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Spectrophotometric Determination of Acidity Constants of Thiamine in Water, Water-Triton X-100 Micellar Media Solutions

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ABSTRACT: *In this work the acidity constants of Thiamine in water and water-Triton X-100 micelle media solutions, at 25 °C, have been determined spectrophotometrically. To evaluate the pH- absorbance data, a resolution based on the combination of soft-and hard-modeling is applied. The acidity constants of all related equilibria are estimated using the whole spectral fitting of the collected data to an established factor analysis model. DATAN program was applied for determination of acidity constants. Results showed that the pKa values of Thiamine were influenced as the percentages of a nonionic surfactant, such as triton X-100, added to the solution of this reagent increased. Effect of surfactant on acidity constants and pure spectrum of each component are also discussed.*

KEY WORDS: *Triton X-100, pKa, Surfactant, Spectrophotometry.*

INTRODUCTION

Acid dissociation constants are important parameters to indicate the extent of ionization of molecules in solution at different PH values. The acidity constants of organic reagents play a fundamental role in many analytical procedures such as acid-base titration, solvent extraction, complex formation and ion transport. It has been shown that the acid-base properties affect the toxicity [1].

The spectroscopic instrumentation used today, however, almost invariably has a capacity to collect data in a full spectral range. Using a single or a few wavelengths, discards most of the information in the collected spectra and requires both the presence of and knowledge of such suitable wavelengths. However, in many cases, the spectral responses of components overlap and analysis is no longer straight forward [2,3].

Data analysis was carried out by DATAN package that was developed by *Kubista* group [2-4]. This package, called physical constraints method, calculates concentrations, obeys an assumed equilibrium expression and demonstrates its applicability by determining the acidity constants of two and four protolytic forms of fluorescence in a possible advantage of the *Kubista et al*.

In this method soft-modeling approach is mixed with a hard-modeling approach. This might be the best and more general strategy, since it can handle different situations, with only a partial knowledge of the chemistry of the system. The physical constants method calculates spectral profiles, concentrations and equilibrium expressions that related the components. The theory and application of physical constraints method has been discussed by kubista et al. in several papers [5-16].

In this work, we have applied the physical constraints approach to determine the acidity constants of Thiamine (Fig. 1) in pure water and water - Triton X-100 micelle media solutions at 25 °C spectrophotometrically. The effect of Triton X-100 was studied on the dissociation constants and pure spectrum of thiamine and the analysis was readily performed with computer program DATAN.

THEORY

The theory and application of the physical constraints method has been discussed by *Kubista et al.*, in several papers [2,5-8] . However, the general method is described briefly here. Spectra of Thiamine at different pH values were digitized and arranged in a data matrix A, which is decomposed into an orthonormal basis set by NIPAL or any equivalent method [2]:

$$A = TP' + E \approx TP' = \sum_{i=1}^{r} t_i p_i' \tag{1}$$

Where the orthogonal target vectors t_i and orthonormal projection vectors p_i' are mathematical constructs that cannot be directly related to component spectra and concentrations; r is the number of independent spectroscopic components, which corresponds to the number of light-absorbing chemical species and is determined by visual inspection of the t and p' vectors or by performing statistical methods, such as, x^2-test [17-19] . E is an error matrix.

By assuming linear responses, the spectra in matrix A are linear combinations of the concentrations, C, and spectral responses, V, of the chemical components.

$$A = CV + E \approx CV \tag{2}$$

If the spectral profiles of the components are known, the concentration of each component can easily be calculated, for example, by least squares minimization.

If standards are not available the common belief has been that the component' spectral responses cannot be separated, which precludes their identification. This is due to ambiguity in determining the rotation matrix, R, in the following equations; from Eqs.(1) and (2) follows that there is a square matrix R (r × r) that satisfies

$$T = CR \tag{3a}$$

$$P = R^{-1}V \tag{3b}$$

Since $A = CV = C(RR^{-1})V = (CR)(R^{-1}V) TP'$.

If R can be determined, the spectral responses V and concentrations C of the components can be calculated from the target T and projection P′ matrices:

$$C = TR^{-1} \tag{4a}$$

$$V = RP' \tag{4b}$$

Among the thermodynamic expression that describes the components, concentration is the main constraint used to determine R, from which thermodynamic parameters and components of spectral responses and concentration are calculated. Therefore, the strategy for determining the rotation matrix R is as follows. Concentrations of the chemical species are calculated from the equilibrium expressions for various trial values of the equilibrium constants, and are fitted to the calculated target vectors according to Eq. (3a). The accuracy of the equilibrium constants and best fit determines their values and the elements of matrix R.

EXPERIMENTAL SECTION
Apparatus

The spectrophotometric measurements were made using a Scinco (SUV-2120) spectrophotometer with a thermostated cell holder and equipped with a 1-cm path length quartz cell was used for UV-Vis spectra acquisition. Spectra were acquired between 240 and 350 nm. All spectrophotometric measurements were made at 25.0 ± 0.5 °C. The pH values were measured using a HORIBA M-12 pH-meter and a combined glass electrode.

Reagents

All reagents used were of analytical grade. Doubly distilled water was used throughout. Thiamine, Triton X-100, hydrochloric acid, sodium hydroxide and

potassium nitrate were from Merck. These reagents were used without further purification. Standard stock solutions consisted of 8×10^{-4} M of Thiamine in water. The stock solutions of surfactant were prepared by dissolving weighted amounts of substances in appropriate amounts of water. All the solutions were prepared in deionized water.

Procedure

For the Thiamine in pure water as well as water-Triton mixtures titrations, absorption spectra were measured with a titration set-up consisting of a computer interfaced to a spectrophotometer. After each pH adjustment, solution is transferred into the cuvette and the absorption spectra are recorded. Ionic strength was maintained at 0.1 M by adding appropriate amounts of KNO_3. All measurements were carried out 25 ± 0.5 °C.

RESULTS AND DISCUSSION

The electronic absorption spectra of thiamine in pure water at various pH values at 240-350 nm intervals were recorded. In order to determine the influence of the nonionic surfactant (Triton X-100) on acidity constant, a series of experiments were run at different Triton X-100 concentrations, above the cmc. Sample spectrum of Thiamine at different pH values in pure water and water-Triton X-100 are shown in Figs. 2, 3 and 4, respectively, these factors could be attributed to the one dissociation equilibria of a triprotic acid, such as, Thiamine. The pK_a value of Thiamine was investigated in pure water and different water-Triton X-100 mixtures spectrophoto-metrically at 25 °C and at an ionic strength of 0.1 M (KNO_3).

Acidity constants of Thiamine in several mixtures were evaluated using the DATAN program using the corresponding 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) evidence 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 output of the program is pK_a values and their standard deviation, the number of principal components, projection vectors
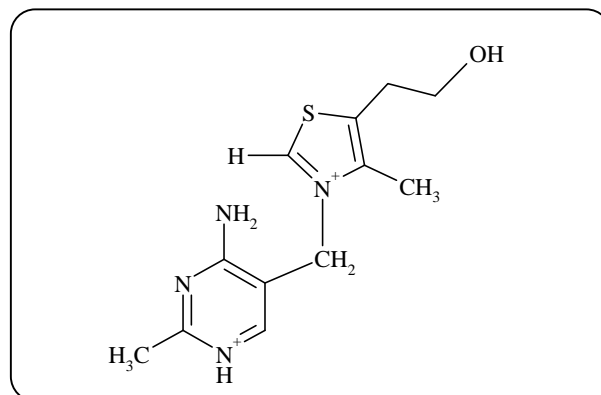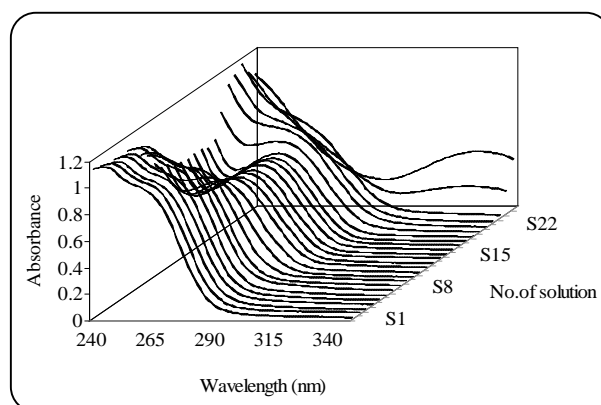

Fig. 1: Structure of thiamine .

Fig. 2: Absorption spectra of Thiamine in pure water at different pH values: (1) 1.06, (2) 1.53, (3) 2.05, (4) 2.53, (5) 3.00, (6) 3.51, (7) 4.03, (8) 4.52, (9) 5.01, (10) 5.52, (11) 6.01, (12) 6.53, (13) 7.01, (14) 7.50 (15) 8.01, (16) 8.51, (17) 9.00, (18) 9.50, (19) 10.00, (20) 10.50, (21) 11.01, (22) 11.50, (23) 12.01, (24) 12.50, (25) 13.06.
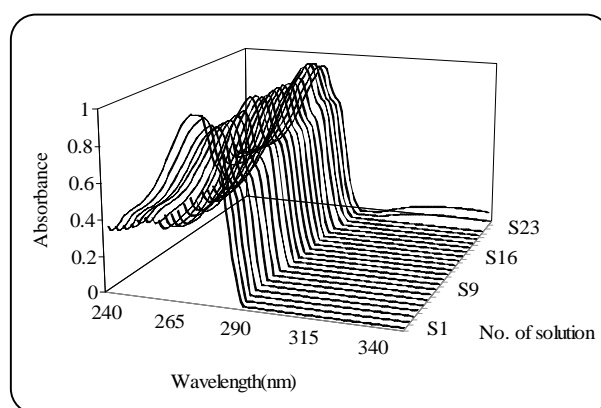

Fig. 3: Absorption spectra of 2 ml Thiamine in 0.02 % (w/v) Triton at different pH values: (1) 1.50, (2) 2.00, (3) 2.50, (4) 3.00, (5) 3.50, (6) 4.00, (7) 4.50, (8) 5.01, (9) 5.50, (10) 6.01 (11) 6.50, (12) 7.00, (13) 7.51, (14) 8.00 (15) 8.50, (16) 9.00, (17) 9.49, (18) 10.00, (19) 10.50, (20) 11.00, (21) 11.50.(22)12.00.(23)12.50.(24)13.00.

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Table 1: Acidity Constant of Thiamine in pure water and at different percentage of Triton X-100 (w/v) at 25 °C and constant ionic strength (0.1 M KNO$_3$).

Surfactant (w/v)(%)	Acidity Constant ± S.D.		
	Triton X-100		
	pKa1	pKa2	pKa3
0.000	5.02	10.69	13.25
0.020	5.07	10.97	12.26
0.010	5.43	11.19	12.36
0.005	5.13	10.84	12.63
0.001	5.18	10.85	12.74

(loadings), concentration distribution diagrams, and the pure spectrum of each assumed species.

The obtained pK$_a$ values are listed in table 1 as function of surfactant concentrations. The pK$_a$ values correspond to the pH dependent variation of absorption spectra in micelle media systems. One of the very important outputs of the DATAN program is the calculated spectrum of different forms of Thiamine in micelle media. Sample spectrum of the calculated spectra of all species in pure water and 0.02 % (w/v) Triton X-100 are shown in Fig. 4. It is interesting to note that the nature of the surfactant has a fundamental effect on each pure spectrum. As it is clear from Fig. 4, this effect is apparently observed in different species of Thiamine. The surfactant effect on this spectrum is very interesting.

Many papers and reviews have discussed the effect of micelle on the apparent pK$_a$ values of acids [20-25]. In the present work we observed the shifts of spectrum in Triton X-100 micelle media systems and then we calculated the pK$_a$ value of this reagent in these media. As is clear from Fig. 4b, Triton X-100 caused little influence on L^{2-} spectrum. The pK$_a$ is decreased with increase of Triton X-100 percentages. However, the effect of surfactant is seen in the spectra of L^{2-} more than HL$^-$ specie. It has been suggested that the effect of micellar systems on acid-base equilibria arises from an intrinsic factor (arising from energy difference between the aqueous and the nonpolar media) and a potential effect due to the electrically charged micelle surface.

The most important features of distribution diagrams are the pH limit of evolving and disappearance of
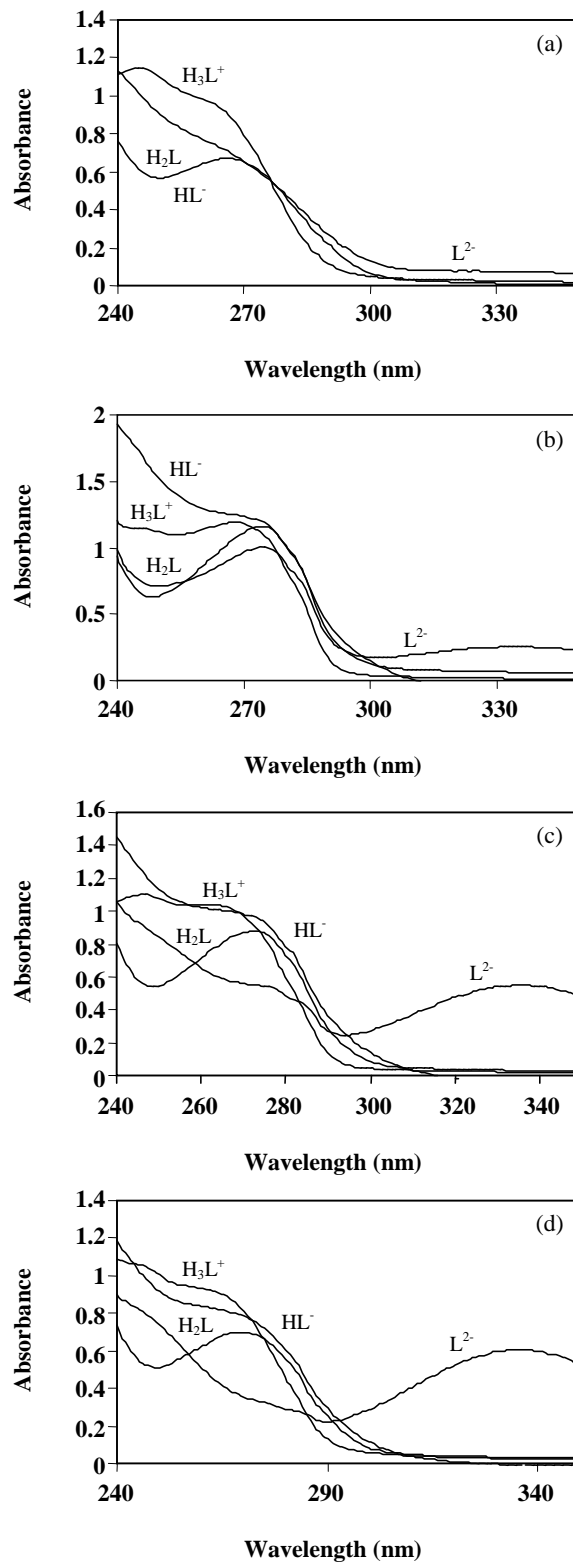
Fig. 4: The pure spectra of different form of Thiamine in (a) Pure water, (b) 0.02 % (w/v) Triton X-100 , (c) 0.01 % (w/v) Triton X-100 (d) 0.001 % (w/v) Triton X-100 (e) 005 % (w/v) Triton X-100 .
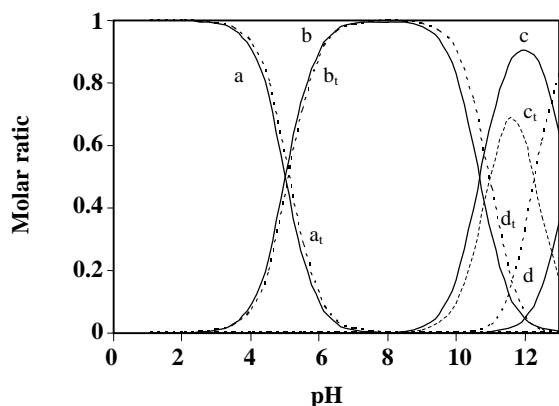
Fig. 5: Distribution diagrams of different species of Thiamine: (a) H_3L^+, (b) H_2L, (c) HL^-, (d) L^{2-} in water (full line), and subscript t comes for showing 0.02 wt % Triton X-100 (dashed line).

components. So, according to the distribution diagrams it may be concluded that the spectra at smaller pH than 4.0 can be assigned to H_3L^+ form because of its dominance at this range. At pH 4.5-10.5 interval the H_2L form dominates and hence the spectra should be mostly attributed to this form. The HL^- and L^{2-} forms appeared at pH intervals of 10.5-12.0 and pH>12.0, respectively. Samples of distribution diagrams are shown in Fig. 5.

CONCLUSIONS

The dissociation constants of the Thiamine were calculated with sectrophotometric titrations using a chemometric method. The striking advantage of the proposed method is the use of the whole spectral information in the computation process which enable us to have more precise and accurate thermodynamics constants in comparison to the classical methods such as single wavelength approach. The effect of surfactant on the acidity constants is investigated. The results show good consistency with the previous reported results. DATAN is a useful tool for resolution of the different species present in equilibria systems. By using this method and without any prior knowledge about the system, we can obtain concentration profiles and pure spectra froms the experimental data. In conclusion, interaction with micellar aggregates induces significant pK_a shifts which can be rationalized in terms of partitioning of species and electrostatic contribution.

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