Anal. Chem. **1994**, *66*, 2232–2239

Micellar Catalysis and Product Stabilization in Hydrazone Formation Reactions and Micellar-Modified Determination of Hydrazine and Phenylhydrazine

Anatoly K. Yatsimirsky,* Natalia T. Yatsimirskaya, and Svetlana B. Kashina†

Facultad de Química, Universidad Nacional Autónoma de México (UNAM), México D.F., 04510 México, and Department of Chemistry, Moscow State University, 119899 Moscow, Russia

Kinetics and equilibria of condensation reactions of hydrazine and phenylhydrazine with *p*-(dimethylamino)benzaldehyde in micellar sodium dodecyl sulfate solutions were studied spectrophotometrically. The reaction with hydrazine involves consecutive reversible addition of two aldehyde molecules. The reaction rate under conditions of high excess of aldehyde is determined by the acid-catalyzed attack of aldehyde by hydrazinium cation. The reaction with phenylhydrazine proceeds slower and is characterized by a much smaller equilibrium constant as compared to the reaction with hydrazine. Micelles strongly enhance the observed rate (ca. 10^2 times) and equilibrium (ca. 10^4 times) constants of the reaction with hydrazine and exert more modest (20–30 times) enhancement of the respective parameters of the reaction with phenylhydrazine. The binding constants of reactants and reaction products to surfactant micelles as well as the intrinsic rate constants of the reactions in the micellar pseudophase were calculated from dependencies of observed rate constants and reaction yields on surfactant concentration. Spectrophotometric and kinetic methods of hydrazine determination based on its interaction with *p*-(dimethylamino)benzaldehyde in micellar medium are suggested, which avoid additions of concentrated acids and organic solvents, use ca. 100 times more diluted reagent solution, and can be performed in a shorter time as compared to the traditional procedure.

Aqueous micelle solutions are unique media characterized, in contrast to common mixed aqueous–organic solvents, by a nonuniform distribution of solutes which give rise to modification of their reactivity, spectroscopic, and acid–base properties, extraction, and chromatographic behavior, etc. These effects find numerous applications in analytical chemistry.[1-4] Currently, much attention is attracted to the use of micellar catalysis for improvement of kinetic[5,6] and flow injection[7] methods. Less familiar micellar effects on reaction equilibria (others than shifts of pK_a values of solubilized molecules) have not yet found application in analysis although they can be in principle[8] even stronger than more extensively studied catalytic micellar effects. In particular, they can be used to promote processes strongly reversible in water, e.g., condensation reactions, such as formation of hydrazones, oximes or Schiff bases from carbonyl compounds.

Schiff base and hydrazone formation condensation reactions are widely used for determination of both carbonyl compounds and amines or hydrazines.[9-11] All these reactions are, however, strongly reversible, and sometimes strictly anhydrous conditions are necessary to obtain a close to quantitative yield of the product.[12,13] Another disadvantage is the slow rate of condensation reactions under mild conditions in the absence of specific or general acid catalysts.[14]

Earlier, we observed[15] that micelles of an anionic surfactant sodium dodecyl sulfate (SDS) strongly increase both the rate and the yield of the product of the condensation of benzaldehyde with aniline in aqueous solution. These effects were found to be general for the reactions between arylamines and arylaldehydes and were used for the improvement of spectrophotometric determinations of arylamines with *p*-(dimethylamino)benzaldehyde (DAB) as reagent.[16-18]

Recently, we have found that SDS micelles exert similar effects on the condensation of DAB with hydrophilic hydrazine molecule.[19] This observation opens an opportunity to improve the common method of hydrazine determination in water based on its condensation with two molecules of DAB in strongly acid media.[20-22]

† Moscow State University.

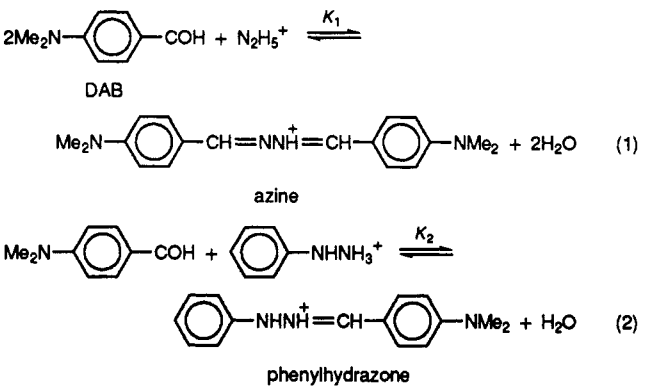
(1) Hinze, W. L. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 1, pp 79–127.
(2) Hinze, W. L., Armstrong, D. W., Eds. *Ordered Media in Chemical Separations*; ACS Symposium Series; American Chemical Society: Washington, DC, 1987; Vol. 342.
(3) Dorsey, J. G. *Adv. Chromatogr.* **1987**, *27*, 167–214.
(4) McIntire, G. L. *CRC Crit. Rev. Anal. Chem.* **1990**, *21*, 257–278.
(5) Mottola, H. A.; Pérez-Bendito, D. *Anal. Chem.* **1992**, *64*, 407R–428R.
(6) Pérez-Bendito, D.; Rubio, S. *Trends Anal. Chem.* **1993**, *12*, 9–18.
(7) Johnson, B. F.; Malick, R. E.; Ghearing, B.; Dorsey, J. G. *Analyst* **1992**, *117*, 1833–1837.
(8) Berezin, I. V.; Martinek, K.; Yatsimirsky, A. K. *Russ. Chem. Rev. (Engl. Transl.)* **1973**, *42*, 787–802.
(9) Siggia, S.; Hanna, J. G. *Quantitative Organic Analysis via Functional Groups*, 4th ed.; Wiley-Interscience: New York, 1979.
(10) Sawicki, E.; Sawicki, C. R. *Aldehydes Photometric Analysis*; Academic Press: London, 1975–1978; Vols. 1–5.
(11) Mázor, L. Methods of Organic Analysis. In *Wilson and Wilson's Comprehensive Analytical Chemistry*; Svehla, G., Ed.; Elsevier: Budapest, 1983; Vol. 15, pp 1–529.
(12) Lopez-Nieves, M.; Wentzell, P. D.; Crouch, S. R. *Anal. Chem.* **1990**, *62*, 304–308.
(13) Lopez-Nieves, M.; Wentzell, P. D.; Crouch, S. R. *Anal. Chim. Acta* **1992**, *258*, 253–258.
(14) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; Dover Publications: New York, 1987.
(15) Martinek, K.; Yatsimirsky, A. K.; Osipov, A. P.; Berezin, I. V. *Tetrahedron* **1973**, *29*, 963–969.
(16) Yatsimirskaya, N. T.; Yatsimirsky, A. K.; Martinek, K.; Berezin, I. V. *Abstr. of Int. Symp. Microchem. Tech.*; Switzerland, 1977; p 216.
(17) Berezin, I. V.; Yasimirskaya, N. T.; Yatsimirsky, A. K.; Martinek, K. *Dokl. Akad. Nauk. SSSR* **1986**, *287*, 643–647.
(18) Krivova, S. B.; Mitiakina, M. G.; Yatsimirskaya, N. T.; Osipov, A. K. *Vestn. Mosk. Univ. Ser. Khim.* **1991**, *32*, 367–372.
(19) Yatsimirsky, A. K.; Krivova, S. B.; Yatsimirskaya, N. T. *Zh. Obsch. Khim.* **1992**, *62*, 916–922; *J. Gen. Chem. (Engl. Transl.)* **1992**, *62*, 752–757.
(20) Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006–2008.

0003-2700/94/0366-2232$04.50/0

The purpose of this study is to determine in more detail and to rationalize micellar effects on the reaction between DAB and hydrazine as well as to explore their analytical utility. These effects are of general interest also since they demonstrate the ability of surfactants to accelerate and to enhance the product yield even in reactions with loosely micellar-bound hydrophilic species like the hydrazine molecule. Normally, micellar effects are small for reactions with such reactants and this observation extends the area of applications of micellar media.

The related reaction of DAB with phenylhydrazine in SDS micellar medium was also studied. Determination of this compound with DAB as a reagent under traditional conditions was recently reported.[23] Phenylhydrazine possesses a hydrophobic phenyl group which can enhance considerably the binding of this reactant to micelles as compared to unsubstituted hydrazine. Therefore, a comparative study of micellar effects on reactions with these two molecules can give interesting information concerning the relationship between binding and catalysis in micellar systems.

The condensation of DAB with hydrazine and phenylhydrazine affording azine and phenylhydrazone products, respectively, proceeds according to stoichiometric equations given below



Both reaction products were isolated and their protonated forms proven to have strong absorption maxima in visible region.[24]

Published analytical procedures use 2–4% (0.13–0.26 M) reagent solution in strongly acidic (1–4 M HCl or H_2SO_4) water or alcohol. The final solution is also strongly acidic (0.3–1 M) and contains 0.02 M or higher concentration of DAB and 0–40% of methyl or ethyl alcohol. The reaction time is rather long, ca. 10 min.[20,22]

The use of SDS solution can allow one to avoid extreme conditions of the traditional method as well as to decrease the reaction time. These improvements can facilitate automation of the procedure. It is worth note that attention continues to be attracted to the development of improved methods of hydrazine determination.[25–28]

EXPERIMENTAL SECTION

Reagents. All reagents were analytical-grade commercial products purified when necessary by standard procedures.[29] Distilled water was used for preparation of all solutions.

Procedure. Reactions of DAB with hydrazine and phenylhydrazine were followed spectrophotometrically using a Specord M-40 or a Hitachi 150–20 UV–vis spectrophotometer equipped with a thermostated cell holder. Weekly prepared 2.0×10^{-3} M solutions of hydrazine dihydrochloride and phenylhydrazine hydrochloride (both from Reakhim) in degassed water kept under argon were used as stock solutions. Solutions of DAB (Merck) (0.010 M) were prepared in 96% ethanol or in 0.020 M aqueous SDS (Sigma).

A constant pH was maintained by using 0.010 M acetate–phosphate buffers in an interval of pH 2–6. In more acidic media the desired pH values were obtained by addition of aliquots of standard 1.0 M HCl solution. Since addition of SDS to acid solutions increases the pH even in the presence of buffers[30] the pH values of surfactant solutions were controlled with a glass electrode initially calibrated with HCl solutions of known concentrations and were adjusted to desired values with 1.0 or 0.10 M HCl.

Critical micelle concentrations (cmc's) of SDS were determined kinetically from the reaction rate vs SDS concentration profiles at low SDS concentrations at pH values 2.0 and 1.0. The following results were obtained: at pH 2.0 cmc = 0.0020 M (lit.[30] cmc = 0.00225 M in 0.010 M HCl) and at pH 1.0 cmc = 0.0010 M.

Kinetic and equilibrium measurements normally used 1.0×10^{-5} M and 3.3×10^{-4} M solutions of hydrazine and phenylhydrazine, respectively. In a typical experiment, 3.0 or 2.5 mL of DAB solution containing the desired concentration of SDS at the desired pH value in a 1.0-cm cuvette was placed in the spectrophotometer and equilibrated thermally for 5 min. The hydrazine (15 μL) or phenylhydrazine (500 μL) solution was then added with a micropipet to initiate the respective reaction. All experiments were carried out at 20.0 °C.

All kinetic studies were performed under conditions of a great excess of DAB over hydrazine or phenylhydrazine. The observed pseudo-first-order rate constants were calculated with the method of Guggenheim.[14]

Calculations of observed rate constants and fitting of experimental dependencies to theoretical equations were performed with an IBM AT computer using the SigmaPlot program.

RESULTS AND DISCUSSION

Characterization of Reaction 1 in Micellar Medium. Mixing of hydrazine with an excess of DAB in 0.01–0.02 M SDS solutions at pH < 3.5 results in the formation of a colored product with the absorption maximum at 468 nm. Its molar absorptivity calculated from the limiting value of absorption at [DAB] ≥ 5×10^{-4} M and pH 1–2 is $\epsilon_a = 7.5 \times 10^4$ M^{-1} cm^{-1} at 468 nm; for isolated azine in 1 M H_2SO_4 in ethanol $\epsilon = 7.5 \times 10^4$ M^{-1} cm^{-1} at 464 nm.[24] In aqueous solution the

(21) Basson, W. D.; Van Staden, J. F. *Analyst* **1978**, *103*, 998–1006.
(22) *Annual Book of ASTM Standards*; 1991; Vol. 11.01, pp 450–452.
(23) Gutierrez, M. C.; Gomez-Hens, A.; Pérez-Bendito, D. *Anal. Chim. Acta* **1989**, *225*, 115–122.
(24) Masly, L. K.; Umetskaya, M. N.; Tikhomolov, A. A.; Timofeeva, T. N. *Zh. Anal. Khim.* **1983**, *28*, 120–125.
(25) Wang, J.; Naser, N.; Angnes, L.; Wu, H.; Chen, L. *Anal. Chem.* **1992**, *64*, 1285–1288.
(26) Hou, W.; Ji, H.; Wang, E. *Talanta* **1992**, *39*, 45–50.
(27) Ratcliffe, N. M. *Anal. Chim. Acta* **1990**, *239*, 257–262.
(28) Atanasiou-Malaki, E.; Koupparis, M. A. *Talanta* **1989**, *36*, 431–436.
(29) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980.
(30) Bunton, C. A.; Wolf, B. *J. Am. Chem. Soc.* **1973**, *95*, 3742–3749.

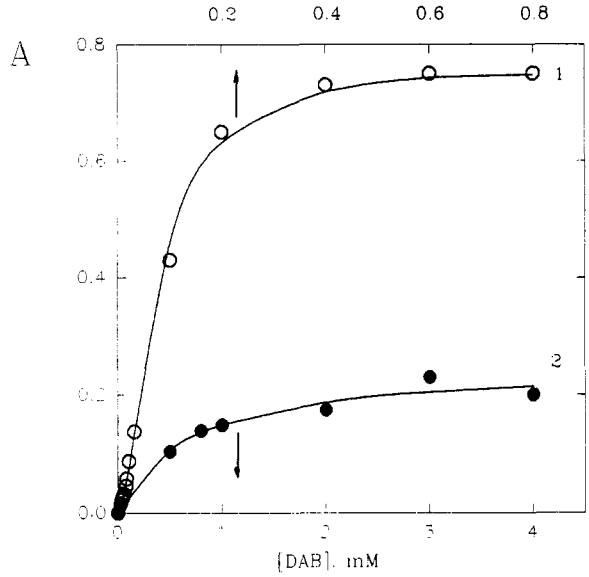
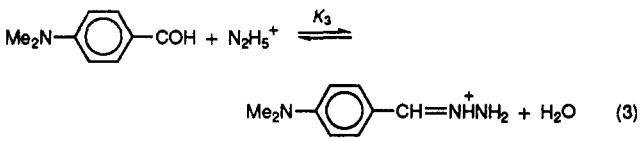


Figure 1. Absorbances of equilibrated solutions of 1.0×10^{-5} M hydrazine, λ 468 nm, pH 1.0 (curve 1) and 1.7×10^{-4} M phenylhydrazine, λ 465 nm, pH 2.0 (curve 2) in 0.020 M and 0.010 M SDS, respectively, vs DAB concentration. The curves are theoretical profiles calculated from eq 5 (curve 1) and the same equation but without the quadratic term and with K_2 instead of K_3 (curve 2) with parameters given in the text and Tables 1 and 2.

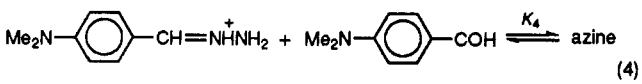
azine absorption maximum lies[23] at 452 nm and in 40% aqueous ethanol[20] at 458 nm. Evidently the azine absorption maximum undergoes a red shift on passing from water to less polar solvents. The fact that micellar medium induces more pronounced red shift than ethanol indicates more or less deep penetration of azine molecules into SDS micelles.

Under the same conditions but with an excess of hydrazine over DAB a more wide and less intensive maximum is observed with $\epsilon_h = 2.8 \times 10^4$ M^{-1} cm^{-1} at 468 nm. This spectrum can be ascribed to the hydrazone formed from one hydrazine and one DAB molecule according to eq 3



(3)

followed by the second condensation step 4



(4)

The existence of an intermediate follows also from the concentration dependence of the absorbance of equilibrated mixtures of hydrazine and DAB, Figure 1, curve 1. Fitting the dependencies of this type obtained at two pH values to the respective theoretical eq 5 gives the equilibrium constants collected in Table 1.

$$\epsilon_{obs} = (\epsilon_h K_3[DAB] + \epsilon_a K_3 K_4[DAB]^2)/(1 + K_3[DAB] + K_3 K_4[DAB]^2) \quad (5)$$

Absorption spectra of azine recorded in the pH interval 1.0–7.8, Figure 2, show the existence of three forms: colorless neutral molecule, monoprotonated form with maximum at 495 nm ($\epsilon = 5.5 \times 10^4$ M^{-1} cm^{-1}), and diprotonated form with maximum at 468 and given above ϵ_a. Evidently, the form actually used for analytical determinations is doubly protonated azine. A routine analysis of pH dependencies of the absorptions at different wavelengths (in the interval 450–500 nm) gives the mean values of $pK_{a1} = 3.35 \pm 0.03$ and $pK_{a2} = 6.76 \pm 0.05$ in 0.020 M SDS. The difference between pK_{a1} and pK_{a2} is surprisingly small, ca. 3.4. The same difference for hydrazine is 8.9. This effect can be explained by delocalization of positive charges on the azine nitrogens due to strong resonance with lone pairs of *p*-(dimethylamino) groups.

Respective pK_a values in aqueous solution are unknown, and one may expect pK_{a1} to be between 0 and 1 since 1 M strong acid is necessary for the complete protonation of azine.[20] Thus, 10^2–10^3 effect of stabilization of doubly protonated azine can be attributed to its incorporation into anionic micelles.

Kinetics of the formation of azine, reaction 1, followed a pseudo-first-order rate law. The dependence of the observed rate constant, k_{obs}, on DAB concentration at pH 1.0 is shown in Figure 3, line 1. As expected for a reversible reaction, this dependence has a positive intercept when extrapolated to zero DAB concentration.

The rate equation derived with a steady-state approximation to the hydrazone intermediate, reaction 3, has the form

$$k_{obs} = (k_{-1}k_{-2} + k_1 k_2[DAB]^2)/(k_{-1} + k_2[DAB]) \quad (6)$$

where the rate constant k_{-1} corresponds to the backward process of step 3 and rate constants k_2 and k_{-2} to the forward and backward processes of step 4. Fitting the results in Figure 3, curve 1, to eq 6 gives $k_2 = 48 \pm 12$ M^{-1} s^{-1}, $k_{-2} = (1.2 \pm 0.4) \times 10^{-3}$ M^{-1} s^{-1}, and $k_2/k_{-2} = K_4 = 4 \times 10^4$ M^{-1} in reasonable agreement with K_4 from the equilibrium study, Table 1.

At high DAB concentrations eq 6 can be presented in a simplified form as eq 7 which corresponds to the linear part

$$k_{obs} = k_1[DAB] \quad (7)$$

of curve 1 in Figure 3 and is indicative of rate-determining forward reaction 3. The respective second-order rate constant k_1 is an apparent parameter which depends on reaction conditions such as SDS concentration and pH. All further discussions are based on values of k_1 which are calculated as slopes of k_{obs} vs [DAB] profiles, like that shown in Figure 3.

Mechanisms of hydrazone formation reactions in the absence of micelles have been studied thoroughly with substituted hydrazines as substrates[14,31,32] (these references contain extensive citation of earlier works). Usually the respective free bases are considered the reacting species. This is not evident for unsubstituted hydrazine, however, since it

(31) Stachissini, A. S.; do Amaral, L. *J. Org. Chem.* **1991**, *56*, 1419–1424.
(32) Somera, N. M.; Stachissini, A. S.; do Amaral, A. T.; do Amaral, L. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1717–1722.

Table 1. Rate and Equilibrium Parameters of Reactions 1 and 2 in Aqueous SDS Solution at 20 °C

reactn	pH	$10^{-3}K_3$[a] (M^{-1})	$10^{-4}K_4$[a] (M^{-1})	k_1[a] (M^{-1} s^{-1})	$k_{1,b}$ (M^{-1} s^{-1})	$k_{H,m}$ (M^{-2} s^{-1})	$k_{H,b}$ (M^{-2} s^{-1})	$10^{-8}K_1$[a,b] (M^{-2})	$10^{-4}K_{1,b}$ (M^{-2})	$10^{-2}K_2$[a] (M^{-1})	$K_{2,b}$ (M^{-1})
1	1.0	2.9 ± 2.1	6.9 ± 0.7	7.5	0.2	0.5 ± 0.1	2.0	2.0	1.0		
1	2.0	6.3 ± 1.4	3.2 ± 0.7	12.0	0.08	1.1 ± 0.4	8.0	2.0	1.0		
2	2.0			2.8	0.1	500 ± 200	7900			6.7 ± 1.4	30

[a] At optimum SDS concentration: 0.020 M for reaction 1 and 0.010 M for reaction 2. [b] $K_1 = K_3K_4$.

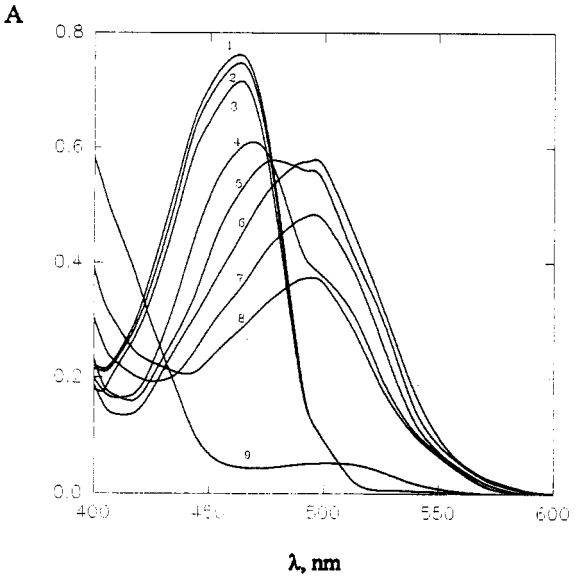


Figure 2. Absorption spectra of 1.0×10^{-5} azine in 0.020 M SDS at pH values 1.0 (1), 2.3 (2), 2.7 (3), 3.4 (4), 4.3 (5), 5.2 (6), 6.6 (8), and 7.8 (9).

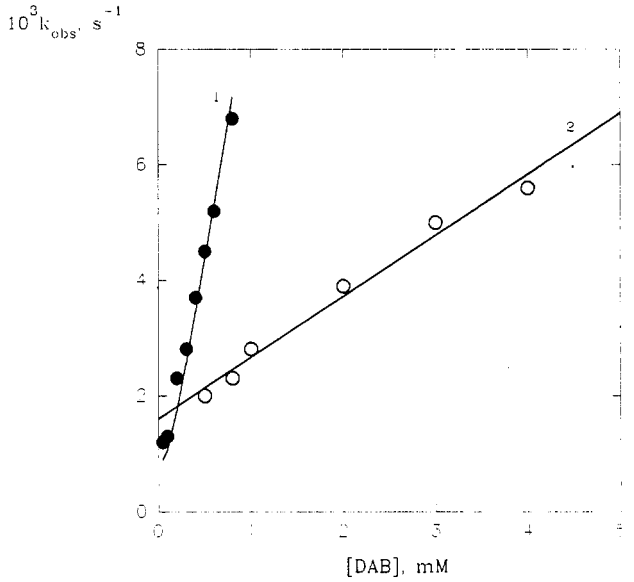


Figure 3. Observed pseudo-first-order rate constants of reactions 1 (curve 1; pH 1.0; 0.02 M SDS) and 2 (line 2; pH 2.0; 0.01 M SDS) vs DAB concentration. Curve 1 is the theoretical profile calculated from eq 6 with parameters given in the text.

is substantially more basic than the usually employed substrates (phenylhydrazine, semicarbazide, etc.) and the concentration of its neutral form in acid solutions can be too small to provide the observed reactivity. To identify the reacting form of hydrazine we studied the pH dependence of k_1 in interval $1 < pH < 4$ and found that at $pH < 3$ the predominant reaction path is a specific acid catalyzed attack of $N_2H_5^+$ cation at DAB with the respective third-order rate constant k_H determined as

$$k_H = k_1/a_{H_3O^+} \quad (8)$$

At $pH > 3$ a noncatalyzed attack of $N_2H_5^+$ at DAB becomes significant. Values of k_1 pass over an optimum at pH ca. 1.7 and decrease at lower pH probably due to protonation of DAB, $pK_a = 1.61$.[33]

Characterization of Reaction 2 in Micellar Medium. Mixing of phenylhydrazine with an excess of DAB under the same conditions as in the case of hydrazine results in the formation of a colored product with a strong absorbance in UV region and a relatively weak maximum at 465 nm which is associated with the protonated form of the phenylhydrazone product. Dependence of the absorbance at this wavelength on DAB concentration at fixed pH and concentrations of SDS and phenylhydrazine is shown in Figure 1, curve 2. The equilibrium constant K_2 calculated from these results, Table 1, is 1 order of magnitude smaller than K_3 for hydrazine.

The formation of the reaction product followed pseudo-first-order kinetics under conditions of an excess of DAB over phenylhydrazine as in the case of hydrazine. The dependence of k_{obs} on DAB concentration at pH 2 and fixed concentration of SDS is shown in Figure 3, line 2. It follows a simple eq 9for a pseudo-first-order reversible reaction with rate constants

$$k_{obs} = k_1[DAB] + k_{-1} \quad (9)$$

of forward and reversing steps $k_1 = 1.1 \pm 0.1$ M^{-1} s^{-1} and $k_{-1} = (1.6 \pm 0.2) \times 10^3$ s^{-1}, respectively. The ratio of these constants $k_1/k_{-1} = 6.9 \times 10^2$ M^{-1} gives the equilibrium constant which is in a good agreement with that found above from thermodynamic data, K_2, Table 1.

The pH dependence of absorbance at 465 nm at fixed concentrations of components was bell-shaped with a maximum at pH 2.0. The molar absorptivity of phenylhydrazone product at pH 2.0, $\epsilon_{Ph} = (1.5 \pm 0.1) \times 10^3$ M^{-1} cm^{-1}, was found by extrapolation of the absorbance to infinite DAB concentration. In more acid solutions the equilibrium constant becomes so small that no "saturation" of the dependence of absorption vs DAB concentration is observed. This can be due to protonation of DAB molecule. From the part of the dependence at $pH > 2$ we found $pK_a = 2.7 \pm 0.1$ for the protonated phenylhydrazone product.

The kinetics of condensation of phenylhydrazine with substituted benzaldehydes in the absence of micelles has been studied comprehensively.[31,32] From published data one can

(33) Pal'm, V. A., Ed. *Tables of Rate and Equilibrium Constants of Organic Heterolytic Reactions*; Acad. Sci. USSR VINITI Publ.: Moscow, 1976; Vol. 2(1), p 97.

conclude that the predominant reaction path in acid solutions is the third-order specific acid-catalyzed addition of phenylhydrazine free base to DAB.

Micellar Effects on Reactions 1 and 2. Yields of the products of reactions 1 and 2 in the absence of SDS and pH > 0.5 were very small. Thus, in 20% ethanol (added to increase DAB and product solubility) at [DAB] = 1.0×10^{-3} M the yield of azine was ca. 1% with respect to hydrazine at pH 1.0, and that of phenylhydrazone at [DAB] = 5.0×10^{-3} M and pH 2.0 was less than 1%. The results obtained under these conditions allowed us to obtain only an approximate evaluation of equilibrium and rate parameters in aqueous solution which were used for the purposes of comparison with respective micellar parameters.

A quantitative treatment of micellar effects on rates and equilibria of chemical reactions can be done with the "pseudo-two-phase" theory which is based on the assumption of equilibrium distribution of reactants between balk aqueous and micellar pseudo-phases and simultaneous transformation of reactants in both "phases".[8,34-36] Binding of organic molecules to micelles is usually described as a partition between aqueous and micellar "phases" and that of small hydrophilic ions as an ion exchange with nonreactive micellar counterions tightly bound to the micellar surface layer.

In our case incorporation of DAB and phenylhydrazine into SDS micelles can be described as their partition between two "phases" with partition constants $P_D = [DAB]_m/[DAB]_b$ and $P_{Ph} = [PhNHNH_2]_m/[PhNHNH_2]_b$, respectively. The binding of hydrazinium ions is an exchange of $N_2H_5^+$ with nonreactive counterions (X) in the surface layer of SDS micelles with the equilibrium constant $K_{N/X} = [N_2H_5^+]_m[X]_b/[N_2H_5^+]_b[X]_m$. Strictly speaking, in acid-buffered solutions used in this study, X corresponds to a mixture of nonreactive sodium (both from SDS and buffer) and hydronium cations, but we will not distinguish between these cations here since the ion-exchange constant between H_3O^+ and Na^+ for SDS micelles is close to unity.[37,38]

There are several simplifications in the derivation of final equations. (i) The total concentration of ions in the micellar surface layer is constant and equals[35]

$$[X]_m + [N_2H_5^+]_m = \beta/V_m \qquad (10)$$

where β is the degree of association of micelles with counterions and V_m is the surfactant molar volume. (ii) Concentrations of reactants are much smaller than that of SDS. (iii) The volume fraction of the micellar pseudo-phase is much smaller than unity (this is true when [SDS] < 0.1 M), $[SDS]V_m \ll 1$. (iv) Partition constants of DAB and phenylhydrazine are much higher than unity (this will be proved experimentally).

Equations presented below are derived with these simplifications using general approaches described in refs 8, 34, and 35.

(34) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844–1850.
(35) Romsted, L. S. In *Surfactants in Solution*; Lindman, B., Mittal, K. L., Eds.; Plenum Press: New York, 1984; Vol. 2, pp 1015–1068.
(36) Bunton, C. A.; Savelli, G. *Adv. Phys. Org. Chem.* **1986**, *22*, 213–310.
(37) Quina, F. H.; Politi, M. J.; Cuccovia, I. M.; Martins-Franchetti, S. M.; Chaimovich, H. In *Solution Behavior of Surfactants*; Mittal, K. L., Fendler, E. J., Eds.; Plenum Press: New York, 1982; Vol. 2, pp 1125–1136.
(38) Perez-Benito, E.; Rodenas, E. *J. Colloid Interface Sci.* **1990**, *139*, 87–92.

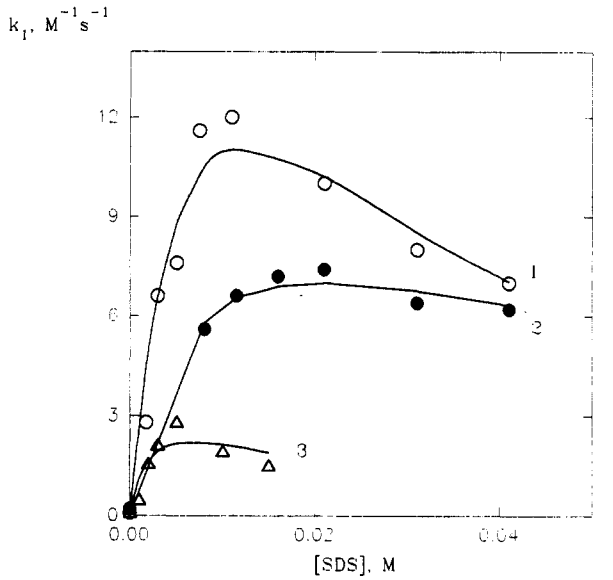


Figure 4. Curves 1 and 2: observed second-order rate constants of reaction 1 vs SDS concentration at pH 2.0 (curve 1) and pH 1.0 (curve 2). The curves are theoretical profiles calculated from eqs 11 and 8 with parameters given in the text and Tables 1 and 2. Curve 3: observed second-order rate constants of reaction 2 vs SDS concentration at pH 2.0. The curve is the theoretical profile calculated from eq 15 with parameters given in the text and Tables 1 and 2.

Micellar Effects on Reaction Kinetics. Figure 4, curves 1 and 2, shows dependencies of observed second-order rate constants k_1 for reaction 1 on SDS concentration at pH 1.0 and 2.0. Qualitatively, these dependencies have typical[8,34-36] forms with maxima. Comparison of the rate constants found in aqueous solution and at optimum SDS concentration (see Table 1) shows observed micellar-induced accelerations to be 150 and 40 times at pH 2.0 and 1.0, respectively.

The above results of the mechanistic study of reaction 1 show that under these conditions the main reaction path is the acid-catalyzed interaction of $N_2H_5^+$ cation with DAB characterized by the rate constant k_H. Therefore, for the quantitative analysis of dependencies in Figure 4 one can apply the theoretical equation for the observed constant k_H which has the form

$$k_H = [k_{H,m}V_m^{-2}K_DK_{N/X}K_{H/X}\beta^2[SDS] + k_{H,b}(\alpha[SDS] + cmc + [B])^2]/[(1 + K_D[SDS])(\alpha[SDS] + cmc + [B])\{(\alpha + \beta K_i)[SDS] + cmc + [B]\}] \qquad (11)$$

where $K_D = P_DV_m$ is an apparent binding constant of DAB to micelles, $\alpha = 1 - \beta$ is the degree of dissociation of micelles, $k_{H,m}$ and $k_{H,b}$ are rate constants in micellar and aqueous "phases" respectively, $K_{H/X}$ is the ion-exchange constant for hydronium ions, and [B] is the concentration of cations from buffer.

To apply eq 11 we used parameters $\alpha = 0.45$ (ref 39), $K_{H/X} = 1$ (refs. 37 and 38), and values of cmc given in the Experimental Section. There is some uncertainty in choosing a proper value of V_m, and reasonable results can be obtained[8,15] with $V_m = 0.35$ M^{-1}. The ion-exchange constant for hydrazonium cation $K_{N/X}$ is unknown, and we used $K_{N/X} = 1$ as an

(39) Frahm, J.; Diekmann, S. In *Surfactants in Solution*; Lindman, B.; Mittal, K. L., Eds.; Plenum Press: New York, 1984; Vol. 2, pp 897–914.

Table 2. Binding Constants (M^{-1}) of Reactants and Products of Reactions 1 and 2 to SDS Micelles

	pH	K_D	K_A	K_{Ph}	K_{PhH}	K_P
DAB	1.0	140 ± 30[a]				
	2.0	16 ± 6				
$PhNHNH_2$	2.0			40[b]	350 ± 200[c]	
					290 ± 130[d]	
azine	2.0		$(3.6 \pm 1.6) \times 10^5$			
phenyl-hydrazone	2.0					$(1.8 \pm 0.5) \times 10^4$

[a] Binding constant of protonated DAB. [b] Calculated indirectly. [c] From kinetic data. [d] From equilibrium data.

approximation since for hydrophilic monovalent cations the values of ion-exchange constants vary depending on the cation's nature in a narrow range from 1 to 2.[40]

Fitting of results in Figure 4 to eq 11 together with eq 8 gives rate and equilibrium parameterrs collected in Tables 1 and 2. Comparison of the rate constants in the micellar "phase" with those in water shows the former to be 4–7 times lower than the latter. Evidently, the main source of the observed micellar effect is the concentration of reactants in micelles. In this connection it is noteworthy that hydrazine can interact with DAB in its protonated form which is attracted and concentrated by anionic micelles.

An increase in K_D on passing from pH 2.0 to pH 1.0 is explicable by protonation of DAB since the protonated molecule can interact with anionic SDS micelles more strongly due to additional electrostatic attraction.

Figure 4, curve 3, shows the dependence of k_1 for reaction 2 on SDS concentration at pH 2.0. Observed micellar-induced acceleration of the reaction with phenylhydrazine is 30-fold, Table 1. For a quantitative treatment of this dependence one must use the respective third-order rate constants k_H as in the case of hydrazine. Interrelation between k_1 and k_H is more complicated here, however. In a general form

$$k_H = k_1(1 + a_{H_3O^+}/K_{a,obs})/a_{H_3O^+} \quad (12)$$

where $K_{a,obs}$ is an observed acid dissociation constant of phenylhydrazinium cation. The factor $(1 + a_{H_3O^+}/K_{a,obs})$ is a correction for protonation of phenylhydrazine. At pH 2.0 the ratio $a_{H_3O^+}/K_{a,obs} \gg 1$ and eq 12 takes the form

$$k_H = k_1/K_{a,obs} \quad (13)$$

Treatment of micellar effects on acid–base dissociation constants in terms of the ion-exchange model[40,41] is more complex than needed for this study. A more simple partition model[8,42] gives the following relationship

$$K_{a,obs} = K_{a,b}(1 + K_{Ph}[SDS])/(1 + K_{PhH}[SDS]) \quad (14)$$

where $K_{a,b}$ is the acid dissociation constant in water and K_{ph} and K_{PhH} are the binding constants of neutral and protonated forms of phenylhydrazine, respectively. Using an equation analogous to eq 11 for k_H together with eqs 13 and 14 we obtain

$$k_1 = k_H K_{a,obs} = [k_{H,m}K_D K_{Ph}\beta V_m^{-2}K_{a,b}[SDS] + k_{H,b}(\alpha[SDS] + cmc + [B])]/[(1 + K_D[SDS])(1 + K_{PhH}[SDS])(\alpha[SDS] + cmc + [B])] \quad (15)$$

Fitting of the results in Figure 4 to eq 15 with the previously determined $K_D = 16\ M^{-1}$ (minimization of a function with three unknown parameters gives large errors) gives the parameters $k_{H,m}K_{Ph}K_{a,b}$ and K_{PhH}. To evaluate K_{Ph} one can suppose the ratio K_{PhH}/K_{Ph} to be approximately the same as the ratio of DAB binding constants in protonated (pH 1.0) and neutral (pH 2.0) forms. This allows one to calculate $k_{H,m}$, K_{Ph}, and K_{PhH}, Tables 1 and 2, from experimentally found parameters.

Evidently in this case the micellar medium is unfavorable for the reaction: the third-order rate constant decreases 16 times on passing from aqueous solution to the micellar "phase". This explains the less pronounced micellar effect on the kinetics of reaction 2 as compared to that on reaction 1. On the other hand the "concentration" accelerating effect which is determined by the binding constants of reactants must be approximately the same in both reactions. This indicates that hydrazinium cation and neutral phenylhydrazine have close affinities to SDS micelles. At the same time phenylhydrazine can be localized in a more hydrophobic part of the micelle, and this explains a stronger negative effect of the micellar microenvironment on its reactivity.

Micellar Effects on Reaction Equilibria. Figure 5 shows dependencies of yields (Y, %) of azine and phenylhydrazone on SDS concentration at pH 2.0 and fixed DAB concentrations.

The yield of azine is connected with the observed equilibrium constant as follows

$$Y = 100(K_1[DAB]^2)/(1 + K_1[DAB]^2) \quad (16)$$

where $K_1 = K_3K_4$. The theoretical equation for the observed equilibrium constant of reaction 1 derived in accordance with refs 8 and 35 has the following form

$$K_1 = K_{1,b}\frac{(1 + K_A[SDS])(\alpha[SDS] + cmc + [B])}{(1 + K_D[SDS])^2\{(\alpha + \beta K_{N/X})[SDS] + cmc + [B]\}} \quad (17)$$

where $K_{1,b}$ is the equilibrium constant of reaction 1 in the absence of SDS and K_A is the binding constant of azine. The concentratioon of hydrazone intermediate is neglected in eq

(40) He, Z. M.; O'Connor, P. J.; Romsted, L. S.; Zanette, D. *J. Phys. Chem.* **1989**, *93*, 4219–4226.
(41) Romsted, L. S.; Zanette, D. *J. Phys. Chem.* **1988**, *92*, 4690–4698.
(42) Yatsimirsky, A. K.; Martinek, K., Berezin, I. V. *Tetrahedron* **1971**, *27*, 2855–2868.

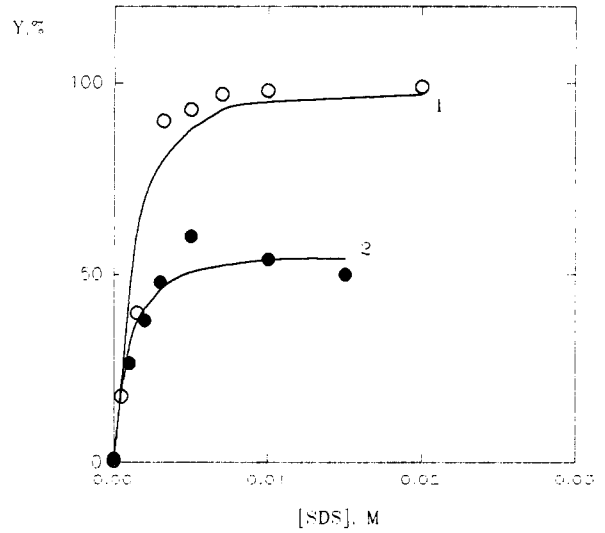


Figure 5. Product yields in reactions 1 (curve 1; 5×10^{-5} M DAB; pH 2.0) and 2 (curve 2; 1×10^{-3} M DAB; pH 2.0) vs SDS concentration. The curves are theoretical profiles calculated from eqs 16 and 17 (curve 1) and eqs 18 and 19 (curve 2) with parameters given in the text and Tables 1 and 2.

16 since under the conditions of Figure 5 its yield is only 6% of the yield of azine, as can be calculated from equilibrium constants K_3 and K_4. It is worth noting that there is a large micellar effect on the equilibrium constant, $K_1/K_{1,b} > 10^4$, Table 1.

Fitting the results in Figure 5, curve 1, to eq 16 with K_1 expressed as eq 17 allowed us to calculate K_A, Table 2. By comparing the binding constants of DAB and azine one can conclude that the micelle-induced shift of the equilibrium originates primarily from much tighter binding of the reaction product as compared with the substrate, $K_A/K_D = 2.1 \times 10^4$. Let us next discuss in more detail the binding constants of reactants and products.

Binding constants for neutral DAB and phenylhydrazine are within the typical range for substituted benzenes.[8,15,43] Their values can be explained by hydrophobic interactions of these molecules with micelles. Azine is the cationic doubly charged species which interacts with SDS micelles both electrostatically and hydrophobically. The contribution of electrostatic interactions to the binding free energy, ΔG_{el}, of a charged species can be evaluated as $\Delta G_{el} = z\Psi_s$, where z is the charge of a species and Ψ_s is the micellar surface potential. For 0.02 M SDS Ψ_s is[44] ca. 100 mV and it gives $\Delta G_{el} = 4.8$ kcal mol^{-1}. This corresponds to a factor of 3×10^3 in the binding constant. The same electrostatic contribution was evaluated above from the observed shift of pK_a of protonated azine as 10^2–10^3. The contribution of hydrophobic interactions can be evaluated as follows. It has been demonstrated[43,45,46] that binding constants of organic molecules to micelles of various surfactants correlate with Hansch hydrophobic parameters π.[47] Parameter π for the p-$C_6H_4NMe_2$ group is[47] 2.3, which corresponds to a factor of 200 in the binding constant K_A due to the presence of such an additional, as compared with DAB, group in the molecule. The combination of both electrostatic and hydrophobic effects can account for the ca. 10^4 times difference between K_A and K_D. This evaluation is of course very rough, but it illustrates that the observed ratio K_A/K_D is quite reasonable.

In the case of phenylhydrazine the yield of phenylhydrazone can be calculated as follows

$$Y = 100(K_2[DAB])/(1 + K_2[DAB]) \quad (18)$$

with K_2 defined by eq 19

$$K_2 = K_{2,b}(1 + K_P[SDS])/\{(1 + K_D[SDS])(1 + K_{PhH}[SDS])\} \quad (19)$$

where $K_{2,b}$ is the equilibrium constant of reaction 2 in the absence of SDS and K_P and K_{PhH} are binding constants of phenylhydrazone product and phenylhydrazinium cation.

The micellar effect on the equilibrium constant $K_2/K_{2,b} = 22$, Table 1, is much lower in this case as compared with that in reaction 1. Fitting the data in Figure 5, curve 2, to eq 18 together with eq 19 gives binding constants K_P and K_{PhH}, Table 2. The latter is in good agreement with the same constant found from kinetic results. A smaller value of K_P as compared to K_A seems quite logical since phenylhydrazone is a monocation while azine is a dication. Contributions of hydrophobic interactions are similar for both compounds since values of π for phenyl ($\pi = 1.96$)[47] and p-(dimethylamino)-phenyl (see above) groups differ insignificantly.

Mathematical analysis of eq 17 shows that K_1 for reaction 1 reaches its maximum value at $[SDS]_{opt} \approx 1/K_D = 0.062$ M and the maximum increase in K_1 relative to $K_{1,b}$ is $(K_1/K_{1,b})_{max} \approx K_A/4K_D = 5 \times 10^3$. For reaction 2 from eq 19 we obtain $[SDS]_{opt} \approx 1/(K_D K_{PhH})^{1/2} = 0.014$ M and $(K_2/K_{2,b})_{max} \approx K_P/(K_D^{1/2} + K_{PhH}^{1/2})^2 = 40$. Equilibrium constants for both reactions pass through maxima, but in accordance with these evaluations an optimum equilibrium constant of reaction 2 is observed at lower SDS concentration than that of reaction 1. This explains why the yield vs SDS concentration profile for reaction 2 passes through a maximum while that for reaction 1 does not. Expressions for $(K_1/K_{1,b})_{max}$ and $(K_2/K_{2,b})_{max}$ show that there are two factors responsible for the higher micellar effect on the equilibrium of reaction 1. First, micelles bind the product of this reaction much tighter than that of reaction 2, $K_A \gg K_P$. This produces a stronger decrease in the free energy of products in the case of reaction 1. Second, micelles bind phenylhydrazinium cation tighter than DAB, $K_{PhH} \gg K_D$. Therefore, micelles decrease the free energy of starting compounds of reaction 2 to a greater extent than those of reaction 1. As a result, $\Delta G°$ of reaction 1 decreases in the presence of SDS micelles to a greater extent than $\Delta G°$ of reaction 2.

ANALYTICAL PROCEDURES

Determination of Hydrazine. Results presented in Figures 4 and 5 show that the highest reaction rate and yield of the product are observed at pH 2.0 in 0.01–0.02 M SDS solutions. The preparation of DAB solution and the use of buffers need

(43) Pramauro, E.; Minero, C.; Saini, G.; Graglia, R.; Pelizzetty, E. *Anal. Chim. Acta* **1988**, *212*, 171–176.
(44) James, A. D.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 10–21.
(45) Treiner, C.; Mannebach, M.-H. *J. Colloid Interface Sci.* **1987**, *118*, 243–250.
(46) Valsaraj, K. T.; Thibodeaux, L. J. *Water Res.* **1989**, *23*, 183–189.
(47) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Bilogy*; Wiley-Interscience: New York, 1979.

some general comments. The efficiency of micellar catalysis is sensitive to the presence of organic cosolvents and inorganic salts. We found that the rate of reaction 1 in the presence of 0.02 M SDS and 5×10^{-4} M DAB at pH 2.0 decreases ca. 15% on addition of a 5% volume of ethanol or duplication of buffer concentration. In view of this, micellar solubilized aqueous rather than alcoholic DAB solution is preferable in this case. To minimize a negative salt effect one can use here a nonbuffered solution containing a known concentration of HCl. It should be noted that SDS micelles behave as a weak electrolyte both with Na^+ and H_3O^+ counterions. This means that acid SDS solutions should have some buffer capacity.

Spectrophotometric Method. The following procedure can be suggested. A known volume of sample or stock hydrazine solution, 1.6 mL of 0.1 M HCl solution, and 1.0 mL of 0.01 M DAB solution in 0.2 M SDS are placed in a 10-mL volumetric flask and diluted with distilled water to 10 mL. After a minimum 5 min the absorbance of solution at 468 nm is measured in a 50-mm cell against the blank. The calibration graph is linear in the range of 0.004–0.1 μg mL^{-1} hydrazine ($r^2 = 0.998$) with a slope 11.7 ± 0.3 μg^{-1} mL and RSD 2.15% for 0.02 μg mL^{-1} hydrazine (11 measurements). The reaction time can be shortened if necessary to 1 min using 0.05 M reagent solution.

Urea, semicarbazide, and ammonia (10 μg mL^{-1} each) tested as possible interfering substances[20] had no effect on the determination of 0.02 μg mL^{-1} hydrazine.

Kinetic Method. The same conditions but with 0.002 M DAB solution in 0.2 M SDS were used. The calibration graph was linear in the range of 0.005–0.5 μg mL^{-1} hydrazine ($r^2 = 0.996$) with a slope of $(2.3 \pm 0.1) \times 10^{-2}$ s^{-1} μg^{-1} mL and RSD of 3.75% for 0.05 μg mL^{-1} hydrazine (11 measurements).

Comparison of characteristics of hydrazine determination in SDS micellar medium with those in classical homogeneous conditions shows the following advantages of the former: (i) no additions of concentrated strong acids and organic cosolvents are necessary, (ii) much more diluted reagent solution can be applied, and (iii) the time of analysis can be shortened considerably.

Determination of Phenylhydrazine. Similar conditions were used for both spectrophotometric and kinetic determinations. The procedure was essentially the same as for spectrophotometric determination of hydrazine. The calibration graph for a spectrophotometric determination was linear in the range of 1–35 μg mL^{-1} phenylhydrazine ($r^2 = 0.997$) with a slope of 0.043 ± 0.001 μg^{-1} mL and RSD of 2.55% for 5 μg mL^{-1} phenylhydrazine (11 measurements) and for kinetic determination in the range of 2–50 μg mL^{-1} hydrazine ($r^2 = 0.996$) with a slope of $(2.7 \pm 0.1) \times 10^{-5}$ s^{-1} μg^{-1} mL and RSD of 2.75% for 5 μg mL^{-1} hydrazine (11 measurements).

The simultaneous determination of hydrazine and phenylhydrazine at the same wavelength can be readily performed since the rates of reactions 1 and 2 differ by 10 times under optimum conditions for hydrazine. It should be noted that DAB is not a suitable reagent for phenylhydrazine due to strong reversibility of condensation and low extinction coefficient of the product although a more sensitive phenylhydrazine determination can be suggested using the absorption below 400 nm. We found in preliminary experiments that much better results can be obtained with other substituted benzaldehydes. Methods of phenylhydrazine determination with the use of micellar media will be presented elsewhere.

ACKNOWLEDGMENT

The work was supported by DGAPA-UNAM, project IN 205393.

Received for review September 2, 1993. Accepted January 11, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1994.