Spectrophotometric Determination of the Dissociation Constant of 5-(*p*-Dimethylaminobenzylidene)rhodanine in Micellar Media

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The investigation of the acidic equilibrium of 5(*p*-dimethylaminobenzylidene)rhodanine (PDR) in aqueous micellar solution by a simple spectrophotometric method is reported. For this purpose, the effect of nonionic (brij-35 and TritonX-100), cationic (CTAB), and anionic (SDS) surfactants on the absorption spectra of PDR at different pH values was studied. The pK_a of PDR in a different concentration of each surfactant was determined (27 °C). It was found that PDR is more dissociated in the presence of CTAB and the lowest dissociation is observed in SDS micellar media. These changes in pK_a can be explained according to the electrostatic contribution of binding of the anionic form of PDR to the micellar pseudophase.

1. Introduction

Aqueous micellar media are widely used in different areas of analytical chemistry. One important property of micelles is their ability to solubilize a wide variety of compounds that are insoluble or slightly soluble in water.[1] The interaction of solutes with micelles leads to apparent changes in their chemical properties, such as shifts in their absorption spectra and acid−base equilibrium. There are different models that explain these changes, such as the binding equilibrium between solute and micelle aggregates and the ion-exchange equilibrium. However, these different models are applied depending on the kind of micelles: the ion-exchange model is applied to explain the behavior of charged species in solutions of ionic surfactants, and the binding model can be applied for ionic and nonionic surfactants.[2]

The apparent pK_a of acids can be shifted in various micellar media. Analytically, these shifts can allow determinations of organic acids in the presence of inorganic acids with equal pK_a values by moving the equivalence points apart. Furthermore, the incorporation of weak acids in micellar media can result in their determination in aqueous media as opposed to nonaqeouse titration.[3]

Various methods for the determination of dissociation constants, such as potentiometric titration, spectrophotometric determination, conductimetry, and spectroscopic methods, have been reported. Of these, potentiometric titration[4] and spectrophotometric determination[1] are the most useful and widely used. For potentiometric titration, the dissociation constants of extremely acidic or basic compounds cannot be accurately determined because of their instability in an extreme pH range or because of the limitations of pH meters. Another essential requirement of this method is that the initial concentration of the samples must be accurately determined; that is to say, the samples must be pure and dry.

The Spectrophotometric method, which was pioneered by Seok et al.,[5] has received widespread attention because it is very simple and rapid for the determination of dissociation constants of organic compounds by means of UV−vis spectrophotometry. It is applied to compounds whose concentrations or extinction coefficient (ϵ) are unknown.

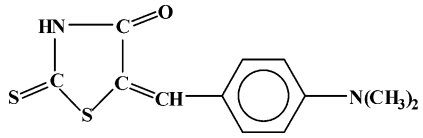

Figure 1. Structure of 5(*p*-dimethylaminobenzylidene)rhodanine (PDR).

5(*p*-Dimethylaminobenzylidene)rhodanine (PDR) is a derivative of rhodanine (Figure 1) that is used as a precipitant for silver, mercury, copper(I), gold, and palladium. The location of the NH group between CO and CS greatly increases its acidic character.[6] Complex formation by a metal ion involves the negatively charged nitrogen in the anion of PDR. Because PDR is slightly soluble in water, it is of interest to investigate the effect of micelle-forming surfactants on its acidic equilibria.

In this study, the Seok et al. method was applied for the determination of apparent dissociation constant values of 5-(*p*-dimethylaminobenzylidene)rhodanine in different micellar media.

2. Experimental Section

Apparatus. The spectrophotometric measurements were made using a Jasco UV−vis spectrophotometer with a thermostated cell holder. All spectrophotometric measurements were made at (27.0 ± 0.1) °C. The pH values were measured using a Metrohm 632 pH meter and a combined glass electrode.

Reagents. All reagents used were of analytical grade. Doubly distilled water was used throughout. An ethanol solution of 5(*p*-dimethylaminobenzylidene)rhodanine (PDR), at approximately 5×10^{-4} M, was prepared by dissolving 0.033 g of PDR in warm ethanol, cooling to room temperature, and diluting to 250 mL with the same solvent. This solution was filtered off before use.

The surfactants cetyltrimethylammonium bromide (CTAB) (Aldrich), polyoxyethylenlauryl ether (brij-35) (Merck), sodium dodecyl sulfate (SDS) (Fluka), and Triton X-100 (Fluka) were used without further purification. The ionic

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strength of the working solutions was kept constant at 0.1 M by the addition of sodium bromide.

Procedure. To 2 mL of an approximately 5×10^{-4} M PDR solution an appropriate volume of surfactant and 2.5 mL of 1 M NaBr were added. The pH of this solution was adjusted to the desired value by the addition of dilute sodium hydroxide or 3 mL of buffer (phosphate or glycine); the solution was then diluted to the mark in a 25-mL volumetric flask. A portion of the solution was transferred to a glass cell. The cell was placed in the holder at 27 °C in the spectrophotometer, and the spectra were recorded. Absorbances at selected wavelengths were obtained from the spectra.

3. Results and Discussion

In a preliminary experiment, PDR was titrated in the presence of CTAB with NaOH. The potentiometric titration results indicate that PDR is a weak acid showing one end point.

In the potentiometric titration of weak acids, there must be a high concentration, and the initial concentration of the samples must be accurately determined. However, spectrophotometry is an ideal method when a substance cannot be analyzed by potentiometry.

The spectrophotometric determination of pK_a, as reported by Seok et al.,[5] has received widespread attention because it is a simple and rapid method for the determination of pK_a values of organic compounds by means of a spectrophotometer and a pH meter. The principle of the method is the following.

The acid−base equilibria can be described by the following reaction:

$$HA + H_2O \rightleftarrows A^- + H_3O^+ \tag{1}$$

Then the apparent dissociation constant K_a^{app} of the acid HA is defined as the equilibrium constant when the solution is sufficiently dilute. We then have

$$K_a^{app} = \frac{[A^-][H^+]}{[HA]} \tag{2}$$

By taking logarithms and rearranging, one can get the Henderson−Hasselbach equation

$$pK_a^{app} = pH - \log\left(\frac{[A^-]}{[HA]}\right) \tag{3}$$

Let $[HA] + [A^-] = T$; T is constant and independent of the pH. Let $\chi = [HA]$ at pH $= I$, and then $[A^-] = T - \chi$. Substituting R for $(T - \chi)/\chi$ and rearranging eq 3 yields

$$I = pK_a^{app} + \log R \tag{4}$$

If the site of protonation/deprotonation is conjugated with a chromophoric group in a compound, then the absorption spectrum of the compound will change as a function of pH. In other words, the spectrum of the system obtained at a pH near the pK_a^{app} will be the sum of those of HA and A^- if Beer's law holds under the experimental conditions used. Suppose that, at an appropriate wavelength that is not the isobestic point, absorbances A_1, A_2, and A_3 are measured at three different pH values, I, $I + a$, and $I + b$ ($a \neq b \neq 0$), respectively, and let ϵ_1 and ϵ_2 be the extinction coefficients of HA and A^- at the selected wavelength, respectively. Then, the effective absorbance of the solution at pH $= I$ is given by

$$\chi\epsilon_1 d + \chi R\epsilon_2 d = A_1 \tag{5}$$

where d represents the path length of light. Let the change in the concentration of HA at pH $= I + a$ be C_a, and the changed absorbance, A_2, of the solution is given by

$$(\chi - C_a)\epsilon_1 d + (\chi R + C_a)\epsilon_2 d = A_2 \tag{6}$$

and from eqn. 3, we can obtain

$$pK_a^{app} = I + a - \log\left(\frac{\chi R + C_a}{\chi - C_a}\right) \tag{7}$$

Similarly, let the change in concentration of HA at pH $= I + b$ be C_b; then the absorbance A_3 and pK_a^{app} are given by

$$(\chi - C_b)\epsilon_1 d + (\chi R + C_b)\epsilon_2 d = A_3 \tag{8}$$

and

$$pK_a^{app} = I + b - \log\left(\frac{\chi R + C_b}{\chi - C_b}\right) \tag{9}$$

The subtraction of eq 4 from eq 7 yields

$$\frac{(\chi R + C_a)\,\chi}{(\chi - C_a)(T - \chi)} = 10^a \tag{10}$$

and thus, we can calculate C_a as

$$C_a = \frac{(10^a - 1)\chi R}{10^a R + 1} \tag{11}$$

Exchanging this C_a with that in eq 6 yields

$$T\epsilon_1 d + 10^a TR\epsilon_2 d = (10^a R + 1)A_2 \tag{12}$$

Similarly the subtraction of eq 4 from eq 9 yields

$$\frac{(\chi R + C_b)\chi}{(\chi - C_b)(T - \chi)} = 10^b \tag{13}$$

From this, we can calculate C_b as

$$C_b = \frac{(10^b - 1)\chi R}{10^b R + 1} \tag{14}$$

Exchanging this C_b with that in eq 8 yields

$$T\epsilon_1 d + 10^b TR\epsilon_2 d = (10^b R + 1)A_3 \tag{15}$$

By combining eqs 12 and 15, one can calculate $\epsilon_1 d$ and $\epsilon_2 d$ given by

$$\epsilon_1 d = \frac{(10^{a+b}R + 10^a)A_3 - (10^{a+b}R + 10^b)A_2}{T(10^a - 10^b)} \tag{16}$$

$$\epsilon_2 d = \frac{(10^a R + 1)A_2 - (10^b R + 1)A_3}{TR(10^a - 10^b)} \tag{17}$$

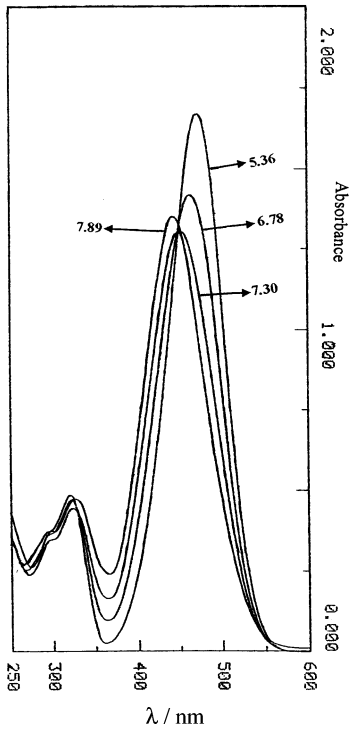

Figure 2. Absorption spectra of 5-(*p*-dimethylaminobenzylidene)-rhodanine in the presence of polyoxyethylenlauryl ether (brij-35) at different pH values.

Introducing eqs 16 and 17 into eq 5 and rearranging yields

$$R = \frac{(10^b - 10^a)A_1 + (1 - 10^b)A_2 + (10^a - 1)A_3}{(10^a - 10^b)A_1 + (10^{a+b} - 10^a)A_2 + (10^b - 10^{a+b})A_3} \quad (18)$$

At an isobestic point, it must be true that $A_1 = A_2 = A_3$, and both the numerator and denominator in eq 18 are zero, thus the equation is not valid.

In eq 18, the ratio of [A$^-$] to [HA] is solely determined by the relative absorbances of the mixture at a randomly selected wavelength at three randomly selected pH values. It is independent of the concentration and extinction coefficient of each species:[5]

$$\mathrm{p}K_\mathrm{a}^{\mathrm{app}} = I - \log \frac{(10^b - 10^a)A_1 + (1 - 10^b)A_2 + (10^a - 1)A_3}{(10^a - 10^b)A_1 + (10^{a+b} - 10^a)A_2 + (10^b - 10^{a+b})A_3} \quad (19)$$

The incorporation of PDR into micellar systems can lead to changes in the acidic equilibrium; therefore, eq 19 was used to determine the p$K_\mathrm{a}^{\mathrm{app}}$ of PDR in different micellar media.

The absorption spectra of PDR in aqueous micellar solutions of brij-35, Triton X-100, CTAB, and SDS were studied over the appropriate pH range. As observed, the absorbance of PDR around λ = 470 nm decreases with increasing pH in the presence of brij-35, Triton X-100, and SDS (Figures 2, 3, and 5), whereas the absorbance around λ = 440 nm increases with increasing pH when using CTAB (Figure 4).

To determine the dissociation constant, the absorbance of PDR solution in the presence of each surfactant was obtained in the wavelength range of 538−386 nm at three

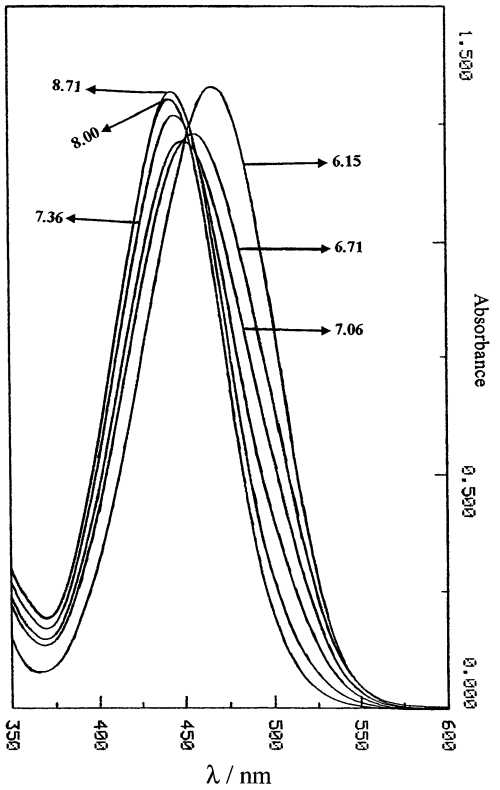

Figure 3. Absorption spectra of 5-(*p*-dimethylaminobenzylidene)-rhodanine in the presence of Triton X-100 at different pH values.

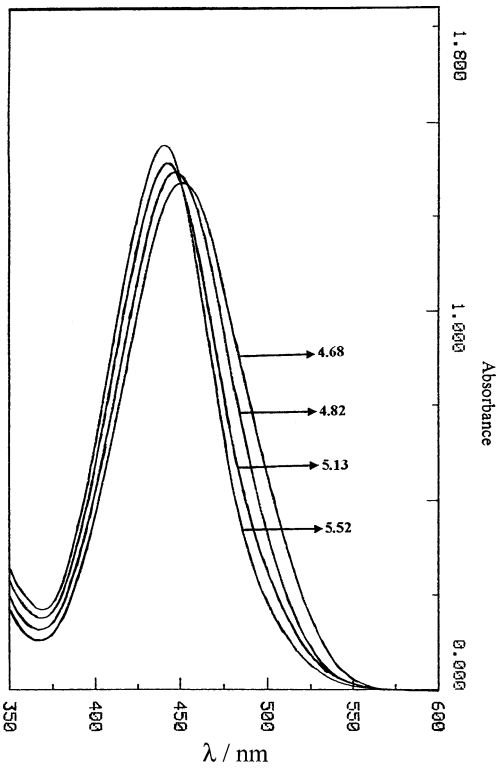

Figure 4. Absorption spectra of 5-(*p*-dimethylaminobenzylidene)-rhodanine in the presence of cetyltrimethylammonium bromide (CTAB) at different pH values.

appropriate pH values. Then the p$K_\mathrm{a}^{\mathrm{app}}$ for each wavelength was calculated from eq 19 (Tables 1−4).

The variation of the p$K_\mathrm{a}^{\mathrm{app}}$ of PDR with a different concentration of each surfactant was studied. According to Tables 5−8, the acid−base equilibrium of PDR is different

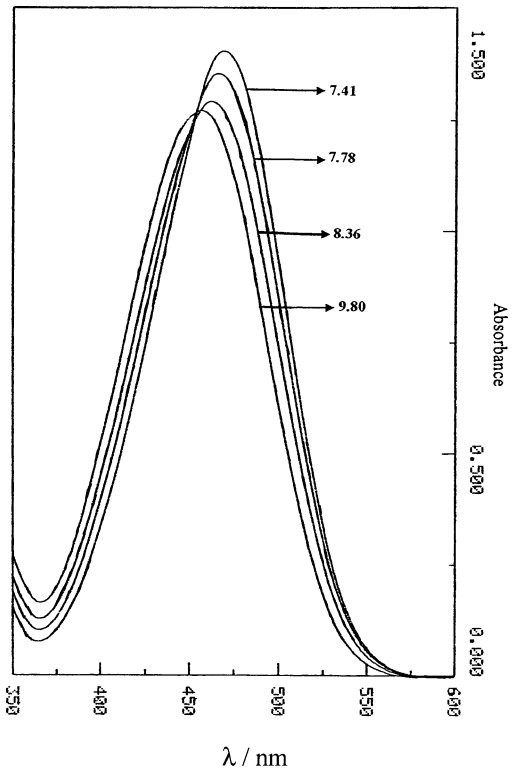

Figure 5. Absorption spectra of 5-(*p*-dimethylaminobenzylidene)-rhodanine in the presence of sodium dodecyl sulfate (SDS) at different pH values.

Table 1. Change in Absorbance of 5-(*p*-Dimethylaminobenzylidene)rhodanine as a Function of pH and pK_a^{app} values in the Presence of 6 × 10^{-3} M Polyoxyethylenlauryl Ether (brij-35)

	Abs in pH			
λ/nm	6.11	6.88	7.35	pK_a^{app} [a]
538	0.128	0.100	0.078	6.97
530	0.219	0.169	0.130	6.96
522	0.355	0.274	0.210	6.97
514	0.539	0.410	0.310	6.96
506	0.750	0.570	0.432	6.95
498	0.982	0.746	0.560	6.97
490	1.187	0.918	0.709	6.97
482	1.350	1.071	0.859	6.94
474	1.437	1.189	1.006	6.91
466	1.445	1.265	1.132	6.92
458	1.360	1.268	1.228	
450	1.215	1.260	1.271	
442	1.055	1.170	1.258	6.95
434	0.890	1.055	1.180	6.94
426	0.736	0.915	1.051	6.94
418	0.591	0.766	0.898	6.94
410	0.466	0.616	0.730	6.94
402	0.336	0.469	0.573	6.97
394	0.232	0.344	0.428	6.94
386	0.147	0.236	0.306	6.92

[a] pK_a^{app}(average) = 6.95 ± 0.02.

in the presence of nonionic, cationic, and anionic micellar media.

It has been suggested that the effect of micellar systems on acid−base equilibria arises from an intrinsic factor (arising from the energy difference between the aqueous and the nonpolar media) and a potential effect that is due to the electrically charged micelle surface. In fact, the micellar systems can be regarded to be a two-phase system consisting of an aqueous phase and a micellar pseudophase. Consequently, by introducing the partition coefficient *P*, $P_{HA} = [HA]_m/[HA]_w$ and $P_{A^-} = [A^-]_m/[A^-]_w$ (where subscripts m and w refer to the micellar and aqueous phases,

Table 2. Change in Absorbance of 5-(*p*-Dimethylaminobenzylidene)rhodanine as a Function of pH and pK_a^{app} Values in the Presence of 0.6% (w/v) TritonX-100

	Abs in pH			
λ/nm	6.22	6.80	7.48	pK_a^{app} [a]
538	0.136	0.098	0.063	6.66
530	0.229	0.165	0.105	6.67
522	0.360	0.259	0.163	6.68
514	0.524	0.378	0.238	6.69
506	0.710	0.513	0.328	6.68
498	0.895	0.655	0.430	6.67
490	1.064	0.799	0.555	6.66
482	1.193	0.937	0.704	6.65
474	1.268	1.057	0.868	6.64
466	1.282	1.149	1.028	6.65
458	1.236	1.197	1.155	
450	1.140	1.189	1.225	
442	1.017	1.135	1.227	
434	0.875	1.030	1.156	
426	0.730	0.893	1.032	6.60
418	0.585	0.743	0.879	6.61
410	0.455	0.592	0.715	6.64
402	0.336	0.451	0.554	6.64
394	0.231	0.328	0.410	6.64
386	0.157	0.225	0.287	6.65

[a] pK_a^{app}(average) = 6.65 ± 0.02.

Table 3. Change in Absorbance of 5-(*p*-Dimethylaminobenzylidene)rhodanine as a Function of pH and pK_a^{app} Values in the Presence of 4 × 10^{-3} M Cetyltrimethylammonium Bromide (CTAB)

	Abs in pH			
λ/nm	5.23	5.54	5.84	pK_a^{app} [a]
538	0.096	0.078	0.056	5.72
530	0.153	0.126	0.091	5.80
522	0.230	0.189	0.139	5.72
514	0.321	0.266	0.200	5.70
506	0.419	0.354	0.274	5.73
498	0.521	0.450	0.364	5.71
490	0.638	0.565	0.480	5.66
482	0.776	0.710	0.635	5.63
474	0.930	0.880	0.819	5.72
466	1.100	1.069	1.033	5.65
458	1.247	1.234	1.232	
450	1.332	1.351	1.373	5.65
442	1.344	1.380	1.426	5.78
434	1.266	1.312	1.365	5.64
426	1.133	1.176	1.228	5.70
418	0.962	1.004	1.054	5.68
410	0.780	0.816	0.859	5.66
402	0.599	0.630	0.668	5.72
394	0.438	0.460	0.487	5.72
386	0.298	0.316	0.340	5.83

[a] pK_a^{app}(average) = 5.70 ± 0.05.

respectively). Thus, an expression for the apparent dissociation constant, K_a^{app}, can be derived[7]

$$K_a^{app} = \frac{K_a(1 + K_{A^-}[C])}{(1 + K_{HA}[C])} \quad (20)$$

where K_a is the acidity constant in the absence of surfactant, [C] is the surfactant concentration exceeding the cmc, and K_{A^-} and K_{HA} are the binding constants with micelles in the deprotonated and protonated forms, respectively.

Equation 20 predicts a monotonic function reaching a plateau value for K_a^{app} at a high concentration of C. For the present conditions, eq 20 describes the data satisfactorily.

The pK_a^{app} values of PDR are shown in Tables 5 and 6 as a function of nonionic surfactant concentrations (brij-35 and Triton X-100). It can be seen that the presence of

Table 4. Change in Absorbance of 5-(*p*-Dimethylaminobenzylidene)rhodanine as a Function of pH and pK_a^{app} Values in the Presence of 0.014 M Sodium Dodecyl Sulfate (SDS)

	Abs in pH			
λ/nm	7.76	8.36	9.84	pK_a^{app} [a]
538	0.143	0.104	0.079	7.76
530	0.234	0.175	0.137	7.76
522	0.361	0.276	0.223	7.73
514	0.520	0.408	0.340	7.71
506	0.707	0.568	0.485	7.69
498	0.890	0.739	0.648	7.70
490	1.070	0.916	0.823	7.70
482	1.218	1.077	0.993	7.69
474	1.314	1.197	1.133	
466	1.344	1.268	1.229	
458	1.304	1.279	1.270	
450	1.208	1.236	1.254	7.76
442	1.098	1.162	1.205	7.80
434	0.965	1.055	1.113	7.76
426	0.823	0.925	0.991	7.76
418	0.681	0.784	0.850	7.76
410	0.547	0.643	0.704	7.75
402	0.425	0.509	0.563	7.76
394	0.315	0.388	0.435	7.76
386	0.220	0.282	0.321	7.74

[a] pK_a^{app}(average) = 7.74 ± 0.03.

Table 5. pK_a^{app} Values of 5-(*p*-Dimethylaminobenzylidene)rhodanine at Different Concentrations of Polyoxyethylenlauryl Ether (brij-35)[a]

10^2C(brij-35)/M	pK_a^{app} ± SD
0.6	6.95 ± 0.02
0.8	6.98 ± 0.01
1.0	7.02 ± 0.03
1.2	7.02 ± 0.04
1.4	7.04 ± 0.02
1.6	7.05 ± 0.01

[a] Conditions: 4×10^{-5} M 5-(*p*-dimethylaminobenzylidene)rhodanine; 0.1 M NaBr; temperature, 27 °C.

Table 6. pK_a^{app} Values of 5-(*p*-Dimethylaminobenzylidene)rhodanine at Different Concentrations of Triton X-100[a]

C(TritonX-100)/% w/v	pK_a^{app} ± SD
0.4	6.58 ± 0.04
0.6	6.65 ± 0.02
0.8	6.82 ± 0.03
1	6.83 ± 0.05
1.2	6.91 ± 0.06
1.4	6.90 ± 0.06

[a] Conditions: 4×10^{-5} M 5-(*p*-dimethylaminobenzylidene)rhodanine; 0.1 M NaBr; temperature, 27 °C.

Table 7. pK_a^{app} Values of 5-(*p*-Dimethylaminobenzylidene)rhodanine at Different Concentrations of Cetyltrimethylammonium Bromide (CTAB)[a]

10^2C(CTAB)/M	pK_a^{app} ± SD
0.4	5.70 ± 0.05
0.6	5.49 ± 0.04
0.8	5.39 ± 0.04
1	5.27 ± 0.04
1.2	5.11 ± 0.04
1.4	5.10 ± 0.04

[a] Conditions: 4×10^{-5} M 5-(*p*-dimethylaminobenzylidene)rhodanine; 0.1 M NaBr; temperature, 27 °C.

the nonionic surfactant leads to slight increase in pK_a^{app} values. Acoording to eq 20, both the acid and base forms of PDR are bound to the micelles through hydrophobic interactions. The results indicate that the interaction of the neutral form of PDR (HA) is probably stronger than

Table 8. pK_a^{app} Values of 5-(*p*-Dimethylaminobenzylidene)rhodanine at Different Concentrations of Sodium Dodecyl Sulfate (SDS)[a]

10^2C(SDS)/M	pK_a^{app} ± SD
1.4	7.74 ± 0.03
1.6	7.97 ± 0.04
1.8	8.05 ± 0.04
2.0	8.06 ± 0.05
2.2	8.11 ± 0.04
2.4	8.15 ± 0.04

[a] Conditions: 4×10^{-5} M 5-(*p*-dimethylaminobenzylidene)rhodanine; 0.1 M NaBr; temperature, 27 °C.

that of the anionic form of PDR (A^-) and that K_{HA} was greater than K_{A^-}. Equation 20 reaches a plateau at higher concentrations of brij-35 and Triton X-100.

The addition of cationic surfactant CTAB to solution of PDR leads to an enhancement of acidic strength. As is obvious from Table 7, the pK_a^{app} values decreased from 5.70 to 5.10 with increasing CTAB concentration. This dependence on the nature of the substrate arises from the fact that species HA and A^- are bound to the micellar pseudophase at pertinent surfactant concentrations. But increases in K_a^{app} reflect the electrostatic contribution to the strong binding of A^- to cationic micelles and increasing K_{A^-}.

According to the ion-exchange model, the ability of the cationic micelles to bind OH^- ions by electrostatic forces and thus to concentrate them within the small volume of the micellar pseudophase favors the dissociation of a weak acid on the micelle surface.[8] Because we used 0.1 M NaBr, OH^- cannot compete effectively with Br^- for a site on the micellar surface, and the ion exchange of OH^- in the micellar pseudophase cannot affect the pK_a^{app} values.

In contrast, the effect of anionic surfactant SDS increased the pK_a^{app} from 7.74 to 8.15 with increasing SDS concentration (Table 8). This behavior is clearly explained by eq 20, assuming that the anionic form of PDR, A^-, does not interact with anionic micelles ($K_{A^-}[C] \ll 1$), and thus eq 20 can be simplified to yield

$$K_a^{app} = \frac{K_a}{(1 + K_{HA}[C])} \tag{21}$$

Equation 21 permits the determination of the binding constant of the undissociation form of PDR, K_{HA}.

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