The influence of surfactants on the acid—base and redox properties of reagents of the diphenylamine series

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The influence of aqueous solutions of surfactants on the redox and acid—base properties of diphenylamine redox reagents was studied by potentiometric titration and UV spectroscopy. The formal redox potentials, the pK_a values of the reagents in aqueous solutions and in the presence of surfactants, and the constants of binding of the reagents by micellar solutions of surfactants were estimated.

Key words: diphenylamine reagents, surfactants, acid—base properties, redox potential, solubilization, binding constants.

Diphenylamine (DPA) and its substituted derivatives are widely used in analytical practice (titrimetry, photometry, catalymetry). Compounds whose molecules contain bulky electron-donating properties at the nitrogen atom are the most promising analytical reagents of this series. Modern analytical chemistry makes use of various ways for increasing the reactivity and changing the properties of organic analytical reagents, in particular, transition from an aqueous medium to aqueous solutions of surfactants. It is known[1] that acid—base equilibria shift in aqueous solutions of surfactants. Cationic surfactants increase the degree of dissociation of weak acids and hamper proton addition to bases, whereas anionic surfactants suppress the dissociation of acids and facilitate protonation of bases. Some studies consider[1—4] the influence of surfactants on the protolytic properties of monoazo compounds, reagents of the triphenylmethane series, and other compounds.

In this work, we study the influence of the nature of surfactant on the protolytic and redox properties of diphenylamine-4-sulfonic acid (DPASA), *N*-methyldiphenylamine-4-sulfonic acid (MDPASA), and triphenylamine-4-sulfonic acid (TPASA).

The cationic surfactants used were cetylpyridinium chloride (CPC); sodium dodecyl sulfate (DDS) was used as the anionic surfactant; and the long-chain alcohol Bridge-35 and oxyethylated alkylphenol Triton X-100 were employed as nonionic surfactants in which the size and the hydrophobicity of the substituent at the reaction center, the nitrogen atom, successively increase.

Experimental

The sodium salts of DPASA and MDPASA (commercial preparations) were used as received and the salts of TPASA, synthesized in the work, were purified prior to use. Commercial samples of surfactants, namely, CPC (Reachim), DDS (Merck), Bridge-35 (Chemapol), and Triton X-100 (Merck) were used as received (the content of the major component was more than 98%).

The UV spectra of the reagents (C_R = 0.0004 mol L^{-1}) were recorded on a UV-Vis Specord M-40 spectrophotometer. The quantitative measurements of constants were performed at λ_{max} = 292, 293, and 303 nm for DPASA, MDPASA, and TPASA, respectively. The concentration was varied from 0 to 0.04 mol L^{-1} in the case of DDS and from 0 to 0.004 mol L^{-1} for CPC, Bridge-35, and Triton X-100.

The quantitative estimation of the basicity of compounds (pK_a) was carried out by spectrophotometry in a H_2SO_4 medium. The acidity of solutions (pH < 0) was estimated using the Hammett acidity function (H_0). The pK_a values for conjugate acids were calculated from the equation

$$pK_a = H_0 + \log[(\varepsilon_{mol} - \varepsilon_i)/(\varepsilon_i - \varepsilon_{ion})],$$

where the subscripts mol, ion, and *i* denote the molar extinction coefficients of the reagent in the molecular, ionic, and intermediate forms, respectively.

The constants of binding of the reagents (K_b) by surfactant micelles were determined by spectrophotometry using the formula

$$K_b = (A_w - A_i)/[(A_i - A_m) \cdot (C_{surf} - CMC)],$$

where the A_w, A_m, and A_i values denote the optical densities of an aqueous solution (w), a micellar solution (m) at the absorption maximum, and a solution containing an intermediate (*i*) amount of the surfactant; C_{surf}/mol L^{-1} is the total surfactant concentration in the solution; and *CMC*/mol L^{-1} is the critical micelle concentration of the surfactant.

The formal redox potentials (E_0') of the reagents in the aqueous medium in the presence of a surfactant were determined by Walden potentiometric titration in 1 *M* H_2SO_4 (DPASA, MDPASA) or 4 *M* H_2SO_4 (TPASA).

Results and Discussion

The reaction center in the molecules of redox reagents of the DPA series is the nitrogen atom with a lone

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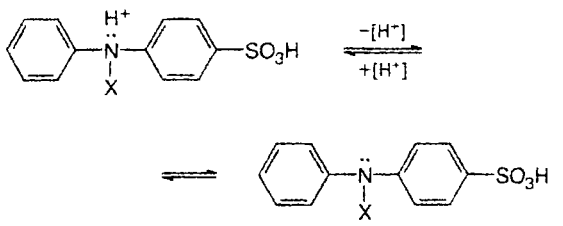
electron pair (LEP), which accounts for the weak basic properties of the compounds. The medium influences the state of the nitrogen LEP and, hence, the acid—base and redox properties of the reagents and thus determines the scope of their application.

The quantitative characteristics used to describe the acid—base equilibria for this series of compounds are dissociation constants of the corresponding conjugate acids (pK_a).



X = H (DPASA), Me (MDPASA), Ph (TPASA)

Table 1 and Fig. 1 present data that illustrate the influence of surfactants on the pK_a value and on the area of existence of ionized forms of the reagents. The pK_a values of the reagents in solutions of CPC decrease in the presence of both ions and micelles of the surfactant. The effect of surfactant cations can be explained by assuming the formation of hydrophobic-hydrated ion associates with participation of the dissociated sulfo

Table 1. pK_a values of the reagents in an aqueous medium and in the presence of various surfactants

Surfactant	$C \cdot 10^{-4}$ /mol L^{-1}	pK_a		
		DPASA	MDPASA	TPASA
CPC	—	−0.90±0.01	−0.86±0.09	−4.4±0.1
	0.4	−1.0±0.1	—	—
	0.8	—	−0.90±0.09	−4.5±0.1
	2	−0.94±0.01	−0.99±0.07	−4.7±0.1
	8	−1.5±0.1	−1.3±0.1	−5.0±0.1
	24	−2.0±0.1	−1.6±0.1	−5.1±0.1
	40	−1.9±0.1	−1.7±0.1	−5.1±0.1
DDS	—	−0.90±0.01	−0.86±0.09	−4.4±0.1
	0.4	−0.91±0.02	−0.77±0.08	−4.3±0.1
	4	−0.93±0.02	−0.77±0.06	−4.6±0.2
	80	−0.94±0.01	−0.91±0.02	−4.8±0.3
	250	−1.0±0.1	−1.2±0.1	−5.3±0.3
	400	−1.2±0.1	−1.2±0.1	−5.8±0.5
Triton X-100	—	−0.90±0.01	−0.86±0.09	−4.4±0.1
	0.4	−0.90±0.02	−0.79±0.06	−4.4±0.1
	2	−0.90±0.01	−0.70±0.02	−4.4±0.1
	8	−0.94±0.01	−0.83±0.04	−4.5±0.1
	24	−1.2±0.1	−1.0±0.1	−4.7±0.3
	40	−1.4±0.1	−1.2±0.1	−4.8±0.1
Bridge-35	—	−0.90±0.01	−0.86±0.09	−4.4±0.1
	0.4	−0.88±0.04	−0.75±0.09	−4.4±0.1
	2	−0.89±0.04	−0.73±0.09	−4.6±0.2
	8	−1.1±0.1	−0.88±0.09	−4.8±0.2
	24	−1.4±0.1	−1.2±0.1	−5.2±0.1
	40	−1.5±0.1	−1.2±0.1	−5.2±0.1

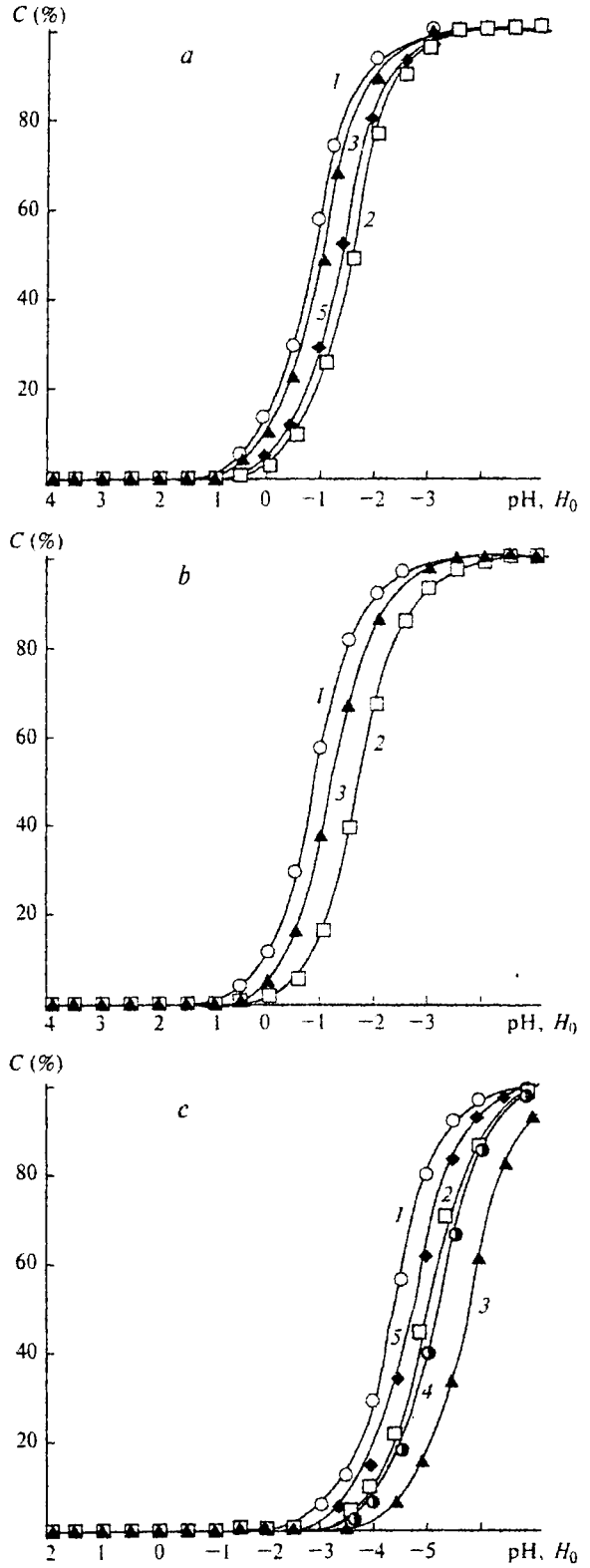


Fig. 1. Proportions of ionic and molecular forms of the reagents DPASA (*a*), MDPASA (*b*), and TPASA (*c*) *vs.* hydrogen ion concentrations in an aqueous medium (*1*) and in the presence of the surfactant CPC (*2*), DDS (*3*), Bridge-35 (*4*), and TX-100 (*5*).

Table 2. Constants of binding of the reagents by micelles of various surfactants (K_b)

Surfactant	$K_b \cdot 10^{-3}$/mol L^{-1}		
	DPASA	MDPASA	TPASA
CPC	7.1±1.7	2.8±0.3	—*
DDS	0.11±0.01	0.28±0.06	—*
Bridge-35	0.45±0.07	0.48±0.04	3.7±1.2
Triton X-100	1.4±0.3	1.3±0.3	2.8±0.7

* Optically nontransparent solutions in the spectral range studied.

group of the reagents (pK_{DPASA} = 3.65; pK_{MDPASA} = 4.12). These associates can be stabilized by both electrostatic and hydrophobic interactions.[1] This transition of the reagents from mainly hydrophilic to a hydrophobic hydrated state might be the main reason for the change in the pK_a value. The decrease in pK_a in the presence of CPC micelles is related to solubilization of the reagents in the micelles. For all the other surfactants studied, this effect is observed only in micellar media and is due to the solubilization effect in the micelle.

The effect of micellar solutions of surfactants on the properties of compounds is associated with the distribution of reagents in the water—micelle system. Quantitative estimation of the reagent solubilization in the surfactant micelles (Table 2) shows that the introduction of a substituent (Me, Ph) to the nitrogen atom and, correspondingly, the increase in the size, conformational rigidity, and hydrophobicity of molecules in the series DPASA < MDPASA < TPASA brings about the following consequences:

— in the presence of CPC, the shift of the acid—base equilibrium decreases ($\Delta pK_a = pK_{a,mol} - pK_a$). Thus the reaction center of the molecule becomes more accessible for a hydronium ion and solubilization becomes less efficient, which is correlated with the change in the constant of binding (K_b) of the reagents;

— in the presence of DDS, the basic properties of compounds become weaker. However, ΔpK_a increases in the series under study, which points to the difficulty of protonation. Hydrophobization of the compound enhances its solubilization in the micelles of anionic surfactants and hampers the access of protons to the nitrogen LEP; this may point indirectly to the localization of MDPASA and TPASA molecules deep in the micelle. These results are also consistent with the change in K_b;

Table 3. Formal redox potentials of reagents of the DPA series (E_o'/V) in an aqueous medium and in the presence of surfactants*

Medium	$C^* \cdot 10^{-4}$ /mol L^{-1}	E_o'/V		
		DPASA	MDPASA	TPASA
H_2O*	2	0.83±0.01	0.80±0.01	0.89±0.02
CPC	6	0.84±0.01	0.85±0.01	0.90±0.02
DDS	80	0.86±0.01	0.77±0.01	—
Bridge-35	1	0.85±0.01	0.82±0.01	0.89±0.02
Triton X-100	9	0.85±0.01	0.83±0.01	0.88±0.01

* The reagent concentration is presented.

— the introduction of nonionic surfactants, results initially in a slight decrease in ΔpK_a followed by its increase in aqueous solutions of both Bridge-35 and Triton X-100. The K_b values increase in the sequence DPASA > MDPASA > TPASA in the presence of Bridge-35. Thus, as in the case of anionic surfactants, solubilization is enhanced.

The use of the DPA redox reagents studied here in analytical practice is largely due to the high values of formal redox potentials (E_o'), which serve as a quantitative measure of the oxidative capacity and the selectivity of redox reagents. Depending on the nature of the reagent and the surfactant, their change of the medium can either increase or decrease the redox potential (Table 3), and, thus, it can be used for controlling the selectivity of determination of various ions.

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