

Note

Spectrophotometric Determination of Acidity Constants of 4-(2-Pyridylazo) Resorcinol in Various Micellar Media Solutions

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Dissociation equilibria of 4-(2-pyridylazo) resorcinol (PAR) in aqueous micellar solutions were determined spectrophotometrically at 25 °C and at the constant ionic strength $I = 0.1 \text{ M KNO}_3$. For this purpose, the effect of nonionic (Brij-35, Triton X-100, Triton X-114, Triton X-405), and anionic (SDS) surfactants on the absorption spectra of PAR at different pH values was studied. Results show that the $\text{p}K_a$ values and pure spectra of each species of PAR are influenced by percentages of a neutral and an anionic surfactant such as Brij-35, Triton X-100, Triton X-114, Triton X-405 and SDS, respectively, added to the solution of this reagent.

Keywords: Acidity constant; PAR; Anionic surfactant; Neutral surfactant; DATAN; Spectrophotometric.

INTRODUCTION

Aqueous micellar media are widely used in different areas of analytical chemistry, and several reviews concerning their analytical applications have been published.¹⁻⁴ One important property of micelles is their ability to solubilize a wide variety of compounds which are insoluble or slightly soluble in water. The incorporation of a solute into micellar systems can lead to important changes in its molecular properties. Another important effect of micellar systems is that they can modify reaction rates and, to some extent, the nature of the products. Micelles can inhibit or accelerate reaction rates (by up to several orders of magnitude) and also shift equilibria (acid-base). Surfactants usually affect spectral parameters: the intensity in the absorption bands can be increased and shifts in the absorption maxima of reagents are observed.⁵ Micelles can affect the apparent $\text{p}K_a$ values of the reagents due to a combination of electrostatic and microenvironmental effects of the micelle.⁶ Moreover, the acid-base equilibria involved in these systems are also influenced by surfactants.⁷⁻¹⁰

Acid dissociation constants (i.e. $\text{p}K_a$ values) can be a key parameter for understanding and quantifying chemical phenomena such as reaction rates, biological activity, biological uptake, biological transport and environmental

fate.¹¹ There have been several methods for the determination of acidity constants, including the use of potentiometric titration, spectrophotometry, capillary electrophoresis, and so on. Spectroscopic methods are in general highly sensitive and as such are suitable for studying chemical equilibria in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and the determination of the equilibrium constant is simple.¹²

For many systems, particularly those with similar components, this is not the case, and these have been difficult to analyze. Therefore, to overcome this problem we have to employ graphical and computational methods. Up to the middle of the 1960s, the evaluation of equilibrium measurements was based on different graphical methods. These methods were reviewed in considerable detail by Rossotti and Rossotti.¹³ Starting from the middle of the 1960s, computers acquired ever-greater importance in the evaluation of equilibrium measurement data using multiple wavelengths or full spectrum to determining the stability and acidity constants. The most relevant reports are on SPECFIT,¹⁴ SQUAD¹⁵ and HYPERQUAD.¹⁶ All these computational approaches are based on an initial proposal of a chemical equilibrium model defining species stoichiometries and based on mass-action law and mass balance

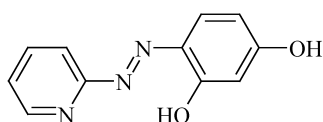
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equations (hard modeling methods) and also involve least-squares curve-fitting procedures. The starting point of using soft modeling was in 1971 when Lawton and Sylvestre¹⁷ introduced a chemometrics-based method for spectral analysis. These approaches are free from the restriction of the mass-action law and do not require an initial model of species to be set up.

Data analysis was carried out by the DATAN package developed by the Kubista group,¹⁸⁻²⁰ called the physical constraints approach, which provides a unique solution by requiring that the calculated concentrations obey an assumed equilibrium expression and demonstrates its applicability by determining the acidity constants of two and four protolytic forms of fluorescein. A possible advantage of the Kubista et al. method is that it mixes a soft modeling approach with a hard modeling approach. This might be best and a more general strategy, since it can handle different situations, with only a partial knowledge of the chemistry of the system. The physical constraints method calculates spectral profiles, concentrations and equilibrium constants by utilizing equilibrium expressions that relate the components. The theory and application of the physical constraints method has been discussed by several workers.²¹⁻³⁰

In this study, we applied the physical constraints approach to determine the acidity constants of 4-(2-pyridylazo) resorcinol (PAR) (Scheme I) in water, water-Brij-35, water-Triton X-100, water-Triton X-114, water-triton X-405 and water-SDS micellar media solutions at 25 °C and an ionic strength of 0.1 M spectrophotometrically. The effects of different surfactants were studied on the dissociation constants and pure spectrum of 4-(2-pyridylazo) resorcinol. The analysis is readily performed with the computer program DATAN.³¹

Scheme I Structure of 4-(2-pyridylazo) resorcinol (PAR)



EXPERIMENTAL

Reagents

Analytical grade PAR, Brij-35, Triton X-100, Triton

X-114, Triton X-405, SDS, hydrochloric acid, sodium hydroxide and sodium perchlorate were commercial products from Merck. These reagents were used without further purification. Standard stock solution of 1.0×10^{-4} M of PAR was prepared by dissolving appropriate amounts of PAR in water. The stock solutions of surfactants prepared by dissolving weighed amounts of surfactants in appropriate amounts of water. All the solutions were prepared in deionized water.

Apparatus

Absorption spectra were measured on an Agilent 8453 UV-Visible Diode-Array spectrophotometer with a thermostated cell holder equipped with a 1-cm path length quartz cell used for UV-Vis spectra acquisition. Spectra were acquired between 360 and 540 nm. All spectrophotometric measurements were made at 25.0 °C (± 0.5). The pH values were measured using a 300 HANA pH-meter and a combined glass electrode.

RESULTS AND DISCUSSION

The absorption spectra of PAR in pure water at various pH values at 360-540 nm intervals were recorded. In order to determine the influence of the nonionic surfactant (Brij-35, Triton X-100, Triton X-114, Triton X-405) and the anionic surfactant (SDS) in acidity constants, a series of experiments were run at different concentrations of Brij-35, Triton X-100, Triton X-114, Triton X-405 and SDS, above the cmc. The effect of cited surfactants on acidity constants of PAR is studied at the concentration range of 0.005-0.2% (w/v). A sample spectra of 4-(2-pyridylazo) resorcinol at different pH values in pure water and water-triton X-405 are shown in Figs. 1 and 2, respectively. The principal component analysis of all absorption data matrices obtained at various pH values show at least four significant factors that are also supported by the statistical indicators of Elbergali et al.³² These factors could be attributed to the three dissociation equilibria of a triprotic acid such as PAR. The pK_a values of PAR were investigated in pure water and different water-Brij-35, water-Triton X-100, water-Triton X-114, water-triton X-405 and water-SDS mixtures spectrophotometrically at 25 °C and an ionic strength of 0.1 M (KNO_3).

Acidity constants of PAR in several mixtures were evaluated using the DATAN program with the correspond-

ing spectral absorption-pH data. From inspection of the experimental spectra, it is hard to guess even the number of protolytic species involved. The four calculated most significant projection vectors with clear spectral features (as compared to noise) show evidence of the presence of four spectroscopically distinguishable components. Their shapes, however, are clearly unphysical and cannot be directly related to the spectral response of the four protolytic forms. The outputs of the program are pK_a values and their standard deviation, the number of principal components, projection vectors (loadings), concentration distribution diagrams, and the pure spectrum of each assumed species.

The obtained pK_a values are listed in Table 1 as the function of surfactant concentrations. The previous reported values of acidity constants are mainly in pure wa-

ter,^{33,34} which are listed in Table 1. The differences observed between the pK_a values are due to probable experimental errors of old methods, against chemometrics-based methods, by using the whole spectral domain, reduce considerably the level of noise. So the obtained acidity constants are more reliable and precise than previous methods.

There is not a definite pattern of relationships between acidity constants and the percentages of surfactants in the various micellar media solutions. The pK_a values depend on absorption spectra variation at different pH in all micelle media systems. One of the very important outputs of the DATAN program is the calculated spectra of different forms of PAR in each micellar media. Sample spectrum of the calculated spectra of all species in pure water, 0.1%

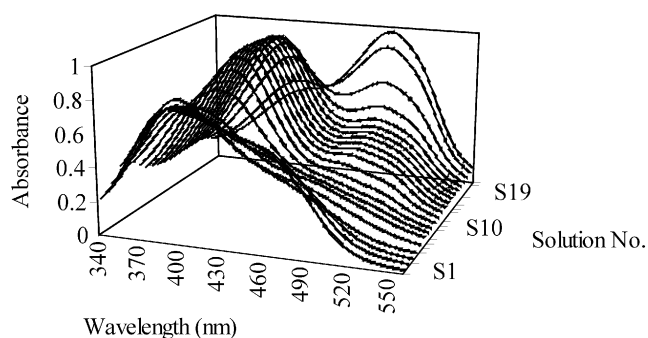


Fig. 1. Absorption spectra of PAR in pure water at different pH values: (1) 1.70, (2) 2.11, (3) 2.62, (4) 3.45, (5) 3.96, (6) 4.57, (7) 5.29, (8) 5.80, (9) 6.26, (10) 6.92, (11) 7.56, (12) 8.10, (13) 8.50, (14) 9.00, (15) 9.56, (16) 10.14, (17) 10.60, (18) 11.06, (19) 11.51, (20) 12.03, (21) 12.32.

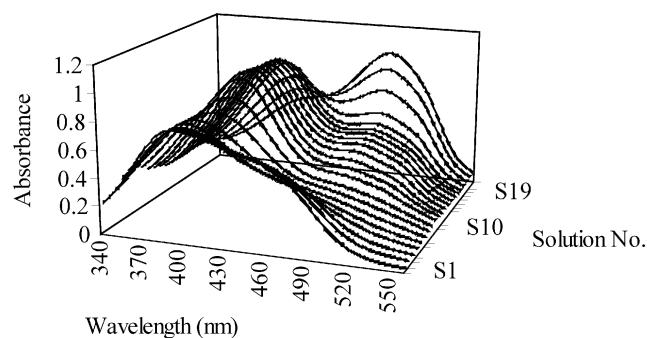


Fig. 2. Absorption spectra of PAR in 0.1% (w/v) Triton X-405 to water at different pH values: (1) 1.59, (2) 2.14, (3) 2.55, (4) 3.18, (5) 3.70, (6) 4.39, (7) 4.92, (8) 5.42, (9) 6.04, (10) 6.55, (11) 7.10, (12) 7.73, (13) 8.50, (14) 9.09, (15) 9.54, (16) 9.98, (17) 10.51, (18) 10.95, (19) 11.50, (20) 11.89, (21) 12.22.

Table 1. Acidity constant of PAR in pure water and different percentages of different of surfactants (w/v) (%) at 25 °C and constant ionic strength (0.1 M NaClO₄)

Concentration (w/v) %	Brij-35 (0.0100) ^a			Triton X-100 (0.0151)			Triton X-114 (0.0113)			Triton X-405 (0.159)			SDS (0.1728)		
	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a1}	pK_{a2}	pK_{a3}
0.00	2.98	5.47	11.98 ^b												
	3.03	5.50	11.99 ^c												
	3.03	5.50	11.95 ^d												
0.005	2.77	5.36	11.69	2.79	5.20	11.72	2.73	5.19	11.66	2.81	5.17	11.75	2.88	5.27	11.72
0.01	2.70	5.55	11.66	2.79	5.23	11.72	2.68	5.25	11.72	2.75	5.18	11.75	2.96	5.31	11.64
0.025	2.68	5.56	11.63	2.76	5.25	11.75	2.69	5.35	11.79	2.76	5.24	11.76	3.32	5.45	11.63
0.05	2.65	5.57	11.63	2.61	5.43	11.78	2.61	5.49	11.78	2.76	5.31	11.78	3.49	5.60	11.62
0.1	2.64	5.73	11.64	2.36	5.73	11.73	2.15	5.88	11.60	2.64	5.39	11.78	3.58	5.78	11.61

^a Values in parentheses are cmc in (w/v) % from ref. 35.

^b This work in pure water.

^c Rouhollahi, A.; Kiaei, F. M.; Ghasemi, J. *Talanta* **2005**, *66*, 653.

^d Kelckova, Z.; Langova, M.; Havel, J. *Collect. Czech. Chem. Commun.* **1978**, *43*, 3163.

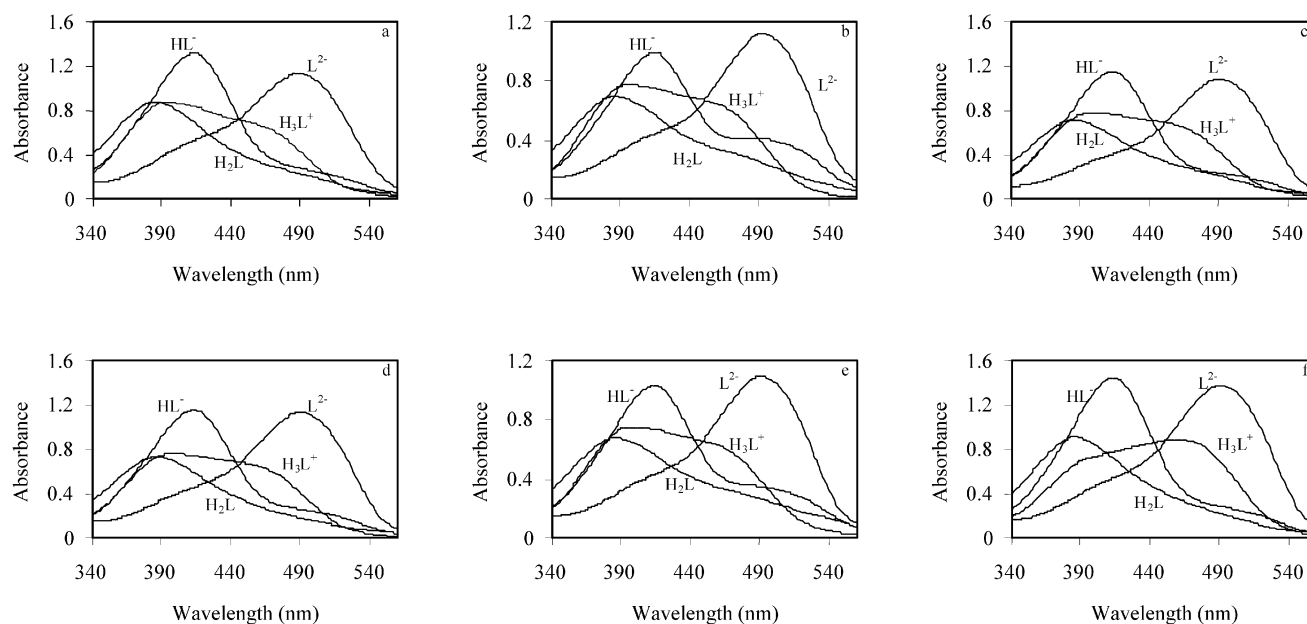


Fig. 3. The pure spectra of different forms of PAR in (a) pure water, (b) 0.05% (w/v) Brij-35 to water, (c) 0.05% (w/v) Triton X-100 to water, (d) 0.05% (w/v) Triton X-114 to water, (e) 0.05% (w/v) Triton X-405 to water and (f) 0.05% (w/v) SDS to water.

(w/v) Brij-35, 0.1% (w/v) Triton X-100, 0.1% (w/v) Triton X-114, 0.1% (w/v) Triton X-405 and 0.1% (w/v) SDS to water are shown in Fig. 3. It is interesting to note that the nature of the surfactant has a fundamental effect on each pure spectrum. As is clear from Fig. 3, this effect is apparently different for different species of PAR.

Many papers and reviews have discussed the effect of micelles on the apparent pK_a values of the acids.^{2-10,30} In the present work we observed the shifts of spectrum in Brij-35, Triton X-100, Triton X-114, Triton X-405 and SDS micelle media systems and then we calculated the pK_a values of this reagent in these media. As is clear from Fig. 3b, when the Brij-35 surfactant is used, it caused an influence on the H_3L^+ and HL^- spectrum and when different Triton surfactants are used, spectra of different species of PAR changed slightly (Figs. 3c, 3d and 3e). Also, when SDS surfactant is used, it caused lot of changes on the H_3L^+ spectrum (Fig. 3f). However, results show that a greater effect of surfactant is seen in the spectra of H_3L^+ and HL^- than H_2L and L^{2-} species. It has been suggested that the effect of micellar systems on acid-base equilibria arises from an intrinsic factor (arising from energy differences between the aqueous and the nonpolar media) and a potential effect that is due to the electrically charged micelle surface. Also, these changes are due to the hydrophobic and electrostatic interactions of

reactants with micellar aggregates.^{3,5,9,36,37}

CONCLUSION

In this work, we distinguish the behavior of acidity constants of PAR in pure water, water-Brij-35, water-Triton X-100, water-Triton X-114, water-Triton X-405 and water-SDS systems at 25 °C and an ionic strength of 0.1 M that are studied by the multiwavelength spectrophotometric method. Results show that the pK_a values of PAR are influenced by addition of the neutral surfactants and an anionic surfactant such as Brij-35, Triton X-100, Triton X-114, Triton X-405 and SDS. The DATAN program was applied for determination of acidity constants. By using this method and without any prior knowledge about the system, we can obtain concentration profiles and pure spectra from the experimental data. In conclusion, interaction with micellar aggregates induces significant pK_a shifts which can be rationalized in terms of the partitioning of species and electrostatic contribution.

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REFERENCES

1. Hinze, W. L. *Solution Chemistry of Surfactants*; Mittal, W. L., Ed.; Plenum Press: New York, 1979; p 79.
2. McIntire, G. L. *Crit. Rev. Anal. Chem.* **1990**, *19*, 257.
3. Beltran, J. L.; Codony, R.; Granados, M.; Izquierdo, A.; Prat, M. D. *Talanta* **1993**, *40*, 157.
4. Pourreza, N.; Rastegarzadeh, S. *J. Chem. Eng. Data* **2005**, *50*, 206.
5. Beltran, J. L.; Prat, M. D.; Codony, R. *Talanta* **1995**, *42*, 1989.
6. Pramaura, E.; Pellezzeti, E. *Anal. Chim. Acta* **1981**, *126*, 253.
7. Pellezzeti, E.; Pramaura, E. *Anal. Chim. Acta* **1985**, *169*, 1.
8. Yuanqin, Z.; Fan, L.; Xiaoyan, L.; Jiming, L. *Talanta* **2002**, *56*, 705.
9. Underwood, A. *Anal. Chim. Acta* **1982**, *140*, 89.
10. Abbaspour, A.; Kamyabi, M. A. *J. Chem. Eng. Data* **2001**, *46*, 623.
11. Kara, D.; Alkan, M. *Spectrochim. Acta Part A* **2000**, *56*, 2753.
12. Safavi, A.; Abdollahi, H. *Talanta* **2001**, *53*, 1001.
13. Rossoti, F. J. C.; Rossoti, H. S. *The Determination of Stability Constants*; McGraw-Hill: New York, 1961; p 40.
14. Gamp, H.; Maeder, M.; Mayer, C. J.; Zuberbuhler, A. *Talanta* **1985**, *32*, 95.
15. Legget, D. J. *Computational Methods for the Determination of Formation Constants*; Plenum Press: New York, 1985; p 159.
16. Gans, P.; Sabbatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739.
17. Lawton, W.; Sylvestre, E. A. *Technometrics* **1971**, *13*, 617.
18. Kubista, M.; Sjoback, R.; Albinsson, B. *Anal. Chem.* **1993**, *65*, 994.
19. Kubista, M.; Sjoback, R.; Nygren, J. *Anal. Chim. Acta* **1995**, *302*, 121.
20. Kubista, M.; Nygren, J.; Elbergali, A.; Sjoback, R. *Crit. Rev. Anal. Chem.* **1999**, *29*, 1.
21. Scarminio, I.; Kubista, M. *Anal. Chem.* **1993**, *65*, 409.
22. Sjoback, R.; Nygren, J.; Kubista, M. *Spectrochim. Acta Part A* **1995**, *51*, L7.
23. Nygren, J.; Andrade, J. M.; Kubista, M. *Anal. Chem.* **1996**, *68*, 1706.
24. Svanvik, N.; Nygren, J.; Westman, G.; Kubista, M. *J. Am. Chem. Soc.* **2001**, *123*, 803.
25. Ghasemi, J.; Niazi, A.; Kubista, M.; Elbergali, A. *Anal. Chim. Acta* **2002**, *455*, 335.
26. Ghasemi, J.; Niazi, A.; Westman, G.; Kubista, M. *Talanta* **2004**, *62*, 831.
27. Ghasemi, J.; Niazi, A.; Kubista, M. *Spectrochim. Acta Part A* **2005**, *62*, 649.
28. Niazi, A.; Yazdanipour, A.; Ghasemi, J.; Kubista, M. *Collect. Czech. Chem. Commun.* **2006**, *71*, 1.
29. Niazi, A.; Ghali, M.; Yazdanipour, A.; Ghasemi, J. *Spectrochim. Acta Part A* **2006**, *64*, 660.
30. Niazi, A.; Yazdanipour, A.; Ghasemi, J.; Kubista, M. *Spectrochim. Acta Part A* **2006**, *65*, 73.
31. <http://www.multide.se>.
32. Elbergali, A.; Nygren, J.; Kubista, M. *Anal. Chim. Acta* **1999**, *379*, 143.
33. Kelckova, Z.; Langova, M.; Havel, J. *Collect. Czech. Chem. Commun.* **1978**, *43*, 3163.
34. Russeva, E.; Kuban, V.; Sommer, L. *Collect. Czech. Chem. Commun.* **1979**, *44*, 374.
35. Rosen, M. J. *Surfactants and Interfacial Phenomena*; John Wiley: New York, 2004.
36. Dario Falcone, R.; Mariano Correa, N.; Alicia Biasutti, M.; Silber, J. J. *Langmuir* **2002**, *18*(6), 2039.
37. Takeshima, M.; Yokoyama, T.; Imamoto, M.; Asaba, H. *J. Org. Chem.* **1969**, *34*, 730.