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Condensation of *p*-Dimethylaminocinnamaldehyde with Aniline and Substituted Anilines in Micellar Media

S. Yu. Doronin, R. K. Chernova, and N. N. Gusakova

Chernyshevskii Saratov State University, Saratov, Russia

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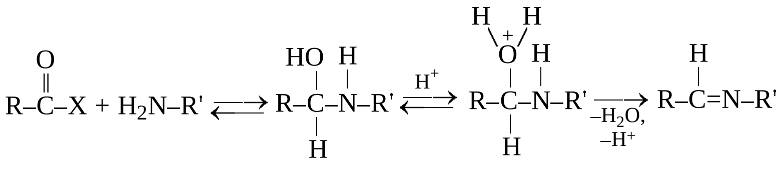
Abstract—Optimal conditions were found for the reactions of aniline and its hydroxy-, carboxy-, methyl-, and nitro-substituted derivatives with p-dimethylaminocinnamaldehyde in the presence of sodium dodecyl sulfate micelles in the pH range 1–6. A correlation was revealed between the optimal pH value pK_a of aromatic amines. The reaction in the model system aniline–*p*-dimethylaminocinnamaldehyde–sodium dodecyl sulfate in micelles formed by anionic surfactants is accelerated more than 1000-fold due to increased concentration of the reactive species in sodium dodecyl sulfate micelles.

Condensation of primary aromatic amines with aldehydes is widely used in organic synthesis (preparation of secondary amines and heterocyclic compounds, protection of aldehyde group, etc) [1] and analytical chemistry (formation of colored Schiff bases) [2–6]. It is known that micellar media formed by surface-active substances are capable of essentially changing the state of reactants in solution, the rate and mechanism of reactions, and their direction [7]. The catalytic effect of surfactant micelles in the condensation of aldehydes with aliphatic and aromatic amines was the subject of a number of publications [8–12]. For example, Martinek *et al.* [8] and Krivova *et al.* [9] reported on the effect of sodium dodecyl sulfate (**I**) micelles on the condensation of aromatic amines (aniline, benzidine, *p*-anisidine) with *p*-dimethylaminobenzaldehyde (**II**). The authors showed that the reaction rate increases due to increase in the reactant concentrations in the micellar pseudophase. The influence of salt **I** on the mechanism and equilibrium in the condensation of hydrazine and phenylhydrazine with vanillin [10] and *p*-dimethylaminobenzaldehyde (**II**) [11, 12] was also studied. It was found that the apparent rate constants increased by more than 2 orders of magnitude for the reaction with hydrazine and by a factor of 20–30 for phenylhydrazine, which was attributed to increase of the reactant concentrations in the surfactant micelles.

In the present work we examined the effect of surfactant micelles on the condensation of *p*-dimethylaminocinnamaldehyde (**III**) with aniline, nitroanilines, aminophenols, toluidines, and aminobenzoic acids. The mechanism of condensation of primary aromatic amines with aldehydes was studied in sufficient detail [13–16]. The condensation includes two steps: the first step is nucleophilic addition of amine at the carbonyl carbon atom to give intermediate α-amino alcohol, and the second step is elimination of water with formation of C=N bond (Scheme 1). The final products are the corresponding Schiff bases.

Scheme 1.



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}X + H_2N{-}R' \rightleftarrows R{-}\underset{H}{\overset{HO}{C}}{-}\overset{H}{N}{-}R' \overset{H^+}{\rightleftarrows} R{-}\underset{H}{\overset{H_2\overset{+}{O}}{C}}{-}\overset{H}{N}{-}R' \xrightarrow[-H_2O,\ -H^+]{} R{-}\overset{H}{C}{=}N{-}R'}$$

Figure 1a shows the electronic absorption spectra of the system aniline–aldehyde **III** at various pH values. It is seen the medium-intensity absorption band with its maximum at λ 520 nm, which is observed in the pH range from 2 to 6, corresponds to the condensation product. The optimal conditions for the reaction of aniline with aldehyde **III** (citrate buffer, pH 2–6; ionic strength 0.1–0.4; temperature 20°C;

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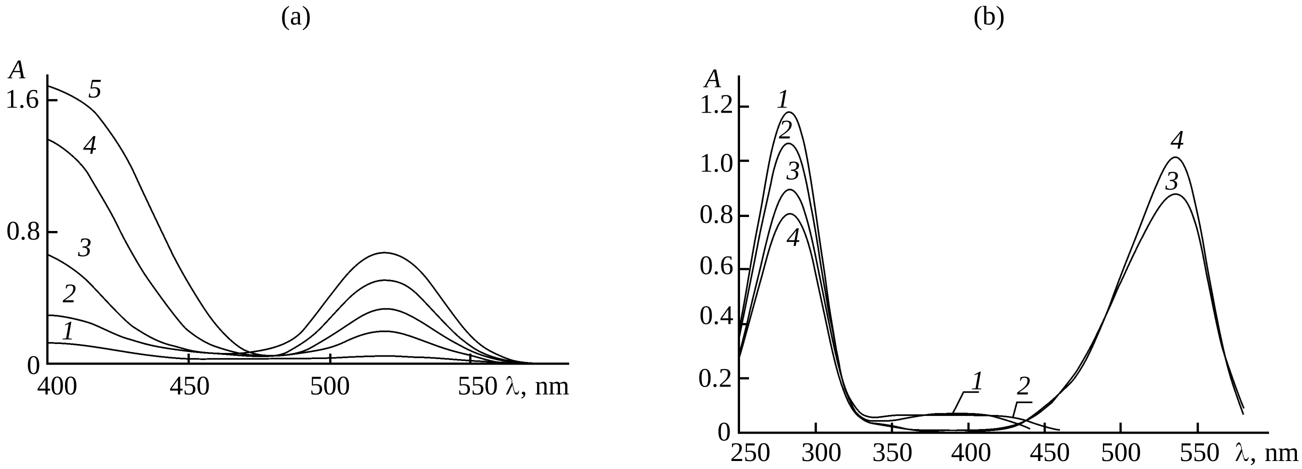
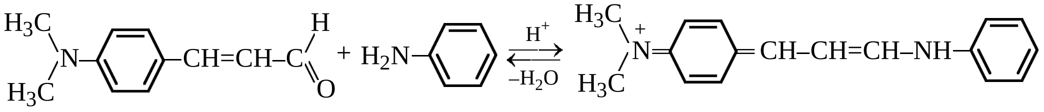


Fig. 1. Electronic absorption spectra of the system aldehyde **III**–aniline (a) in the absence of salt **I** at pH (*1*) 2, (*2*) 3, (*3*) 4, (*4*) 5, and (*5*) 6 (c_{III} = caniline = 10^{-4} M) and (b) in the presence of (*1*) 0, (*2*) 10^{-3}, (*3*) 2×10^{-3}, and (*4*) 5×10^{-3} mol/l of salt **I** ($c_{aniline}$ = c_{III} = 5×10^{-6} M, pH = 4.0).

absorption of the product at λ_{max} 520 nm develops during 20 min) differ from those ensuring formation and stability of most known Schiff bases [1]. It is known that a number of Schiff bases are stable in alkaline medium due to their low basicity and that they undergo hydrolysis in acid medium. The presence in molecule **III** of an electron-donor dimethylamino group radically changes the behavior of the condensation product with aniline in acid medium, where quinoid form **IV** of the protonated Schiff base is stable [17] (Scheme 2). Hydrolysis is a competing process which reduces the concentration of *N*,*N*-dimethyl-4-(3-phenylamino-2-propenylidene)-2,5-cyclohexadienylideneammonium ion (**IV**).

Scheme 2.



III **IV**

Depending on the nucleophile nature, the rate and mechanism of the reaction are strongly influenced by pH. Here, two main factors are to be taken into account: first, the nucleophile should exist in its active form, i.e., it should possess an unshared electron pair capable of attacking the carbonyl group, and second, the process is catalyzed by solvated proton. Substituents in the nucleophile differently affect the reaction rate, for example, the presence of an electron-donor substituent in a primary aromatic amine increases its basicity, which should increase the reaction rate due to acceleration of the nucleophile addition at the carbonyl group. On the other hand, increased basicity of an arylamine requires greater pH for its protonation, which reduces the rate of dehydration of intermediate amino alcohol.

In order to reveal some general relations holding in the reactions under study and find optimal conditions, we examined the effect of various substituents in the benzene ring of the aromatic amine (Table 1). Each of the above amines (except for *o*-nitroaniline) reacted with aldehyde **III** in a citrate buffer to give colored Schiff bases with λ_{max} 505–560 nm. From the obtained data we have drawn a correlation between the optimal pH value (pH_{opt}) and pK_a of amines: $pH_{opt} = (pK_{amine} + 3.18)/2$, where 3.18 is the basicity constant of aldehyde **III** (Table 1). Using this correlation we can predict optimal conditions for the reaction of aldehyde **III** with any primary aromatic amine. The lesser the pK_a value, the lesser pH_{opt} and the shorter the time necessary for the reaction equilibrium to establish; correspondingly, the absorption maximum of the product shifts to longer wavelengths.

As follows from Fig. 1b, a strong absorption band with its maximum at λ 540 nm appears in the electronic absorption spectra starting from a sodium do-

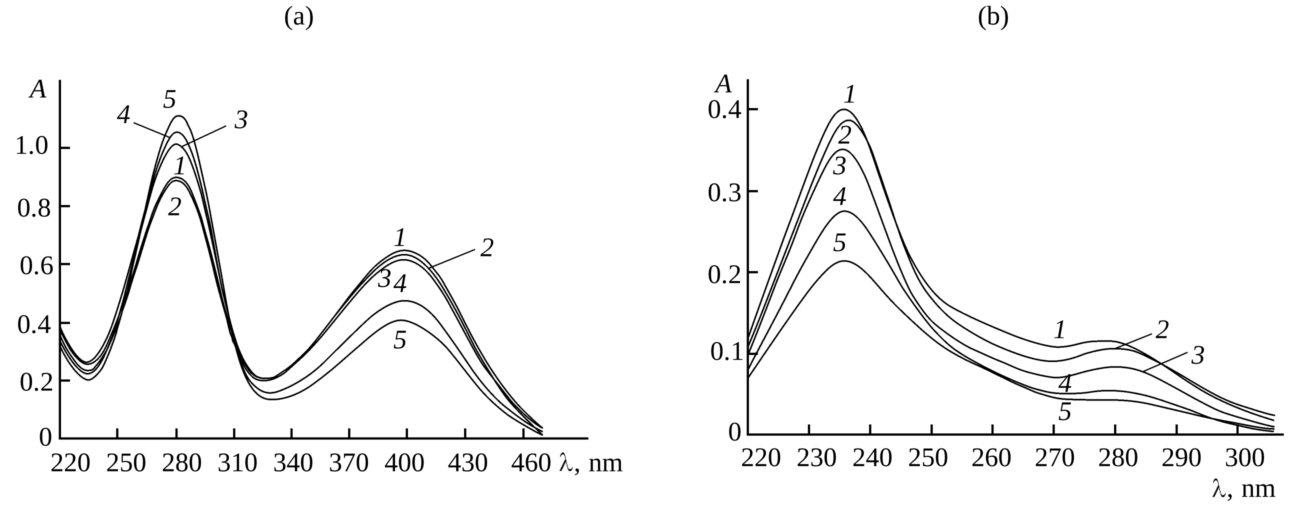


Fig. 2. Electronic absorption spectra in citrate buffer of (a) aldehyde **III** (pH = 3.0) and (b) aniline (pH = 4.0) in the presence of (*1*) 0, (*2*) 10^{-3}, (*3*) 2×10^{-3}, (*4*) 4×10^{-3}, and (*5*) 4×10^{-3} mol/l of salt **I**.

decyl sulfate concentration of 2×10^{-3} M. It reaches the maximal intensity at $c_{\mathbf{I}} = 5\times10^{-3}$ M. The optimal concentration of salt **I** for the reaction of aniline with aldehyde **III** is considerably lower than critical micelle concentration (CMC) of sodium dodecyl sulfate in water, $(8\text{–}9)\times10^{-3}$ M [19]. Many factors are capable of affecting CMC of surfactants [7]; therefore, it was reasonable to determine the CMC of **I** under the optimal conditions, i.e., in a citrate buffer at pH 4.0.

The measurements were performed using viscometric and spectrophotometric techniques [20]. In the first case, the CMC of salt **I** was estimated at 1.8 ± 0.3 mM (number of parallel runs $n = 3$, confidence probability $p = 0.95$); in the second case, a value of 1.60 ± 0.05 mM ($n = 3$, $p = 0.95$) was obtained. Thus the optimal concentration of sodium dodecyl sulfate (5×10^{-3} M) exceeds its critical micelle concentration in citrate buffer; this means that micelles of salt **I** are formed in the given concentration range. Reduction in the CMC of **I** is likely to result from the high ionic strength created by citrate buffer.

One of the main factors determining the rate of the reaction under study is the state of the reactants in aqueous and micellar media at different pH values. Therefore, we examined the electronic absorption spectra of aldehyde **III** and aniline in citrate buffers at pH 1–6 in the presence of micelles **I**.

Figure 2a shows that the equilibrium between the neutral (λ_{max} 400 nm) and protonated (λ_{max} 280 nm) forms of aldehyde **III** shifts toward the latter as the concentration of micelles rises. This follows from the corresponding redistribution of the absorption intensities and from the presence of an isosbestic point at λ 310 nm. We can conclude that under the optimal conditions sodium dodecyl sulfate micelles stabilize the reactive protonated form of aldehyde **III** via electrostatic interaction, which leads to acceleration of the process.

The absorption pattern of aniline also changes with rise in micelle concentration (Fig. 2b). However, the intensity of absorption of both neutral (λ_{max} 280 nm)

Table 1. Reactions of aniline and its derivatives with *p*-dimethylaminocinnamaldehyde (**III**)

Aromatic amine	λ_{max}, nm	τ_{eq},[a] min	pH_{opt}[b]		pK_a [18]
			experimental	calculated	
Aniline	520	15–20	4.0	3.88	4.58
o-Aminophenol	520	15–20	4.0	3.95	4.72
m-Aminophenol	525	15–20	3.7	3.68	4.17
p-Aminophenol	515	50–60	4.3	4.34	5.50
o-Toluidine	505	15–20	3.9	3.79	4.39
m-Toluidine	525	15–20	4.0	3.94	4.69
p-Toluidine	520	25–30	4.0	4.15	5.12
o-Aminobenzoic acid	545	2–5	2.75	2.65	2.11
m-Aminobenzoic acid	530	2–5	3.3	3.15	3.12
p-Aminobenzoic acid	545	30–35	2.9	2.80	2.41
o-Nitroaniline	–	–	–	1.44	–0.29
m-Nitroaniline	540	25–30	3.0	2.84	2.50
p-Nitroaniline	560	5–10	2.0	2.1	1.02

[a] τ_{eq} is the time necessary for equilibrium to establish.

[b] Calculated by the correlation equation given in the text.

and protonated species (λ_{max} 235 nm) decreases, and no definite conclusions on the state of aniline in micellar solution can be drawn. Therefore, we tried to determine pK_a of aniline in micelles by potentiometric titration. The titration was performed using the half-neutralization technique which is analogous to the procedure described in [21]. As titrant we used solutions of NaOH and of NaOH and salt **I**, which were freed from CO_2. The results showed an apparent shift of the pK value for protonation of aniline in the presence of micelles, i.e., pK_a increased relative to the corresponding value in aqueous phase (5.30 ± 0.05 against 4.60 ± 0.02; $n = 3$, $p = 0.95$). This may be due to binding of the reactant by micelles according to the following scheme:

$$(PhNH_3^+)_{aq} + (Na^+DDS^-)_{micelle}$$
$$\rightleftarrows (Na^+)_{aq} + (PhNH_3^+\ DDS^-)_{micelle}.$$

Deprotonation of aniline is favored by specific features of its solubilization in the bulk micelle due to hydrophobic properties of the aromatic ring and relatively small size of the molecule. Our results are consistent with the data of [22].

Thus, the concentrations of the protonated form of aldehyde **III** and neutral form of aniline increase in going to sodium dodecyl sulfate micelles. Insofar as both these are reactive species and protolytic equilibrium is displaced toward their formation in the presence of micelles **I**, the rate of the condensation of aniline with aldehyde **III** increases.

The reactant distribution over aqueous–micellar system can be estimated directly from the kinetic data obtained by studying the formation and hydrolysis of protonated Schiff base **IV**.

Before proceeding to kinetic studies in the presence of surfactant **I**, we deduced a general kinetic equation for the condensation of aniline with aldehyde **III** in aqueous medium under the optimal conditions. For this purpose, we plotted the kinetic curves in the coordinates *A*–*t* (using spectrophotometric technique) upon variation of the reactant concentrations and calculated partial orders of the reaction with respect to each reactant. As a result, the following equation was obtained (pH 2.5–6.0):

$$dc/d\tau = k_1 c_1 c_2 c_{H^+}. \tag{1}$$

Here, c_1 and c_2 are the concentrations of aldehyde **III** and aniline, respectively. Using this equation, we calculated the rate constant for the forward reaction in aqueous medium: $k_1 = (6.5 \pm 0.9) \times ^{105}$ min^{-1} mol^{-2} l^2 ($n = 5$, $p = 0.95$).

The hydrolysis of **IV** is a process concurrent with its formation, which reduces the concentration of the product. Therefore, we examined the kinetics of the hydrolysis of the Schiff base prepared from aniline and aldehyde **III** as described in Experimental. The kinetic equation for the hydrolysis of **IV** looks as follows:

$$dc/d\tau = k_2 c_3 c_{H^+}. \tag{2}$$

Here, c_3 is the concentration of protonated Schiff base **IV** (quinoid form). The calculated rate constant for the hydrolysis of **IV** in aqueous medium k_2 is equal to $(1.6 \pm 0.2) \times 10^3$ min^{-1} mol^{-1} l ($n = 5$, $p = 0.95$). The equilibrium constant for the reaction of aniline with aldehyde **III** in aqueous medium (K^{aq}) was calculated as the ratio of rate constants k_1 and k_2: $K^{aq} = k_1/k_2 = (4.1 \pm 0.5) \times 10^2$.

The kinetics of the reaction of aniline with aldehyde **III** in surfactant micelles were studied in terms of the micellar catalysis concept [8, 23] according to which increase in the order of a reaction by unity leads to a *P*-fold increase of its efficiency; here, *P* is the coefficient of reactant distribution between the aqueous and micellar phases. Preliminarily, we found that the general appearance of the kinetic equations for the formation and hydrolysis of Schiff base **IV** does not change in going from aqueous to micellar phase.

We then calculated the rate constants of the forward and reverse reactions in micelles **I**. For this purpose, we determined by spectrophotometry the rates of formation and hydrolysis of **IV** upon variation of the concentrations of aniline (from 0.8×10^{-5} to 6.0×10^{-5} M), Schiff base (from 0.8×10^{-5} to 4.0×10^{-5} M), and salt **I** (from 0.2×10^{-2} to 4.0×10^{-2} M). For each series of solutions we measured the slope of the linear part of the kinetic curve and calculated the apparent molar absorption coefficient from the limiting optical density at λ_{max} 540 nm. The results are summarized in Table 2. As follows from the plots of k_1^m and k_2^m vs. $c_\mathbf{I}$ (Fig. 3a), increase in the concentration of salt **I** initially leads to increase of the formation rate constant k_1^m (curve *1*) and decrease of the hydrolysis rate constant k_2^m (curve *2*); the optimal ratio is reached at $c_\mathbf{I} = 5 \times 10^{-3}$ M. Further rise in the concentration of salt **I** ($c_\mathbf{I} > 5 \times 10^{-3}$ M) is accompanied by increase of the hydrolysis rate constant and decrease of the formation rate constant. Figure 3b shows the dependence of the apparent equilibrium constant in the micellar medium (K_{ap}^m) on the salt **I** concentration, which clearly indicates that the optimal concentration of **I** equals 5×10^{-3} M.

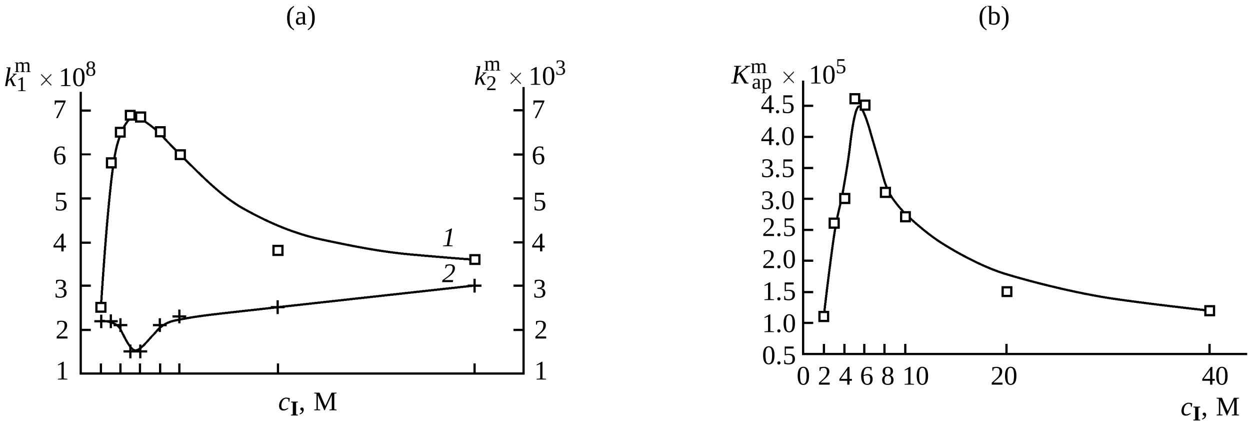


Fig. 3. Plots of (a) (*1*) k_1^m and (*2*) k_2^m and (b) K_{ap}^m versus concentration of salt **I**.

According to the pseudo-two-phase model of micelle effects [14], the apparent constant K_{ap}^m is related to the equilibrium constant of the same reaction in aqueous medium (K^{aq}) and binding constants of aldehyde **III** (K_1), aniline (K_2), and protonated Schiff base **IV** (K_3) in aqueous–micellar medium by equation (3):

$$K_{ap}^m = K^{aq} \frac{1 + K_3[\mathbf{I}]}{(1 + K_1[\mathbf{I}])(1 + K_2[\mathbf{I}])}. \qquad (3)$$

Here, [**I**] is the equilibrium concentration of salt **I**, calculated from the difference between the total salt concentration and its critical micelle concentration in citrate buffer: $[\mathbf{I}] = c_\mathbf{I} - \mathrm{CMC}_\mathbf{I}$. Equation (3) allows us to calculate the binding constants of the reactants under the constraint K_3 [**I**] >> 1 since the apparent rate constant k_1^m in the presence of micelles **I** is greater by three orders of magnitude than in aqueous medium (Table 2). Then, Eq. (3) may be represented as follows:

$$F_1 = \frac{K^{aq}[\mathbf{I}]}{K_{ap}^m} = \frac{1}{K_3} + \frac{K_2 + K_1}{K_3}[\mathbf{I}] + \frac{K_2K_1}{K_3}[\mathbf{I}]^2. \qquad (4)$$

If the equilibrium concentration of salt **I** is not high, the dependence $F_1 = f([\mathbf{I}])$ is linear, and the intercept on the y axis is equal to $1/K_3$. As shown in Fig. 4a, the $F_1 = f([\mathbf{I}])$ plot is linear until the overall concentration of **I** does not exceed (6–8) × 10^{-3} M. Therefore, in the subsequent calculations we used the first five points of this dependence, and K_3 was estimated at 9.09×10^5. Equation (4) can be transformed into Eq. (5):

$$F_2 = \frac{K^{aq}[\mathbf{I}]}{K_{ap}^m} = \frac{1}{K_3[\mathbf{I}]} - \frac{K_2 + K_1}{K_3} + \frac{K_2K_1[\mathbf{I}]}{K_3}. \qquad (5)$$

The plot of F_2 versus [**I**] is shown in Fig. 4b. Here, the intercept on the *y* axis is equal to $(K_2 + K_1)/K_3$, and the slope, to K_2K_1/K_3. The calculated binding constants are as follows: $K_1 = (2.9 \pm 0.7) \times 10^2$, $K_2 = (2.1 \pm 0.5) \times 10^2$, $K_3 = (9.1 \pm 1.1) \times 10^5$ ($n = 3$, $p = 0.95$). Using the formula $K = (P - 1)/V$, where K is the binding constant of a reagent, and V is the molar volume of micelles **I** ($V = 0.29$ l/mol [8]), we calculated the corresponding distribution constants P between the aqueous and micellar phases: aldehyde **III**, $P_1 = (1.00 \pm 0.02) \times 10^3$; aniline, $R^2 = (0.81 \pm 0.05) \times 10^3$; protonated Schiff base **IV**, $R^3 = (3.10 \pm 0.06) \times 10^6$ ($n = 3$, $p = 0.95$). On the basis of these values we determined the true equilibrium constant K^m for the condensation of aniline with aldehyde **III** in the micellar medium, which is related to the equilibrium constant in aqueous medium K^{aq} by the following equation:

$$K^m = K^{aq} \frac{P_3}{P_1P_2}. \qquad (6)$$

Thus the calculated true equilibrium constant in

Table 2. Rate constants for the formation (k_1^m) and hydrolysis (k_2^m) of compound **IV** in the micellar phase ($n = 5$, $p = 0.95$)[a]

$c_\mathbf{I} \times 10^{-2}$, M	$(k_1^m \pm \Delta k_1^m) \times 10^8$, min^{-1} mol^{-2} l^2	$(k_2^m \pm \Delta k_2^m) \times 10^3$, min^{-1} mol^{-1} l
0.2	2.5 ± 0.3	2.2 ± 0.9
0.3	5.8 ± 0.4	2.2 ± 0.9
0.4	6.4 ± 0.5	2.1 ± 0.8
0.5	6.9 ± 0.4	1.5 ± 0.8
0.6	6.6 ± 0.4	1.5 ± 0.7
0.8	6.5 ± 0.3	2.1 ± 0.9
1	6.2 ± 0.3	2.3 ± 0.7
2	3.8 ± 0.4	2.5 ± 0.9

[a] (*n*) is the number of parallel runs, and (*p*), confidence probability.

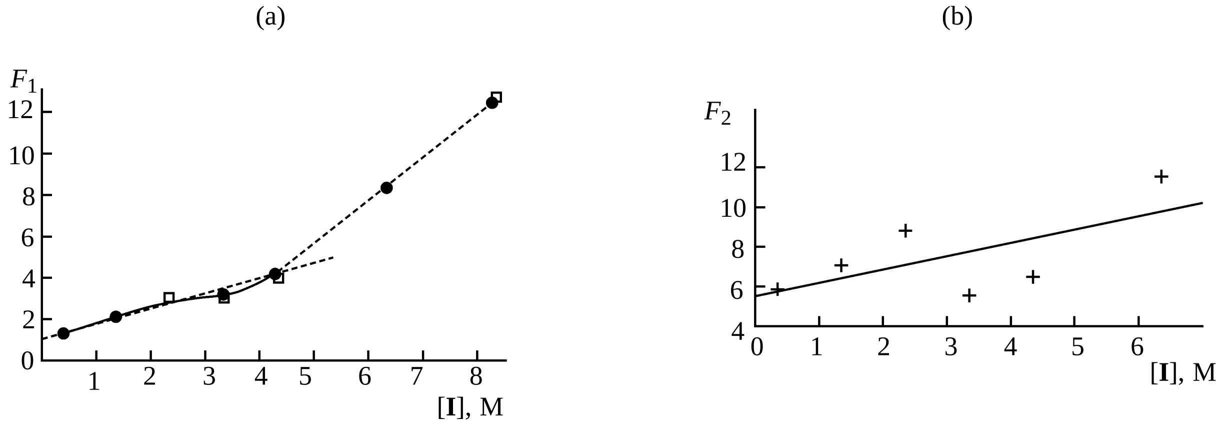


Fig. 4. Plots of (a) F_1 [Eq. (4)] and (b) F_2 [Eq. (5)] vs. [**I**].

sodium dodecyl sulfate micelles, $K^m = 1.57 \times 10^3$, exceeds the corresponding value for aqueous phase by a factor of ~4, while the rate constant for formation of **IV** in the micellar phase is greater by 3 orders of magnitude than that in aqueous phase.

Our results led us to conclude that the observed acceleration of the model reaction originates mainly from increased concentration of the reactive aniline and *p*-dimethylaminocinnamaldehyde species in micelles formed by anionic surfactants, as follows from the calculated distribution coefficients in aqueous–micellar system. The general relations found in the present study can be applied to condensations of other primary aromatic amines with *p*-dimethylaminocinnamaldehyde in micellar media containing anionic surfactants.

EXPERIMENTAL

The electronic absorption spectra were recorded on SF-46 and Specord M-40 spectrophotometers using quartz and glass cells with an absorbing layer thickness of 1–5 cm. The optical densities of solutions were measured with KFK-2 and KFK-3 photoelectrocolorimeters. The pH values were monitored using pH-121 and pH-673 pH meters.

Commercial *p*-dimethylaminocinnamaldehyde (**III**) (from Merck) was used. Aniline was distilled just before use; *ortho*-, *meta*-, and *para*-substituted anilines (aminophenols, aminobenzoic acids, nitroanilines, and toluidines) were purified according to the procedures described in [24].

Determination of the critical micelle concentration of sodium dodecyl sulfate (I). For viscometric determination of CMC, solutions of salt **I** with concentrations of 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, and 5 mM were prepared, and the time of draining of each solution from a viscometric capillary was measured. The ratios of the specific viscosities of the solutions to the concentration of salt **I** ($\eta_{sp}/c_\mathbf{I}$) vs. $c_\mathbf{I}$ were plotted, and CMC was determined by the graphical technique. Spectrophotometric determination of CMC of salt **I** was performed by measuring the optical density at λ_{max} 540 nm for a series of solutions containing 5×10^{-6} mol/l of the reactants and 1.0 to 2.0 mol/l of salt **I** through a step of 0.1 mol/l, followed by plotting differential dependences in the coordinates $dA/dc_\mathbf{I}$–$c_\mathbf{I}$.

Synthesis of Schiff base from aniline and *p*-dimethylaminocinnamaldehyde. A solution of equimolar amounts of aniline and aldehyde **III** in 20 ml of toluene containing 3 drops of glacial acetic acid as catalyst was heated for 0.5 h under reflux with simultaneous removal of the liberated water as azeotrope. The product was purified by quadruple recrystallization from 1-butanol until constant melting point (mp 133 ± 1°C).

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