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ARTICLES

Analytical Aspects of Reactions of Primary Aromatic Amines with *p*-Dimethylaminocinnamic Aldehyde in the Presence of Surfactant Ions and Micelles

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Abstract—The effect of surfactants on reactions of primary aromatic amines with *p*-dimethylaminocinnamic aldehyde is studied. It is shown that the performance characteristics of the photometric determination of primary aromatic amines with *p*-dimethylaminocinnamic aldehyde can be substantially improved by using anionic surfactant micelles. On the basis of the observations, it is shown that anionic surfactants play a multiple role in the systems in study. Namely, surfactant anions select photometrically significant protonated quinoid forms of the condensation products of primary aromatic amines with *p*-dimethylaminocinnamic aldehyde (at a premicellar concentration) to form poorly soluble ion pairs. Next, anionic surfactant micelles dissolve them to form intensely colored solutions that possess aggregative stability. Additionally, anionic surfactants increase the condensation rate. Procedures are developed for photometric and test determinations of aniline and its toxic and medicinal derivatives in the environmental samples, pharmaceutical formulations, and biological fluids. The procedures exhibit low detection limits; they are simple and precise.

Condensation of aldehydes with primary aromatic amines is widely used for the photometric determination of the latter [1]. Among the known aldehydes proposed as reagents for primary aromatic amines, *p*-dimethylaminobenzaldehyde and *p*-dimethylaminocinnamic aldehyde are of particular interest. The lowest detection limit for primary aromatic amines (0.1 μg/mL) is achieved with *p*-dimethylaminocinnamic aldehyde. The peculiarity of the reactions of primary aromatic amines with these reagents results from the influence of the electron-donating dimethylamino group on the chromophore system of the resulting analytical forms (Schiff bases) [2]. Unlike most Schiff bases, which are stable in alkaline media, the Schiff bases formed by primary aromatic amines and *p*-dimethylaminocinnamic aldehyde or *p*-dimethylaminobenzaldehyde are stable in acid media [2–7], which makes them valuable for analytical purposes.

Earlier, we studied systematically the condensation of the simplest primary aromatic amine, aniline, with *p*-dimethylaminocinnamic aldehyde [7]. A comprehensive physicochemical examination showed that the protonated form of the Schiff base, which can exist in two equilibrium resonance forms **I** and **II** (Fig. 1), is formed in this system. It is the presence of the protonated

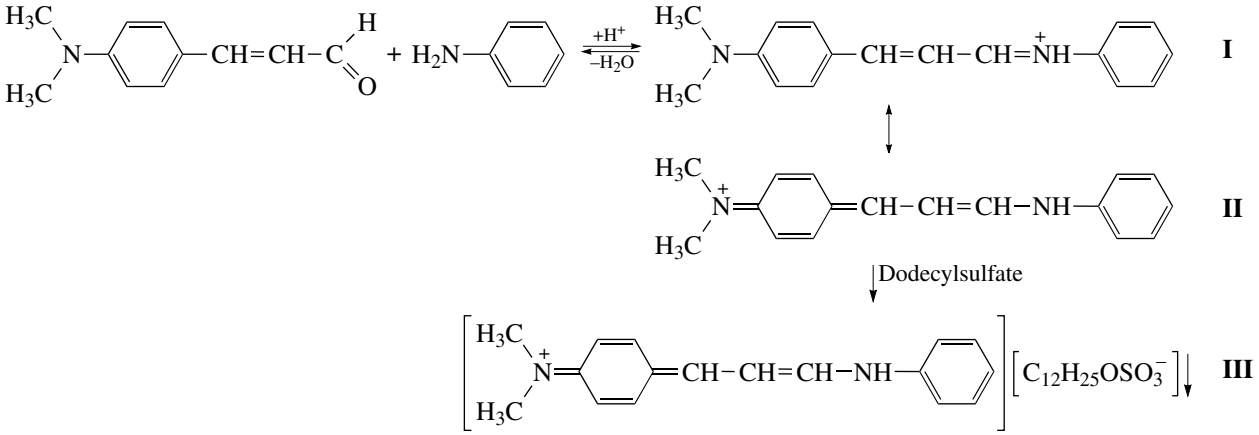

Fig. 1. Interaction of primary aromatic amines with *p*-dimethylaminocinnamic aldehyde in aqueous media and in the presence of anionic surfactants.

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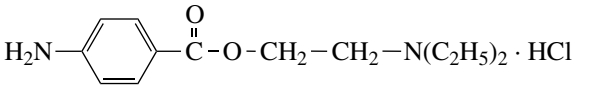
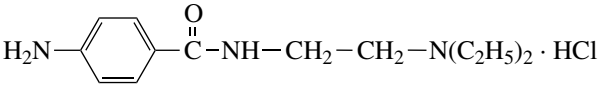
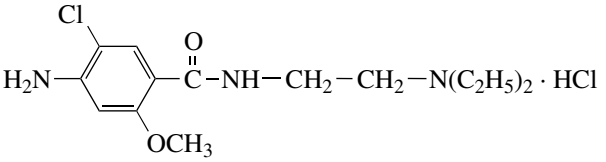
Table 1. Studied surfactants

Surfactant	Name	Mr	% of major constituent
$C_{12}H_{25}$–CH(SO_3Na)COONa	Sodium α-myristate	330.3	95.9
R–O–SO_3Na	Sodium alkylsulfate with R =		
	$C_{16}H_{33}$ (hexadecyl),	344.5	92.9
	$C_{14}H_{29}$ (tetradecyl),	316.4	89.2
	$C_{13}H_{27}$ (tridecyl),	302.4	88.5
	$C_{12}H_{25}$ (dodecyl), and	288.0	96.4
	$C_{10}H_{21}$ (decyl)	260.3	98.2
$(CH_2–CH_2O)_{10}H$	Ethoxylated alkylphenol, OP-10	441.0	99.0
$C_6H_5N^+–C_{16}H_{33}$	Cetylpyridinium chloride	339.5	95.7

Table 2. Medicinal derivatives of *p*-aminobenzoic acid

Formula	Name
	Novocaine (procaine), *p*-aminobenzoic acid β-diethylaminoethyl ester hydrochloride
	Novocainamide (procainamide), *p*-amino-*N*-(β-diethylaminoethyl)-benzamide hydrochloride
	Cerucal (metoclopramide, reglan), 4-amino-5-chloro-*N*-(2-diethylaminoethyl)-2-methoxybenzamide hydrochloride

quinoid form **II** that gives rise to the analytical effect of the reaction.

The effect of surfactant ions and micelles on the analytical reactions of this type is poorly known. In this connection, the goal of this paper is to study the effect of various surfactant ions and micelles on the analytical performance of primary aromatic amine–*p*-dimethylaminocinnamic aldehyde systems.

EXPERIMENTAL

We used *p*-dimethylaminocinnamic aldehyde (Merck) as the main organic reagent. Table 1 shows the surfactants used in this work and some of their characteristics. Aniline (freshly distilled) and its hydroxy (aminophenols), carboxy (aminobenzoic acids), nitro (nitroanilines), methyl (toluidines), sulfo (sulfoanilines), and amino (phenylenediamines) *ortho*-, *meta*-, and *para*-substituted derivatives were purified according to [8]. The medicinal derivatives of aniline—cerucal, procainamide, and novocaine—were used without purification (Table 2).

The absorption spectra were recorded using SPECORD M-40 and SF-46 spectrophotometers. The absorbance of the solutions was measured using KFK-3 and FEK-56M photoelectric colorimeters. pH was monitored by pH-121 and pH-673 pH-meters.

RESULTS AND DISCUSSION

Our preliminary study of the influence of various type surfactants on the interaction of *p*-dimethylaminocinnamic aldehyde with primary aromatic amines showed that the effects important for analytical application are observed only in the systems with anionic surfactants of linear structure. For all the studied primary aromatic amine–*p*-dimethylaminocinnamic aldehyde–anionic surfactant systems, a series of common phenomena was observed. Namely, precipitation occurred at low anionic surfactant concentrations; intensely colored stable solutions characterized by substantial changes in the absorption spectra of the analytical form (bathochromic and hyperchromic effects) (Fig. 2) formed at certain conditions accompanied; a change in reaction rates and an increase in aggregative stability took place.

Further studies of the primary aromatic amine–*p*-dimethylaminocinnamic aldehyde–sodium dodecylsul-

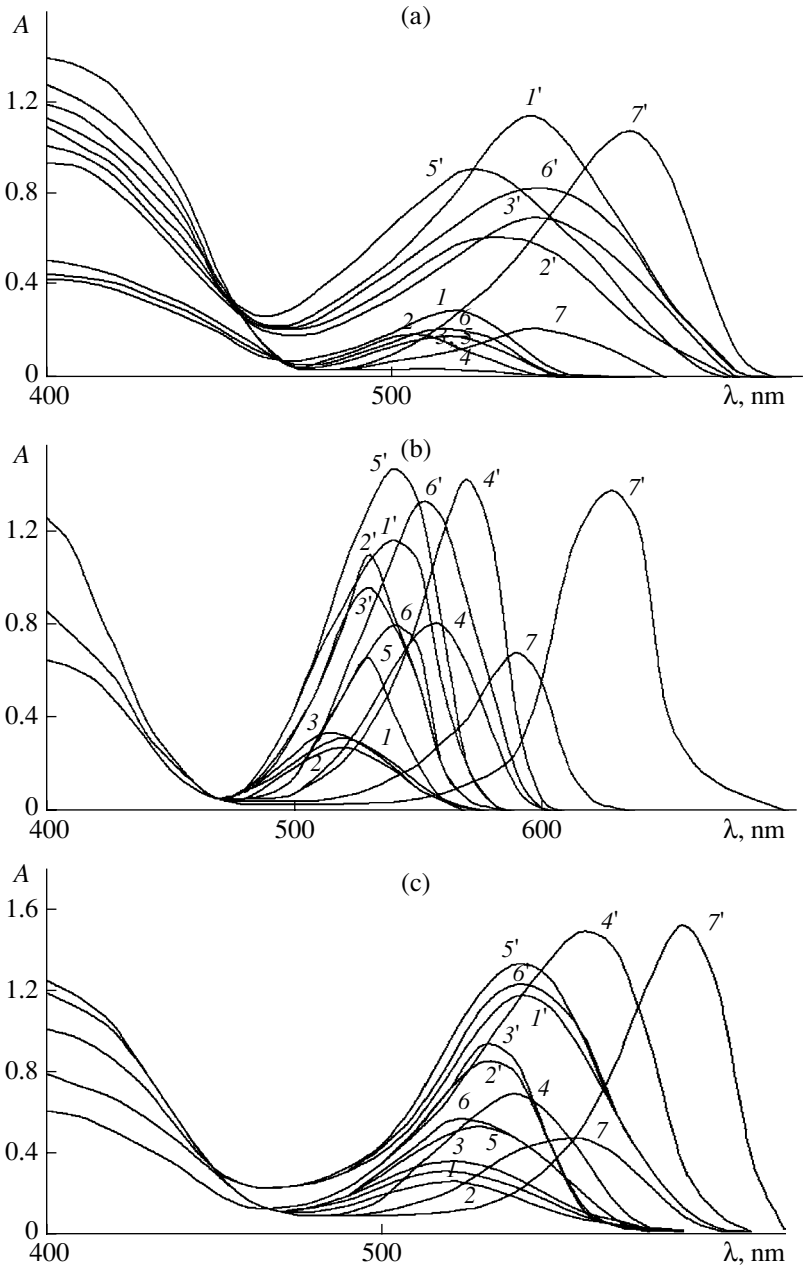


Fig. 2. Absorption spectra of the primary aromatic amines–*p*-dimethylaminocinnamic aldehyde and primary aromatic amines–*p*-dimethylaminocinnamic aldehyde–sodium dodecylsulfate systems for the following (a) *ortho*-, (b) *meta*-, and (c) *para*-substituted primary aromatic amines: (*1* and *1'*) aniline, (*2* and *2'*) toluidines, (*3* and *3'*) aminophenols, (*4* and *4'*) nitroanilines, (*5* and *5'*) aminobenzoic acids, (*6* and *6'*) aminobenzenesulfonic acids, and (*7* and *7'*) phenylenediamines. $c_{\text{primary aromatic amine}} = 2 \times 10^{-5}$ M, $c_{p\text{-dimethylaminocinnamic aldehyde}} = 4.6 \times 10^{-5}$ M, $c_{\text{sodium dodecylsulfate}} = 4 \times 10^{-3}$ M, pH 3.0.

fate systems in a wide concentration range (5×10^{-5}–5×10^{-2} M) showed that the performance characteristics of the binary systems improve substantially only in the micellar solutions of sodium dodecylsulfate. In particular, aggregatively stable and intensely colored solutions suitable for the photometric determination of primary aromatic amines are formed regardless of the nature of the substituents in the amine molecules. The contrast of the reactions increases from 20 to 45 nm (Table 3). For the amines with electron-withdrawing substituents, this analytical effect is more pronounced than for the primary aromatic amines with other substituents. Molar absorptivities (ε_{mol}) of the analytical forms also substantially increase, which reduces the detection limit of amines down to some fractions of their maximum permissible concentrations (Table 3). The stabil-

Table 3. Performance characteristics of the primary aromatic amines–*p*-dimethylaminocinnamic aldehyde and primary aromatic amines–*p*-dimethylaminocinnamic aldehyde–sodium dodecylsulfate systems

Amine	λ_{max} of the analytical form		pH_{opt}	*t*, min, sodium dodecylsulfate	Analytical range, μg/mL	Δλ, nm	ε_{mol}, $a \times 10^{-4}$	
	in H_2O	in sodium dodecylsulfate micelles					in H_2O	in sodium dodecylsulfate micelles
Aniline	520	540	3.5–4.5	15–20	0.01–1.0	20	1.50	9.90
o-Aminophenol	520	540	3.5–4.5	15–20	0.1–6.0	20	0.38	2.40
m-Aminophenol	520	530	3.2–4.2	15–20	–	10	0.76	4.60
p-Aminophenol	515	540	3.7–4.9	50–60	0.05–9.0	20	0.64	4.80
o-Toluidine	505	530	3.4–4.4	15–20	–	25	0.40	2.60
m-Toluidine	520	530	3.5–4.5	15–20	–	10	0.56	4.30
p-Toluidine	520	530	3.7–4.9	25–30	0.05–2.0	10	0.83	5.50
o-Aminobenzoic acid	525	520	2.3–3.9	15–20	0.04–6.0	–	0.36	1.80
m-Aminobenzoic acid	530	540	2.7–3.9	15	0.05–5.0	10	1.60	6.80
p-Aminobenzoic acid	530	540	2.4–3.4	3–5	0.05–4.0	10	2.80	7.40
o-Nitroaniline	–	–	–		–	–	–	–
m-Nitroaniline	540	555	2.5–3.5	25–30	0.01–8.0	15	1.80	7.40
p-Nitroaniline	560	570	1.7–2.7	5–10	0.01–12.0	10	2.00	7.10
Orthanilic acid	520	540	3.2–4.5	25–30	0.05–6.0	20	0.40	2.20
Metanilic acid	525	540	2.8–3.5	5–10	0.05–5.0	15	1.40	6.20
Sulfanilic acid	540	550	2.7–3.5	3–5	0.01–6.0	10	1.90	6.60
o-Phenylenediamine	545	580	3.5–4.5	15–20	0.04–0.8	35	1.10	8.60
m-Phenylenediamine	555	590	4.0–4.5	1–2	0.04–0.8	35	2.60	9.50
p-Phenylenediamine	590	630	4.0–5.0	1–2	0.04–0.9	40	3.10	10.50
Benzidine	570	615	3.0–4.5	1–2	0.02–3.0	45	2.50	10.80
Dianisidine	565	585	3.0–4.5	1–2	0.02–3.0	20	1.90	9.6
Novocaine	540	570	2.0–3.6	3–5	0.04–5.6	30	–	6.3
Procainamide	540	570	3.5–4.5	3–5	0.04–4.0	30	–	5.9
Cerucal	540	560	1.5–3.0	5–10	0.05–8.0	20	–	5.7

ity of the micellar solutions should be noted: unlike the binary systems, the absorbance of the analytical forms is stable for 6–8 h.

Unlike the properties of the micellar solutions of the primary aromatic amine–*p*-dimethylaminocinnamic aldehyde–sodium dodecylsulfate systems mentioned above, a solid phase of intensely colored precipitates was observed below the critical micelle concentration of sodium dodecylsulfate [$(0.1–1) \times 10^{-3}$ M] and above 5×10^{-5} M for other reagents. In the case of the model aniline–*p*-dimethylaminocinnamic aldehyde–sodium dodecylsulfate system, the precipitate (**III**, Fig. 1) was isolated and examined by thermogravimetry, elemental analysis, and IR spectroscopy [9]. The associate **III** formed by the protonated quinoid form of the Schiff base and dodecylsulfate anion is poorly soluble in water but is readily solubilized in anionic surfactant micelles, which shifts the reaction equilibrium towards the formation of the analytical form. This results in an intense color of micellar solutions in the primary aromatic amine–*p*-dimethylaminocinnamic aldehyde–sodium dodecylsulfate systems.

In addition to the large hydrophobic dodecylsulfate anion, 3-(*p*-dimethylammonium quinonimino)-1-aminophenyl-1-propene forms similar associates with some inorganic anions. Their solubility decreases in the series $SCN^- > NO_3^- \approx Cl^- > SO_4^{2-} > ClO_4^-$. The structure of the associates was elucidated using the poorly soluble associate of 3-(*p*-dimethylammonium quinonimino)-1-aminophenyl-1-propene with perchlorate as an example [7]. The quinoid form of the protonated Schiff base 3-(*p*-dimethylammonium quinonimino)-1-aminophenyl-1-propene (IV) also takes part in the formation of the associate. When the above anions are present in the systems to be analyzed, this fact should be taken into account as an adverse factor that hampers the photometric determination of arylamines at low concentrations of anionic surfactants.

It is shown using various primary aromatic amine–aromatic aldehyde–anionic surfactant systems that the equilibrium is almost completely shifted towards the formation of ion associates similar to 3-(*p*-dimethylammonium quinonimino)-1-aminophenyl-1-propene–sodium dodecylsulfate in the micelles of linearly structured anionic surfactants. When solubilized by the micellar phase of the anionic surfactant, these associates form aggregatively stable and intensely colored solutions of the analytical form similar to III. These processes form the basis for reducing the detection limit and increasing the contrast of the photometric determination of primary aromatic amines (substituted anilines) in the anionic surfactant micelles (Table 3).

In addition to the above effects, sodium dodecylsulfate micelles catalyze the reaction of aniline (and other primary aromatic amines) with *p*-dimethylaminocinnamic aldehyde. One of the rate-determining factors for this reaction is the condition of the reagents in aqueous and micellar media at various pH. Therefore, we studied the condition of *p*-dimethylaminocinnamic aldehyde and aniline in citrate buffer solutions (pH 1–6) in the presence of sodium dodecylsulfate micelles [9]. It was found that, according to the Hartley rule, sodium dodecylsulfate micelles stabilized the protonated reactive form of *p*-dimethylaminocinnamic aldehyde under the best reaction conditions (pH 4).

The deprotonation of aniline in the presence of sodium dodecylsulfate micelles was revealed by potentiometry [9]. This process can be explained by the character of aniline solubilization in the depth of the micelles due to the hydrophobic aromatic ring and relatively small size of the molecule. The results obtained agree with the data reported in [10].

Thus, the protonated form of *p*-dimethylaminocinnamic aldehyde and the neutral form of aniline are preconcentrated in sodium dodecylsulfate micelles. Because both forms are reactive, the overall rate of aniline condensation with *p*-dimethylaminocinnamic aldehyde increases, so that the yield of the analytical form increases as well (an increase in the absorbance) [11]. The regularities found can be extended to the condensation of other primary aromatic amines with *p*-dimethylaminocinnamic aldehyde in anionic surfactant micelles.

The analytical effects caused by anionic surfactant ions and micelles and resulting in a lower detection limit of primary aromatic amines (Table 3) form the basis for a procedure of the photometric and test determination of aniline and its derivatives in various samples: biological fluids (blood and saliva), animal organs (liver and heart), industrial waste water, working area air, solid and liquid drug formulations, and primary aromatic amine impurities in drugs.

Thus, a procedure is developed for the determination of toxic impurity of *p*-aminophenol in paracetamol-containing drugs. The condensation of aminophenol with *p*-dimethylaminocinnamic aldehyde in sodium dodecylsulfate micelles reduced the detection limit of aminophenol by an order of magnitude. This made it possible to analyze samples as small as 0.2000 g (one tablet) with a relative standard deviation of 2–5% [12].

On the basis of *p*-dimethylaminocinnamic aldehyde, indicator tubes with chemisorbed packing are developed for the test determination of aniline, toluidines, and chloroanilines in air. The indicator tubes allow the *in situ* determination of 0.1–1 mg/m^3 volatile aniline derivatives with an error of the semiquantitative determination of primary aromatic amines of no more than 10% (by the color chart) [13].

A simple procedure was developed for the photometric determination of cerucal in oral cavity fluid with the aim of pharmacodiagnosis. After the precipitation of proteins, the reaction with *p*-dimethylaminocinnamic aldehyde was performed in a solution of citrate buffer (pH 1.2–4.0) and sodium dodecylsulfate (5×10^{-3}–5×10^{-2} M) [14]. The analytical range of the procedure was 1.00–12.00 μg/mL.

Some procedures for the determination of primary aromatic amines in other samples based on the studied systems are described below.

Determination of novocaine in blood. To construct a calibration plot, portions of the standard 100 μg/mL novocaine solution (0.1, 0.3, 0.5, 0.8, 1.0, 1.2, and 1.4 mL) are placed in seven 25-mL volumetric flasks. *p*-Dimethylaminocinnamic aldehyde (0.2% or 1.14×10^{-2} M) in 0.1-mL portions and 0.1 M sodium dodecylsulfate in 1-mL portions are added to each flask, and the solutions are diluted to the mark with citrate buffer solution with pH 3. The prepared solutions are stirred thoroughly, and the absorbance is measured by FEK-56M (l = 1 cm, λ_{max} = 560 nm). The reference solution contains all the components but for novocaine. The $A = f(c)$ curve is constructed from the absorbances obtained. Beer's law is obeyed in the range of 0.4–5.6 μg/mL of novocaine.

If lower concentrations of novocaine are to be determined, a 10 μg/mL novocaine solution is prepared. Portions of the novocaine solution (0.1, 0.4, 0.7, and 1.0 mL) are placed in four 25-mL volumetric flasks and processed as described above. The calibration plot is linear in the range of 0.04–0.4 μg/mL of novocaine.

To determine novocaine in blood, 2 mL of blood is placed in a volumetric test-tube, and proteins are immediately precipitated with 2 mL of 20% trichloroacetic acid. The mixture is stirred vigorously and centrifuged for 5 min (at 3000 rpm). The reagent can contact with blood for 5–30 min. After centrifugation, the filtrate is decanted to a volumetric cylinder; the precipitate is washed with 2 mL of citrate buffer solution (pH 3) and centrifuged again for 5 min; and the secondary filtrate is also decanted to the volumetric cylinder. An aliquot portion of the pooled filtrate is placed in a 25-mL volumetric flask, 0.1 mL of 0.2% *p*-dimethylaminocinnamic aldehyde and 1 mL of 0.1 M sodium dodecylsulfate are added, and the solution is diluted to the mark

Table 4. Determination of procainamide in rat organs ($n = 3$, $P = 0.95$)

Dose, mg/kg	Organ	Survival time, h				
		1	3	6	12	24
		Procainamide concentration, mg/100 g				
10	Liver	0.45 ± 0.03	0.18 ± 0.02	0.15 ± 0.01	–	–
	Heart	0.80 ± 0.05	0.18 ± 0.02	0.15 ± 0.01	–	–
	Blood	0.25 ± 0.01	0.10 ± 0.01	–	–	–
200	Liver	3.80 ± 0.08	3.40 ± 0.04	3.10 ± 0.03	1.60 ± 0.04	0.20 ± 0.01
	Heart	4.80 ± 0.05	6.70 ± 0.07	6.60 ± 0.07	3.50 ± 0.05	0.50 ± 0.02
	Blood	0.60 ± 0.03	2.20 ± 0.05	1.50 ± 0.06	0.30 ± 0.02	–
500	Liver	4.50 ± 0.06	5.80 ± 0.06	6.80 ± 0.08	4.50 ± 0.04	2.60 ± 0.02
	Heart	5.70 ± 0.09	7.30 ± 0.07	10.8 ± 0.09	12.5 ± 0.05	6.00 ± 0.05
	Blood	4.90 ± 0.08	4.40 ± 0.05	4.20 ± 0.03	3.40 ± 0.04	0.70 ± 0.01

with citrate buffer solution (pH 3). The absorbance is measured by FEK-56M as described above relative to the blank solution. Novocaine concentration is found from the calibration plot.

Determination of procainamide in rat organs. To construct the calibration plot, portions (0.1, 0.4, 0.7, and 1.0 mL) of the standard 10 μg/mL procainamide solution are placed in four 25-mL volumetric flasks. *p*-Dimethylaminocinnamic aldehyde (0.2%) in 0.1-mL portions and 0.1 M sodium dodecylsulfate in 1-mL portions are added to each flask. The solution is diluted to the mark with a citrate buffer solution with pH 3. The prepared solutions are stirred, and the absorbance is measured at 555 nm relative to the blank solution. The calibration plot is linear for 0.2–4.0 μg/mL of procainamide at $l = 1$ cm and 0.04–0.4 μg/mL of procainamide at $l = 5$ cm.

To determine procainamide in rat heart and liver, the corresponding organs are extracted at desired exposure intervals and triturated with glass until homogeneous. A portion (2 mL) of 30% trichloroacetic acid is added to precipitate proteins. The mixture is stirred thoroughly with a stirring rod and centrifuged for 5 min (3000 rpm). The filtrate is transferred to a 25-mL volumetric flask, and the reagents are added as described above. Procainamide concentration is found from the calibration plot. The results of the determination of procainamide in rat organs are given in Table 4.

One can see from Table 4 that a therapeutic dose (10 mg/kg) of procainamide was not found in organs after 12 h, and after 6 h it was found only in rat liver and heart. Only drug traces were found in most organs after 3 h. The dose of 200–400 mg/kg of procainamide was not found in organs after 36 h, and the dose of 500 mg/kg was found in a negligible amount. The maximum procainamide amount was concentrated in heart. The lethal dose of the drug in rats is 600 mg/kg.

Test determination of some primary aromatic amines on a chromatographic paper. On the basis of the studied systems, test facilities are developed for the identification and semiquantitative determination of primary aromatic amines. For this purpose, a drop (~0.005 mL) of primary aromatic amine solution to be analyzed was applied to a filter paper strip using a micropipet. Next, a drop of solution consisting of a buffer solution or HCl (pH_{opt}, Table 3), *p*-dimethylaminocinnamic aldehyde (1×10^{-4} M), and sodium dodecylsulfate [$(5–8) \times 10^{-2}$ M] (the best component ratio is 5 : 2 : 2 v/v/v) is applied to the dry spot. A blank experiment is performed for each determination. For all the primary aromatic amines in study, the analytical effect of the reactions should be observed after the spot on the chromatographic paper dries completely. The best analytical effect was observed in an acid medium (0.5–1 M HCl or a citrate buffer solution with pH 1.0); the reagent (blank experiment) is colorless under these conditions. In other cases, the reagent in the blank experiment is yellow. Performing the reaction in sodium dodecylsulfate makes it possible to reduce the limit of the semiquantitative determination of primary aromatic amines on the chromatographic paper by the order of magnitude (according to the corresponding color chart) (Table 5).

Photometric Determination of Aniline and Some Its Derivatives in Waste Water

Calibration plot for the determination of *m*-nitroaniline. Portions (0.25, 0.75, 1.25, 1.75, and 2.50 mL) of the standard 1 μg/mL *m*-nitroaniline solution are placed in five 25-mL volumetric flasks. *p*-Dimethylaminocinnamic aldehyde (0.2%) in 0.1-mL portions and 0.1 M sodium dodecylsulfate in 1-mL portions are added to each flask, and the solution is diluted

Table 5. Performance characteristics of the detection of the primary aromatic amines in study with *p*-dimethylaminocinnamic aldehyde on the chromatographic paper with and without sodium dodecylsulfate

Primary aromatic amines	Detection limit, μg/0.005 mL		Color	
	without sodium dodecylsulfate	with sodium dodecylsulfate	of the reaction products	of the blank
Aethazol	0.1	0.05	Pink	White
Phthalazol	0.1	0.05	Same	Same
Sulfapyridazin	0.2	0.025	″	″
Sodium sulfacyl	0.1	0.05	″	″
Norsulfazole	0.2	0.025	″	″
White streptocid	0.2	0.025	″	″
Sulfalene	0.2	0.01	″	″
Sulfadimesine	0.1	0.025	″	″
Sulfadimethoxine	0.1	0.025	″	″
Norsulfazole	0.1	0.025	″	″
Urosulfan	0.1	0.025	″	″
Sulfamonomethoxine	0.1	0.025	″	″
Phthazin	0.2	0.05	″	Yellow
4-Phenylenediamine	0.01	0.004	Blue	Same
3-Phenylenediamine	0.01	0.04	Lilac	″
2-Phenylenediamine	0.1	0.01	Same	″
4-Chloroaniline	0.1	0.01	Pink	White
Anthranilic acid	0.1	0.01	Same	Yellow
2-Nitroaniline	–	–	–	–
1-Naphthylamine	0.1	0.025	Blue	Yellow
4-Nitroaniline	0.1	0.01	Same	White
4-Toluidine	0.1	0.01	Pink	Yellow
2-Toluidine	0.1	0.05	Same	Same
Sulfalene	0.1	0.025	″	White

to the mark with citrate buffer solution (pH 3.0). The absorbances are measured by FEK-56M (l = 5 cm, λ_{max} = 555 nm). Beer's law is obeyed in the range of 0.01–0.1 μg/mL. The $A = f(c)$ curve is constructed from the absorbances obtained.

Calibration plot for the determination of *p*-nitroaniline. Portions (0.25, 0.75, 1.25, 1.75, 2.50, and 3.75 mL) of the standard 100 μg/mL *p*-nitroaniline solution are placed in six 25-mL volumetric flasks. *p*-Dimethylaminocinnamic aldehyde (0.2%) in 0.1-mL portions and 0.1 M sodium dodecylsulfate in 1-mL portions are added to each flask, and the solution is diluted to the mark with citrate buffer solution (pH 2.0). The absorbances are measured by FEK-56M at l = 1 cm and λ_{max} = 570 nm. The $A = f(c)$ curve is constructed from the absorbances obtained. Beer's law is obeyed in the range of 0.1–12.0 μg/mL of *p*-nitroaniline.

o-Nitroaniline does not enter the condensation with *p*-dimethylaminocinnamic aldehyde [15]. To preconcentrate primary aromatic amines by freezing, 1 L of the water to be analyzed is placed in a freezing mixture and frozen by 90–95%. The unfrozen concentrate is decanted, and primary aromatic amines are determined in it from the corresponding calibration characteristics.

The accuracies of the determination of aniline and some its derivatives in various samples are presented in Table 6.

Our studies allow the following conclusions:

1. A multiple role of the anionic surfactants in the condensation of primary aromatic amines with *p*-dimethylaminocinnamic aldehyde is ascertained. The protonated quinoid form of the Schiff base (IV) forms poorly soluble ion pairs with anionic surfactant ions below the critical micelle concentration of the surfactant. Next,

Table 6. Accuracy of the determination of some primary aromatic amines in various samples ($n = 5$, $p = 0.95$)

Primary aromatic amine to be determined	Sample	Primary aromatic amines added, mg/L	Primary aromatic amines found, mg/L	RSD, %
p-Aminophenol	Paracetamol	0.03	0.032 ± 0.003	5
White streptocid	Ointment	25.0	25.0 ± 0.3	2
Cerucal	O(I) Rh(+) Blood	30.0	29.1 ± 0.6	3
Procainamide	Oral cavity fluid	100.0	99.2 ± 0.9	2
Aniline	Air	0.1	0.11 ± 0.02	10
Aniline	Tap water	0.1	0.09 ± 0.02	20
p-Toluidine	Same	0.6	0.54 ± 0.08	10
p-Aminobenzoic acid	″	0.2	0.19 ± 0.03	10
Metanilic acid	″	0.5	0.46 ± 0.07	10
p-Phenylenediamine	″	0.2	0.22 ± 0.04	20
m-Phenylenediamine	Purified waste water	0.05	0.04 ± 0.01	20
Benzidine	Same	0.08	0.09 ± 0.02	20
p-Nitroaniline	″	0.3	0.25 ± 0.07	20
Sulfanilic acid	″	1.0	0.98 ± 0.12	10

these ion pairs are solubilized into the anionic surfactant micelles. The reaction rate also changes.

2. The analytical effects caused by the anionic surfactants in the *p*-dimethylaminocinnamic aldehyde–primary aromatic amine systems form a basis for the procedures of the photometric determination of aniline and its derivatives in environmental samples, pharmaceutical formulations and biological fluids. The procedures exhibit low detection limits (fractions of the maximum permissible concentrations); they are simple and precise.

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