The influence of ionic surfactants on the acid-base properties and tautomeric equilibrium of 2-dimethylaminomethylphenol

R. A. Shagidullina, I. S. Ryzhkina, A. B. Mirgorodskaya,*
L. A. Kudryavtseva, V. E. Bel'skii, and B. E. Ivanov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center
of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: +7 (843) 275 2253

Shifts in the acid-base and tautomeric equilibria have been observed in aqueous solutions of 2-dimethylaminomethylphenol (DAMP) containing surfactants. Cationic micelles of cetyltrimethylammonium bromide increase the dissociation constants of DAMP ($\Delta pK_1 \sim 0.3$, $\Delta pK_2 \sim 0.5$), and anionic micelles of sodium dodecyl sulfate reduce them ($\Delta pK_1 \sim 1.5$, $\Delta pK_2 \sim 0.3$). The constant of tautomeric equilibrium decreases when ionic surfactants are added. This is connected with the better solubilization of the neutral form by micelles.

Key words: 2-dimethylaminomethylphenol; acid-base equilibrium; tautomerism; micelle; cetyltrimethylammonium bromide; sodium dodecyl sulfate; solubilization.

The different types of ionogenic groups in 2-aminomethylphenols form a complex system of acid-base equilibria involving the transfer of a proton[1] that makes these compounds a convenient model for extensive studies of the properties of hydrogen bonds and prototropic tautomeric equilibrium[2] that play an important role in biological systems. It is known that shifts in acid-base equilibria occur in micellar solutions of surfactants. Cationic surfactants increase the dissociation of weak acids and hamper the addition of a proton to bases, whereas anionic surfactants decrease the dissociation of acids and favor the protonation of bases.[3–6] However, these concepts do not allow one to judge the behavior of systems with intramolecular interactions in micellar solutions.

In the present work, the influence of the cationic surfactant, cetyltrimethylammonium bromide (CTAB), and the anionic surfactant, sodium dodecyl sulfate (SDS), on the acid-base and tautomeric equilibria in aqueous solutions of 2-dimethylaminomethylphenol (DAMP) has been studied.

Experimental

DAMP and its phenolate were prepared by the procedure described previously.[1] The samples of CTAB and SDS (Chemapol) were reprecipitated with ether from an ethanolic solution. Phenol and benzylamine were purified by the usual methods.

The values of pK_1 and pK_2 were determined by potentiometric titration on a pH-340 instrument (concentrations of DAMP and its phenolate were 0.002 *M*). 0.1 *M* HCl was used as the titrant. The CTAB concentration varied from 0 to 0.008 *M*; that of SDS varied from 0 to 0.2 *M*.

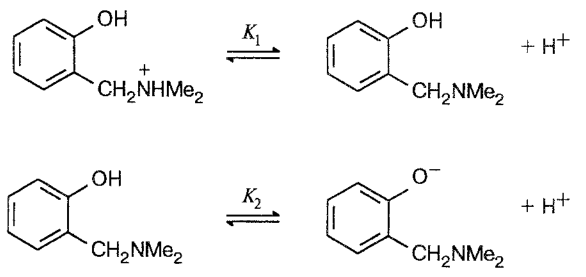
UV spectra of DAMP were recorded on a Specord UV-VIS instrument. Optical density was measured at 238 and 294 nm for the calculation of K_T.

Parameters of the regression equations were calculated by a program based on the least-squares method. The algorithm was programmed in the Turbo-Pascal language.

Results and Discussion

Acid-base equilibria in aqueous solutions of DAMP are characterized by two measurable constants, pK_1 and pK_2, which correspond to the processes presented below (Scheme 1).

Scheme 1



However, the complete scheme is described by a more complicated system of equilibria due to the tautomeric equilibria between the neutral and zwitter-ionic forms of this compound (Scheme 2).

The specific constants of acid-base equilibria are related to the measurable values of pK_1 and pK_2 and to

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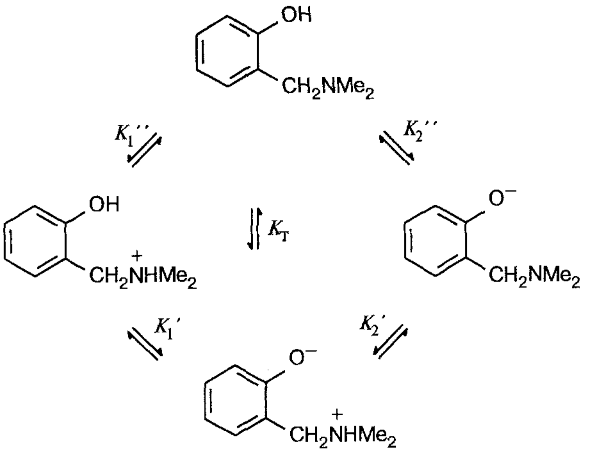
Scheme 2



the constant of the tautomeric equilibrium (K_T) by the following relationships:[1]

$$K_1' = K_1K_T/(1 + K_T),$$
$$K_1'' = K_1/(1 + K_T),$$
$$K_2' = K_2(1 + K_T)/K_T,$$
$$K_2'' = K_2(1 + K_T).$$

The influence of ionogenic surfactants on the acid-base properties and tautomeric equilibrium of DAMP may be explained by the unequal Coulomb interactions of various forms of this compound with the charged surface of micelles. When the charges on the substrate and head groups of micelles are different binding by the micelle increases, and when the charges are the same the opposite effect occurs.

The change in the pK_1 and pK_2 values determined for DAMP in aqueous solutions in the presence of cationic CTAB is presented in Table 1 and Fig. 1.

The constants of the tautomeric equilibrium and the specific constants of acid-base equilibria were determined by the combined use of potentiometric titration data and UV spectroscopic data for fixed pH values of the solution by the method described previously[1] (see Table 1).

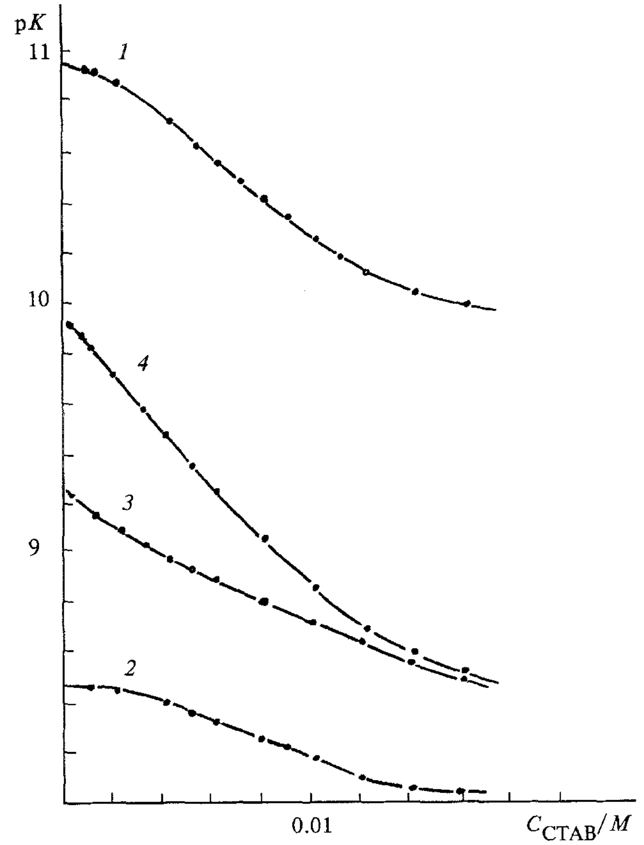


Fig. 1. Effect of CTAB micelles on pK_a of DAMP (*1*, pK_2, *2*, pK_1), phenol (*3*), and *N,N*-dimethylbenzylamine (*4*). Concentration of the compounds studied was 0.002 *M*; 25 °C.

The character of the effect of CTAB concentration on the specific constants of DAMP is nonlinear. When the surfactant concentration is lower than that of DAMP ($C_{surf} \leq 2 \cdot 10^{-3}$ *M*), the changes in K_T and p*K* are insignificant, which may be related to the insufficient formation of micellar aggregates, which solubilize DAMP. Increasing the surfactant content results in the enhancement of its effect on the equilibrium constants, and when $C_{surf} > 0.007$ *M*, the p*K vs.* surfactant concentra-

Table 1. Effect of CTAB on the constants of acid-base and tautomeric equilibria of DAMP in water at 25 °C (C_{DAMP} = 0.002 *M*)

C_{CTAB}/M	pK_1	pK_2	K_T	pK'_1	pK''_1	pK'_2	pK''_2
0	8.45	10.90	2.50	8.60	8.99	10.75	10.36
0.0005	8.45	10.90	2.50	8.60	8.99	10.75	10.36
0.001	8.45	10.90	2.48	8.60	8.98	10.75	10.36
0.002	8.45	10.88	2.45	8.59	8.98	10.74	10.31
0.003	8.45	10.79	2.21	8.60	8.96	10.63	10.28
0.004	8.42	10.72	2.00	8.61	8.90	10.62	10.24
0.005	8.35	10.62	1.50	8.55	8.75	10.40	10.22
0.006	8.32	10.52	1.33	8.56	8.69	10.28	10.15
0.008*	8.24	10.42	1.10	8.62	8.66	10.14	10.10

* A further increase in the CTAB concentration results in optically nontransparent solutions in the spectral range studied.

tion plots reach a plateau, which is associated with the saturation of the micelles and the establishment of an equilibrium between the aqueous and micellar pseudophases.

The value K_T for DAMP over the surfactant concentration range studied (from 0 to 0.008 *M*) decreases twofold, which must attest that CTAB micelles solubilize the neutral form of DAMP more readily than the zwitter-ionic form. The change in pK_2 that characterizes the formation of the phenolate form is greater in the presence of CTAB than the change in pK_1 (see Table 1). This indicates the lower sensitivity of the equilibrium involving the protonated form of DAMP to the existence of cationic micelles in the solution.

The analysis of the specific constants of the acid-base equilibrium of DAMP allows one to judge the solubilization of its various forms by the CTAB micelles (see Table 1). The constant pK_1 is insensitive to changes in the CTAB concentration in the solution, which is likely associated with weak solubilization both of the protonated and the zwitter-ionic forms of DAMP by micelles. The Coulomb interaction of anions with the positively charged head groups of CTAB is manifested in the changes in pK_2' (ΔpK_2' = 0.6), which reflect the shift of the equilibrium to this form and a decrease in the content of the poorly solubilized zwitter-ionic form. The weak influence of CTAB on pK_1'' (ΔpK_2'' = 0.25) as compared with that of pK_2' also testifies that solubilization of the neutral form is preferable to that of the zwitter-ionic form.

The behavior of DAMP in aqueous solutions differs from that of related benzylamines and phenols due to the influence of the intramolecular hydrogen bond (IHB). The influence of CTAB on the pK_a of the compounds studied is shown in Fig. 1.

The value ΔpK_a ~ 1 (C_{CTAB} = 0.008 *M*) for phenol is significantly higher than for *N,N*-dimethylbenzylamine (ΔpK_a ~ 0.5) due to the negative charge of the phenolate anion. The character of the changes in pK_a for phenol and *N,N*-dimethylbenzylamine is similar to that observed for DAMP, although for the latter ΔpK_2 is lower than that of the non-substituted phenol. This may reflect a change in the stability of IHB in the less polar water-micellar medium. A similar increase in the effect of IHB on pK_a in the presence of CTAB has been previously observed[7] for Schiff's bases.

In accordance with the predominantly electrostatic nature of the micelle effect on the acid-base equilibria of DAMP, the anionic surfactant (SDS) affects the pK_1 value to a greater extent than pK_2. The values of pK_1 and pK_2 increase in this process (Table 2). pK_1 increases to a greater extent (ΔpK_1 ~1.5) in the concentration range studied (C_{SDS} = 0 to 0.2 *M*), while the change in pK_2 is small. The most abrupt change in pK_1 is observed for the surfactant concentration higher than the critical concentration of the micelle formation (CCM). pK_2 is almost independent of the concentration of SDS. The anionic SDS like the cationic CTAB decrease K_T from ~2.5 to 1.0, *i.e.*, the equilibria shift to the increase in the content of the neutral form of DAMP that attests to its preferable solubilization as compared with that of the zwitter-ion independently of the charge of the micelles.

The data on the influence of the surfactants on the specific equilibrium constants (see Table 2) show that SDS preferably solubilizes the cationic form of DAMP strongly increasing pK_1 values and enhancing pK_2 to a lesser extent, which agrees well with the character of the changes in K_T. The absence of the influence of the SDS micelles on pK_2 testifies an approximately equally low solubilization both of anionic and zwitter-ionic forms, and the change in pK_2 attests to a somewhat better solubilization of the neutral form of DAMP by the SDS micelles.

Thus, the effect of the surfactant on the solubilization of various forms of DAMP estimated from the change in the specific constants of acid-base equilibria increases in the series: anion ~ zwitter-ion < neutral molecule $\ll$ cation (for SDS) and cation ~ zwitter-ion < neutral

Table 2. Effect of SDS on the constants of acid-base and tautomeric equilibria of DAMP in water at 25 °C (C_{DAMP} = 0.002 *M*)

C_{SDS}/M	pK_1	pK_2	K_T	pK'_1	pK''_1	pK'_2	pK''_2
0	8.45	10.90	2.50	8.60	8.99	10.75	10.36
0.002	8.50	10.95	2.20	8.67	9.00	10.79	10.44
0.005	8.75	10.98	1.90	8.93	9.21	10.79	10.51
0.010	8.95	11.00	1.67	9.15	9.37	10.80	10.57
0.015	9.25	11.04	1.52	9.47	9.65	10.82	10.64
0.020	9.58	11.06	1.40	9.81	9.96	10.83	10.68
0.025	9.76	11.08	1.32	9.99	10.11	10.83	10.75
0.030	9.85	11.09	1.26	10.10	10.20	10.83	10.73
0.035	9.90	11.09	1.20	10.16	10.24	10.83	10.75
0.050	10.00	11.10	1.09	10.28	10.32	10.82	10.78
0.080	10.00	11.10	1.02	10.34	10.38	10.82	10.80
0.200	10.00	11.10	1.00	10.35	10.39	10.82	10.80

molecule < anion for CTAB. The wide range of SDS concentrations tested allowed us to use the method described previously[6,8] and to calculate the binding constants for the separate forms of DAMP by the equation:

$$\frac{K_{\text{exp}} - K_{\text{a}}}{C_{\text{surf}}} = K'_{\text{b}}K_{\text{exp}} - K_{\text{b}}K_{\text{exp}},$$

where K_{b} is the binding constant of the non-dissociated form; K'_{b} is the binding constant of the ionic form; K_{a} is the dissociation constant in the absence of the surfactant; and K_{exp} is the observed dissociation constant for the fixed surfactant concentration (in the range higher that CCM). The binding constants estimated by the regression method from the data in Table 2 for the cation, neutral molecule, zwitter-ion, and anion equal 635, 117, 44, and 30 mol^{-1}, respectively.

The values obtained confirm the validity of the conclusions based on the analysis of the influence of surfactants on specific dissociation constants about the relative ability of various forms of DAMP to undergo solubilization.

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