

Micellar Catalysis in the Systems Arylamine–Diphenylamine–NO₂⁻

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Abstract—By methods of UV and IR spectroscopy and thermogravimetry reactions of diazotization and azo coupling were studied in the systems of primary arylamine (*p*-nitro-, *p*-carboxy- and *p*-sulfoaniline)–diphenylamine–nitrite ion in water and micellar media on the basis of surfactants. The micellar catalysis effect of sodium dodecylsulfate in the micellar media was revealed. Rate of diazotization was shown to be independent of the surfactants of various types. Formation of ionic associates of azo dyes with dodecylsulfate anions in pre-micellar region was established and physicochemical characteristics of the associates were estimated.

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Reactions of diazotization and azo coupling found wide application in organic [1] and analytical [2] chemistry. The reactions of diazotization of primary arylamines followed by azo coupling of the formed diazonium salts with amines and phenols have been well enough studied and some general conditions for these reactions were formulated [1–3]. However, effect of surfactants of various types on the physicochemical parameters of such reactions remains practically not studied. It is known that in the presence of micellar nanoreactors, the micelles of surfactants, micellar catalysis is possible [4] that affects some physicochemical characteristics of the system including its stability, degree of formation of azo dye, and others.

Published data on the micellar catalysis of diazotization and azo coupling reactions are scanty and contradictory [5–8]. In a review [5] results were presented of the study of kinetics of several azo coupling reactions. In the presence of micelles of sodium dodecylsulfate and hexadecyltrimethylammonium bromide a deceleration (up to 15-fold) occurred of azo coupling reactions of 4-nitrobenzenediazonium with 1-naphthol-6-sulfoacid and 2-naphthol-3,6-disulfoacid. On the contrary, sodium dodecylsulfate micelles accelerate azo coupling reactions of 4-methoxybenzenediazonium with 1-naphthylamine and 1-amino-2-methylnaphthalene (up to 1100-fold). The data of the study on the azo coupling reactions

involving diazonium cation and azo components bearing different charges allowed to conclude that micellar effects are controlled by formal charges of both reactants.

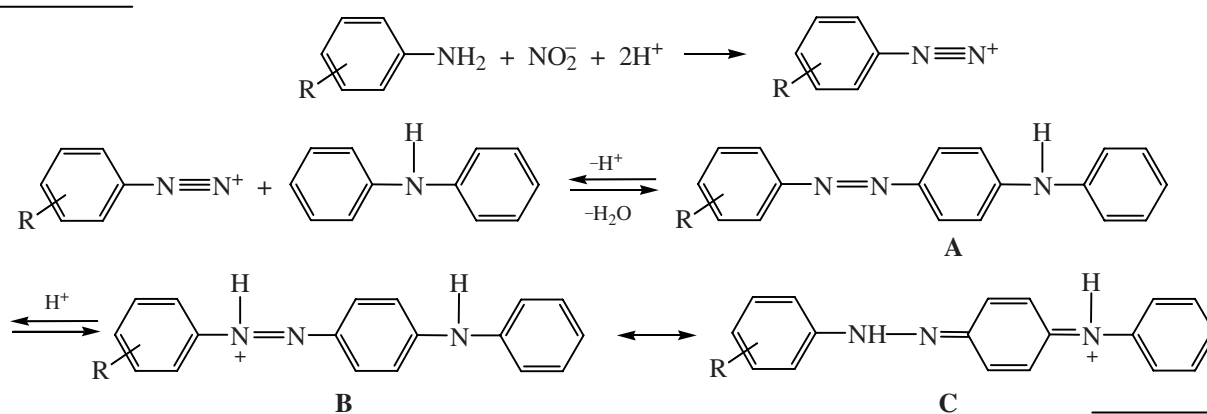
In [8] the effect of sodium dodecylsulfate micelles on the azo coupling reactions was studied of twelve benzenediazonium tetrafluoroborates (XC₆H₅BF₄, where X = H, *p,m*-NO₂, *p,m*-Cl, *p,m*-Br, *p,m*-CH₃, *p,m*-OCH₃ and *p*-OC₂H₅) with 1-naphthol-4-sulfonic acid. In all cases a decrease was observed in the reaction rate with anionic micelles by 1.41 to 11.82 times. Sallo and Tomescu treated the reaction deceleration from the viewpoint of Hartley's "sign rule."

Despite a significant contribution of Coulomb interaction of diazonium ions with azo components in these reactions, no unambiguous prediction was suggested with respect to the effect of surfactants on the stage of the azo coupling. This situation suggests a necessity of detailed experimental study of the influence of surfactants on the kinetics of each azo coupling reaction in dependence on the nature of reactants. Earlier we revealed micellar catalysis effect of sodium dodecylsulfate in the Griss reaction [9] leading to more than 2-fold decrease in the reaction rate due to separating effect of micellar nanoreactors on the reactive forms of the reactants. Now we present the results of the complex study of the effect of micelles as well as ions of surfactants on the reactions of

diazotization and azo coupling in the systems of primary arylamine–diphenylamine–nitrite ion.

We studied three model systems: **(I)** NO_2^- -*p*-nitroaniline–diphenylamine; **(II)** NO_2^- -*p*-aminobenzoic acid–diphenylamine; **(III)** NO_2^- -sulfanilic acid–diphenylamine. This choice of amines for diazotization is defined by their high reactivity and by difference in the nature of substituents of the second type ($-\text{NO}_2$, $-\text{COOH}$ and $-\text{SO}_3\text{H}$) in *para*-position of benzene ring, enhancing the electrophilicity of the diazonium cation. The substituent nature affects also the solubility of arylamine, *p*-aminobenzoic acid derivatives are poorly soluble in water while derivatives of sulfanilic acid are

well soluble. Besides, by varying pH it was possible to vary electrostatic properties of the chosen arylamines (protonated and non-protonated $-\text{COOH}$ and $-\text{SO}_3\text{H}$ groups) that was significant for the consideration of the phenomenon of micellar catalysis. The choice of diphenylamine as an azo component was stipulated by its pronounced hydrophobic character governing its low solubility in water and hence good solubility in the micelles of surfactants. Diphenylamine being a secondary amine is not capable of diazotization, hence some side reactions are excluded (in particular, the autocoupling that is characteristic, e.g., of 1-naphthylamine [1], see the scheme).



We studied stage by stage the effect of various types of surfactants (anionic, sodium dodecylsulfate; cationic, cetylpyridinium chloride; non-ionic, oxyethylated alkylphenol OP-10) on the diazotization of *p*-nitroaniline, *p*-aminobenzoic and sulfanilic acids and on the coupling of the respective diazonium salts with diphenylamine.

Diazotization stage. Diazonium salts formed in solution at pH 1 (Fig. 1) are characterized by absorption peaks with λ_{max} 260, 265 and 270 nm for the systems I, II and III, respectively, in agreement with the data in [10]. The spectra character and intensity of absorption peaks do not suffer any change at the transfer from aqueous medium to micellar one regardless the surfactant type. In addition, in the micellar media formed with different type surfactants did not change the rate of formation of diazonium salt compared with the aqueous medium. Thus, we can conclude that micelles formed by the surfactants of various type do not influence the step of diazotization, due to a sufficiently high rate of this reaction proceeding either in the aqueous medium, or in the presence of a surfactant micelle.

Azo coupling stage. In the systems I and II at pH > 1 the azo coupling reaction does not occur, at pH = 1 azo dyes A formed (see the scheme) precipitate in 15–20 min (Fig. 2) due to their low solubility. Therefore photometric analysis in aqueous medium at the concentration of reagents above 2×10^{-5} M is impossible. In system **III** the azo dye A is soluble in water (pH = 1). Formation of solid phase in such systems occurred after 24 h, or in 2–3 h when sulfanilic acid concentration was above 1×10^{-2} M.

The precipitates formed in the systems I–III were isolated and identified by IR spectroscopy (Fig. 3c) after preliminary thermogravimetric investigation (Fig. 3a). The analysis of IR spectra of the synthesized azo compounds by an example of system I (Fig. 3c) revealed the presence of characteristic bands of NO_2^- group at 1515, 1333 cm^{-1} , of secondary amino group $>\text{NH}$ at 3401 cm^{-1} , and of the system of conjugated bonds including $-\text{N}=\text{N}-$ in the region of 1600–1400 cm^{-1} . Besides, in the IR spectrum there are two bands in the region of 3500–3300 cm^{-1} characteristic of primary amino group of the parent arylamine. The study showed that the product of azo coupling reaction

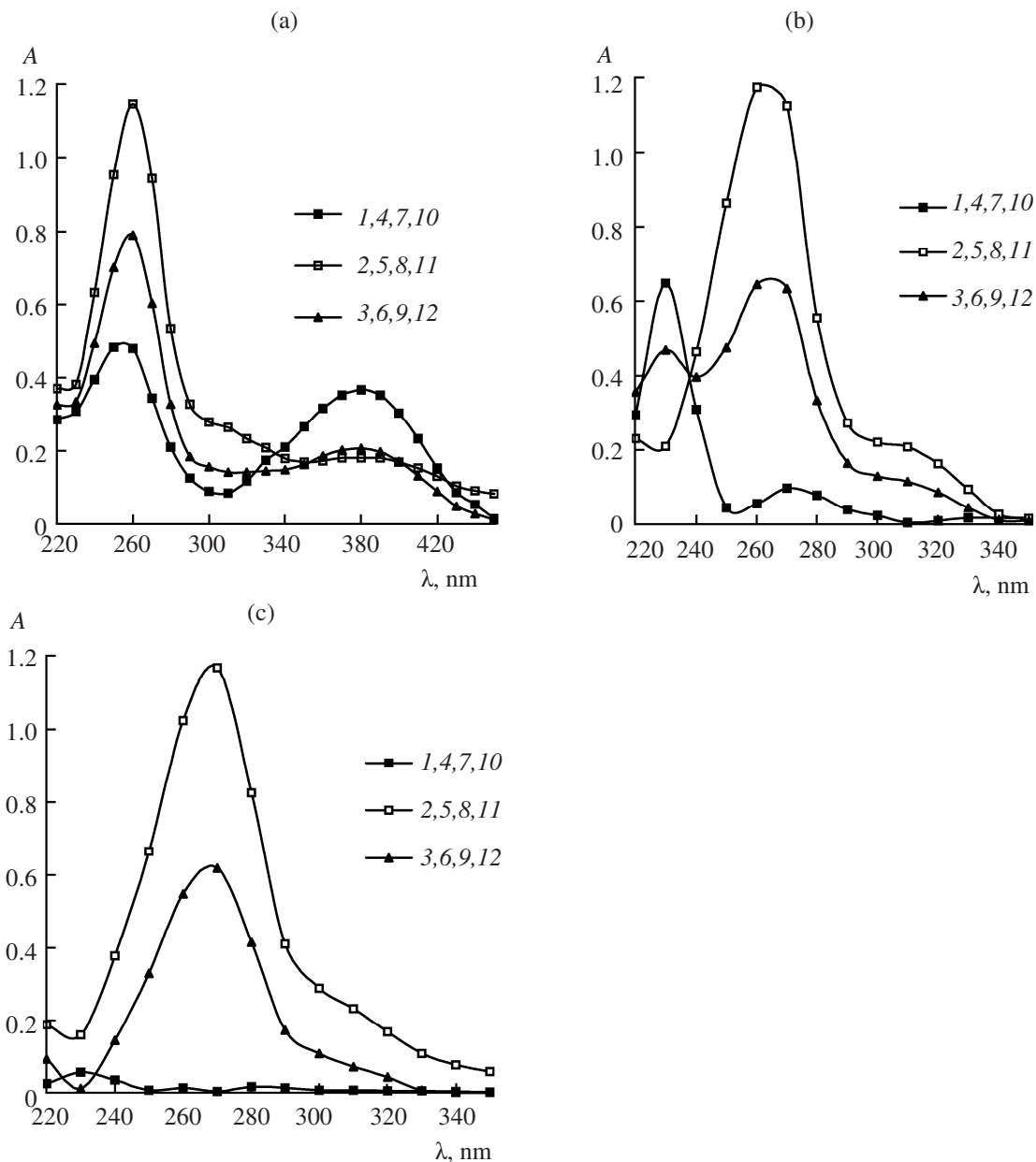


Fig. 1. Electron absorption spectra of model systems (a) I, (b) II, and (c) III. (1–3) aqueous medium, (4–6) in dodecylsulfate solution, 2×10^{-2} M, (7–9) in dodecylsulfate solution, 1×10^{-3} M, (10–12) in the solution of cetylpyridinium chloride in 5×10^{-4} M solution of OP-10. Concentration of NaNO₂: 0 (1, 4, 7, 10); 1×10^{-4} M (2, 5, 8, 11); 5×10^{-4} M (3, 6, 9, 12). $c(\text{arylamine}) 1 \times 10^{-4}$ M, pH 1, l 1 cm.

in the system I is 1-(4-diphenylamino)-4-nitroazobenzene, in the systems II and III were obtained related azodyes of A type (see the scheme). Thus, the poorly soluble azo dyes A formed in aqueous medium decrease the concentration of the most colored (photometrically meaningful) protonated forms B and C (see the scheme).

Preliminary examination showed that introducing to the model systems the micelles of anionic type surfactants (sodium dodecylsulfate) leads to a change in the azo coupling reaction rate, to stabilization of optical density of the solutions under photometry for several hours, and to hyperchromic and bathochromic effects in electron absorption spectra. As seen from

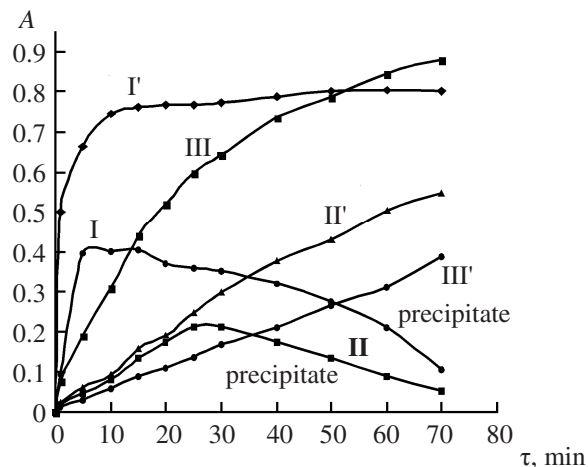


Fig. 2. Plots $A-\tau$ for systems I, II and III in aqueous medium and for systems I', II' and III' in micellar medium of sodium dodecylsulfate, 2×10^{-2} M. Concentrations of arylamine and diphenylamine are 1×10^{-3} M, $c(\text{NaNO}_2)$ 2×10^{-5} M, pH 1, λ_{max} 530 nm.

kinetic curves (Fig. 2), the formation of precipitate in the systems I' and II' does not occur, the solutions are homogenous, and the optical density is stable for 24 h.

Contrary to the effect of sodium dodecylsulfate micelles, at the concentration of this surfactant below critical for the micelle formation $(0.1-1) \times 10^{-3}$ M, in the systems I'–III' occurred formation of the solid phase as strongly colored precipitate, the associate of azo dye protonated form C (see the scheme) with dodecylsulfate ions. The formed precipitates were isolated and identified by analogy with the azo dyes A (Figs. 3b, 3d).

In the IR spectrum of ionic associate appear characteristic bands of NO_2^- group at $1515, 1333 \text{ cm}^{-1}$ and of conjugated bonds system in the region of $1600-1400 \text{ cm}^{-1}$. Two bands in the region of $3500-3300 \text{ cm}^{-1}$ characteristic of NH_2 group of the parent arylamine

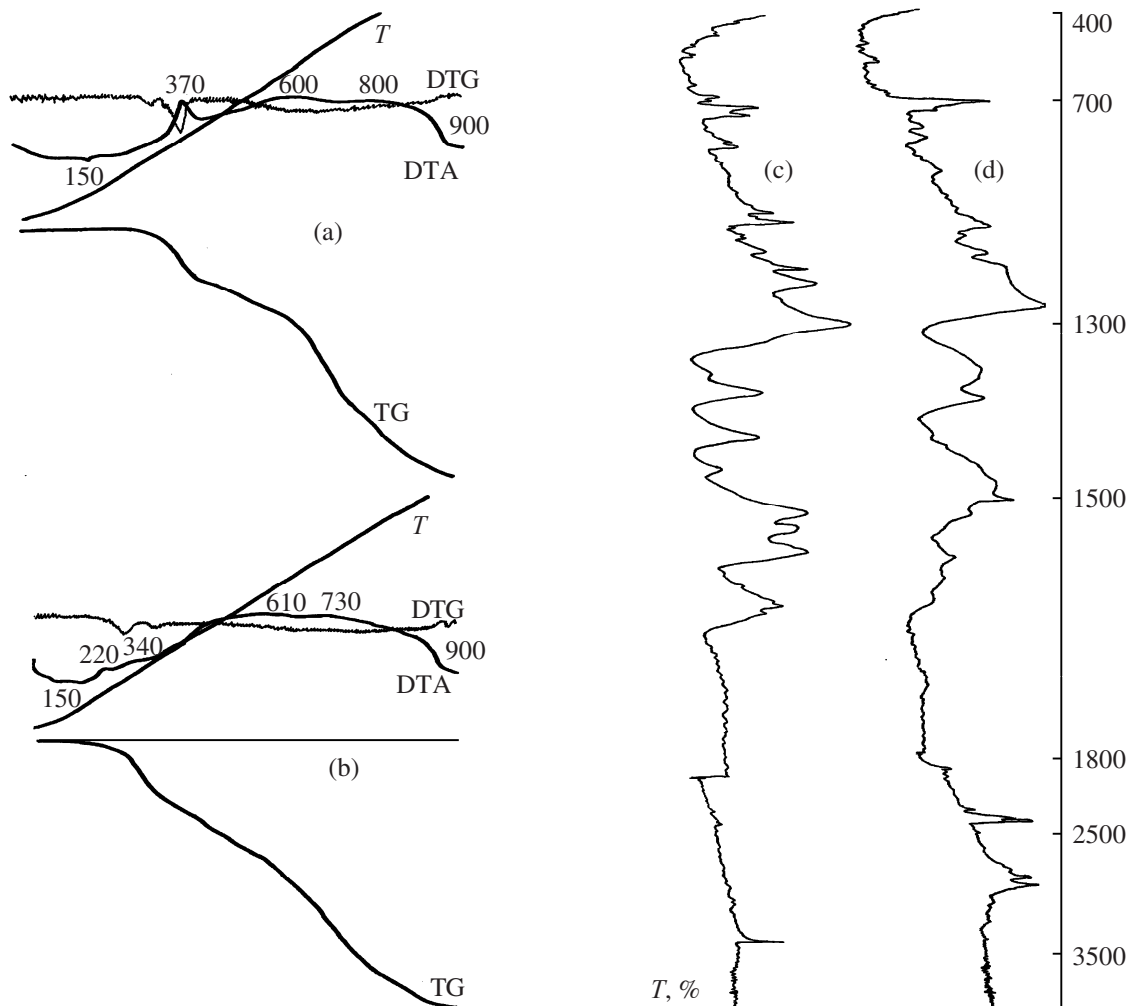


Fig. 3. Derivatograms and IR spectra of (a, c) 1-(4-diphenylamino)-4-nitroazobenzene and (b, d) its ionic associate with dodecylsulfate ion.

were not observed. Compared to the IR spectrum of azo dye (Fig. 3d), in the IR spectrum of associate appear characteristic bands of CH₂ groups at 2940–2915, 2870–2845 cm⁻¹ and of SO group at 1440–1350, 1230–1150 cm⁻¹. The characteristic band of secondary amino group at 3401 cm⁻¹ is not observed, owing probably to the formation of an intramolecular hydrogen bond. Analysis of IR spectra of the synthesized products suggests the formation of dodecylsulfate ions associates with protonated quinoid form of azo dyes **C**. Thus, in the model systems I, II, and III are formed ion pairs of azo dyes with dodecylsulfate ions. The ion pairs are poorly soluble in water but are well solubilized by sodium dodecylsulfate micelles that leads to the shift of the reaction equilibrium to the side of maximal formation of azo dyes in analytical form **C** providing strong coloration of the micellar solutions in the systems I–III.

Solubility of azo dye and its associate with dodecylsulfate ion is determined qualitatively on the example of system I. The solubility both of the dye itself and of its ion pair with dodecylsulfate under optimal conditions in going from aqueous medium (molar solubility 2×10⁻⁶ mol l⁻¹) to micellar one (molar solubility 1.6×10⁻⁴ mol l⁻¹) increases approximately 80-fold, resulting from the solubilization with the sodium dodecylsulfate micelles.

As follows from Fig. 2, transfer from aqueous medium to micellar one changes the rates of the studied reactions. In the model systems I and II the reaction rate grows, in system III falls. For quantitative characterization of reaction rates we investigated kinetics of these reactions and calculated respective rate constants.

Rate of formation of azo compounds depends on the concentration of reacting components. The kinetics equation is as follows:

$$\frac{d[C]}{dt} = k[A]^a[B]^b. \quad (1)$$

Here $d[C]/dt$ is rate of azo coupling reaction, k is the rate constant, $[A]$ and $[B]$ are equilibrium concentrations of diazo compound and diphenylamine, respectively.

It is known that in acid media diphenylamine undergoes protonation (pK_a 0.9). However, only the nonprotonated form enters into the azo coupling

reaction; that is understandable from the viewpoint of the orientation theory. Total concentration of diphenylamine is a sum of concentrations of protonated and nonprotonated forms.

$$c_i = [B] + [BH^+]. \quad (2)$$

Here c_i is the total concentration of diphenylamine, $[B]$ is the equilibrium concentration of nonprotonated form of diphenylamine, $[BH^+]$ is the equilibrium concentration of protonated form of diphenylamine. Introducing protonation constant we can express concentration of protonated form of diphenylamine as:

$$k_a = \frac{[B][H^+]}{[BH^+]}. \quad (3)$$

Here k_a is the constant of diphenylamine protonation.

$$[BH^+] = \frac{[B][H^+]}{k_a}. \quad (4)$$

Hence

$$C_i = [B] + \frac{[B][H^+]}{k_a} = \frac{k_a[B] + [B][H^+]}{k_a}, \quad (5)$$

$$C_i k_a = k_a[B] + [B][H^+] = [B](k_a + [H^+]), \quad (6)$$

$$[B] = \frac{C_i k_a}{k_a + [H^+]}. \quad (7)$$

Introducing relation (7) into Eq. (1) we obtain the equation of the reaction kinetics.

$$\frac{d[C]}{dt} = k[A]^a \left(\frac{C_i k_a}{k_a + [H^+]} \right)^b.$$

Insofar as the reaction rate depends on the concentrations of both diazonium salt and diphenylamine, we had to study the reaction order with respect to each reagent. The reaction orders, estimated according to Van't Hoff differential method [11], were found to equal unity both with respect to diazo and azo components. Therefore for all the studied systems the general kinetic equation is expressed as follows:

$$\frac{d[C]}{dt} = k[A] \frac{C_i k_a}{k_a + [H^+]}$$

The reaction rate constant is:

$$k = \frac{v}{\varepsilon l [A] \frac{C_i k_a}{k_a + [H^+]}}$$

Reaction rate constants for systems I–III in water and sodium dodecylsulfate micelles

System	$k_s, l^2 \text{ mol}^{-2} \text{ min}^{-1}$	
	H ₂ O	Dodecylsulfate micelles
I	80±5	271±19
II	35±1	85±2
III	38±4	7.20±0.17

Here ϵ is the molar extinction coefficient of analytical form, $\epsilon = A/(Cl)$; l is the optical route length, $pK_a = 0.9$ for diphenylamine.

The calculated values of rate constants in aqueous medium and in sodium dodecylsulfate micelles (at optimal concentration 2×10^{-2} M, see the table) show that azo coupling reaction in the systems I and II is accelerated by dodecylsulfate micelles respectively ~3.4- and 2.4-fold while in the system III it is ~5-fold decelerated, that is consistent with Hartley's rule.

According to Hartley's "sign rule," the reactants possessing charges of same sign are concentrated by the oppositely charged micelle of surfactant, and this leads to increase in the reaction rate (systems I and II). When reactants are oppositely charged (system III) the micelles of ionic surfactants will separate them leading to the decrease in the reaction rate, as is observed for the studied systems.

EXPERIMENTAL

Electron absorption spectra and kinetic curves were registered on a SF-46 spectrophotometer in fused glass and glass cells with the length of the absorbing layer 1–5 cm. The pH values were measured on a pH-121 device. The thermogravimetric studies of samples with a mass 100 mg were carried out on an OD-103 derivatograph in the temperature range from 20 to 1000°C with the rate of heating 10 deg min⁻¹. The IR spectra were registered on a Fourier IR spectrometer FSM 1201 from mulls in mineral oil and in hexachlorobutadiene at 25±1°C.

The chemicals used were: NaNO₂ of "chemically pure" grade, 4-nitroaniline, 4-aminobenzoic and sulfanilic acids were twice recrystallized from hot water; diphenylamine of "analytically pure" grade was recrystallized from petroleum ether; sodium dodecylsulfate "pure" of grade corresponding to Technical Requirements TU 6-09-07-1816-93 and other surfactants were not additionally purified. Acetate–chloride buffer solutions were of pH in the range 0.65–4.0.

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