} = 0.2 mol L^{-1}, 25 °C.
* pH 7.0

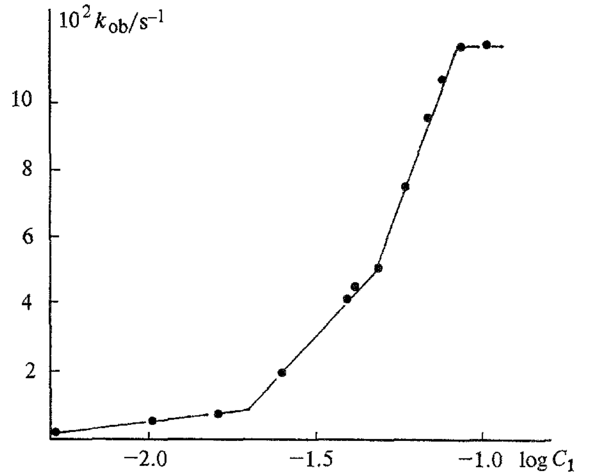

Fig. 1. Dependence of the observed rate constant of the reaction between **1** and **2** on the logarithm of the concentration of **1** at C_{SDS} = 0.2 mol L^{-1}, pH 8.0, 25 °C.

Thus, the reactivity of the zwitter ionic form of **1** in SDS micellar solutions depends on the concentration of this compound, which can be considered as an organic electrolyte additive, changing parameters of micelles and affecting kinetic parameters of the process.

It is known[8] that in the SDS—water system in a certain concentration and temperature zone, hexagonal, lamellar, and nematic lyomesophases are formed, whose liquid-crystalline properties are proved by X-ray diffraction analysis and polarization microscopy. In particular, it is established that the system containing from 38 to 50 wt.% of SDS and water forms at 40 °C the liquid-crystalline mesophase with hexagonal packing of cylinders of indefinite length. On cooling a sample to 20 °C, the liquid-crystalline state is retained for some time, and then the system is laminated.

To study the effect of the hexagonal lyomesophase of the SDS—water double system on the kinetics of the reaction between **1** and 4-nitrophenyl phosphates, we obtained samples[8] containing 40 and 46 wt.% of SDS and compound **1** with a concentration of $5 \cdot 10^{-3}$ mol L^{-1}. Polarization microscopy shows that the texture of samples at 40 °C and above (to ~70 °C) is typical of the hexagonal liquid-crystalline mesophase and is retained after cessation of the reaction with 4-nitrophenyldiphenylphosphate, which is added ($1 \cdot 10^{-4}$ mol L^{-1}) to the cell with the sample. Study of the kinetics of the reaction between **1** and this substrate in the hexagonal liquid-crystalline mesophase by the known procedure[10] shows that, unlike the rate constant in the micellar phase, which increases as the temperature increases (see Table 2), the observed rate constant in the liquid-crystalline phase is independent of temperature and SDS concentration within the range studied and is equal to $0.2 \cdot 10^{-3}$ s^{-1}. The comparison of $k_{\rm ob}$ values in the liquid-crystalline and micellar phases (see Table 2) shows that $k_{\rm ob}$ at 60 °C in the hexagonal phase is 1.5 times lower than in the micellar phase, while at 45 °C it is ~4 times higher.

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