

Spectrophotometric Determination of Conditional Acidity Constant of Some Sulfonephthalein Dyes as a Function of Anionic, Neutral and Cationic Surfactants Concentrations Using Rank Annihilation Factor Analysis

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Abstract

Rank annihilation factor analysis (RAFA) is proposed to the spectrophotometric studies of acid-base equilibrium of some sulfonephthalein dyes in the presence of sodium dodecyl sulfate (SDS), triton X-100 (TX-100) and cetyltrimethylammonium bromide (CTAB). When the conditional acidity constant (surfactant concentration dependent acidity constant) acts as an optimizing object, and simply is combined with the pure spectrum of acidic or basic forms, the rank of original data matrix can be reduced by one by annihilating the information of the acidic or basic spectrum from the original data matrix. The residual standard deviation (R.S.D.) of residual matrix is regarded as the evaluation function. Spectrophotometric studies of bromothymol blue, bromophenol blue and bromocresol green in the presence of varying amounts of above surfactants are used as experimental model systems and the amounts of conditional acidity constants are calculated. The conditional acidity constants decrease by increasing of SDS and TX-100 concentrations for all three investigated dyes. But increasing of CTAB concentration has different effects on the dissociation constants of three dyes.

Keywords:

RAFA; Conditional acidity constant; Sulfonephthalein dyes; TX-100; SDS

1. Introduction

Dye-surfactant interactions in aqueous buffered systems have been drawing interest of many researchers due to their industrial applications [1] and pertinence to biological process [2]. Such studies play a very fundamental role in many analytical and pharmaceutical fields [3-6]. 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 order of magnitude) and also shift equilibrium, including acid-base equilibrium. In presence of surfactants usually, the intensity and shifts in the absorbance bands can be increased and shifts in the absorption maxima of reagents are observed [7]. Micelles can affect the apparent pKa values of the reagents due to combination of electrostatic and micro environmental effects of the micelles [8-10]. Moreover, the acid - base equilibrium involved in these systems is also influenced by surfactants [11-13]. Observed shifts in pKa of aqueous indicator dyes by surfactants have been attributed to an electrostatic potential at the micelle surface [14, 15],

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ion-exchange between the micelle surface and bulk aqueous phase [16], ion pair formation between oppositely charged indicator species and head group of monomeric surfactant [17], low interfacial effective relative permittivity, interfacial salt effect, partition of dye between micelle and water, and other specific molecular interactions [15].

Acid dissociation constants (i.e. pKa 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 [18]. Several methods have been reported 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 suitable for studying chemical equilibrium 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 easy [19]. Several spectrophotometric methods have been developed to determine the equilibrium constants of chemical processes. Occasionally, problems arise because of strong overlapping of spectra of chemical components involved in equilibrium and some uncertainties from using some complex mathematical algorithms, to solve such problems [20]. However, much more information can be extracted if multivariate spectroscopic data are analyzed by means of an appropriate multivariate data analysis method.

The predefined model, known as hard-modeling analysis, cannot be applied if crucial information is missing. Soft modeling or model free approaches based on much more general prerequisites, such as positive molar absorbance, positive concentration of all species, unimodality of concentration profiles, and closure (concentration of all species are the same for all solutions). Naturally, if the strengths of hard-modeling and soft-modeling methodologies are combined, a much more powerful method of data analysis can be expected [21]. Rank annihilation factor analysis (RAFA) is an efficient chemometrics technique based on rank analysis for two-way spectrum data and can be employed to analyze the gray system with unknown background quantitatively. RAFA was originally developed by Ho et al. as an iterative procedure [22]. It was modified by Lorber to yield a direct solution of a standard eigenvalue problem [23]. Sanchez and Kowalski extended the method to the general case of several components that are not necessarily present in both the calibration and the unknown samples, obtained the solution by solving a generalized Eigen problem and called the method generalized rank annihilation method (GRAM) [24]. RAFA was used to analyze the two-way chromatographic spectral data [25] for determination of environmental pollutants such as polyring aromatic compounds [26, 27] and recently for spectrophotometric study of chemical kinetics [28, 29], complex formation equilibrium [30] and acidity constant [31, 32].

In this study, we used RAFA for the spectrophotometric determination of acidity constant of three sulfonphthaleins indicators as bromothymol blue (BTB), bromophenol blue (BPB) and bromocresol green (BCG) without any surfactant and in the presence of varying amounts of TX-100, SDS and CTAB surfactants at 25 °C and ionic strength of 0.1 mol L⁻¹.

2. Theory

As it is known [30, 31], the acid-base equilibrium can be described by the following reaction:



Then the apparent constant (K_a) of the acid HA is defined as the equilibrium constant:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (2)$$

Let

$$[HA] + [A^-] = C \quad (3)$$

C is constant and independent of the pH. With Eqs. (2) and (3), we can calculate concentration profiles of [HA] and [A⁻]:

$$[HA] = \frac{C[H^+]}{[H^+] + K_a} \quad (4)$$

$$[A^-] = \frac{CK_a}{[H^+] + K_a} \quad (5)$$

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 will be the sum of those of HA and A⁻, if Beer's law holds under the experimental conditions used.

The concentration profile of acid or base can be calculated for certain K_a value, by obtaining the roots of this equation as a function of pH. The equilibrium concentrations of HA and A⁻ at different pHs can form two column vectors [HA] and [A⁻], and they are referred to as the concentration profiles of the HA and A⁻ species. A two way data matrix A with rank 2 can be formed by measuring absorbance under different wavelengths at a series of chosen pH and constant analytical concentrations of species.

$$A = A_{HA} + A_{A^-} + R = \varepsilon_{HA}[HA]^T + \varepsilon_{A^-}[A^-]^T + R = EC^T + R \quad (6)$$

Where A_{HA} and A_{A⁻} are the bilinear measuring matrix of pure acidic and basic forms, respectively, and each one can be decomposed into the corresponding molar absorptivity spectrum ε_{HA} and ε_{A^-} (column vectors) and the concentration profiles [HA]^T and [A⁻]^T (row vectors, superscript T denotes the transpose of matrix or vector). E and C^T represent matrices formed by the molar absorptivity spectrum and the concentration profile of each species, respectively. R is the residual matrix and should contain only noise. The size of matrix A is w x p, where w denotes the number of wavelengths and p is the number of pH for which absorbances were recorded (p is smaller than w). Obviously, the size of matrices E and C^T are w x 2 and 2 x p, respectively. The pure spectrum of [HA] and [A⁻] can be readily measured at low pH and at high pH, respectively. Let

$$R = A - A_{HA} - A_{A^-} = A - \varepsilon_{HA}[HA]^T - \varepsilon_{A^-}[A^-]^T \quad (7)$$

The aim of RAFA approach is to find a suitable K_a so that the rank of matrix R can be reduced by two forms that of matrix A through introduction of the concentration profiles of [HA] and [A⁻] forms obtained from the roots of Eqs. (4) and (5).

Based on principal component analysis (PCA), the residual standard deviation (R.S.D.) method is widely used to determine the number of principal component [33, 34]. The R.S.D. is a measure of lack of fit of a principal component model to a data set. The R.S.D. is defined as:

$$\text{R.S.D.}(n) = \left[\frac{\sum_{i=1}^c g_i}{n(c-1)} \right]^{1/2} \quad (8)$$

Where g_i is the eigenvalue and n is the number of considered principal component.

3. Experimental

3.1. Reagents

Bromothymol blue (7.4×10^{-4} mol L⁻¹), bromophenol blue (7.5×10^{-4} mol L⁻¹) and bromocresol green (8.0×10^{-4} mol L⁻¹) were prepared by dissolving appropriate amounts of these indicators in 20% of ethanol solution, respectively. The stock solutions of surfactants of TX-100, SDS and CTAB were prepared by dissolving weighted amounts of substances in appropriate amounts of water. Phosphate buffer solutions with different pH amount were prepared and ionic strength was maintained at 0.1 mol L⁻¹ by adding appropriate amounts of NaCl or KCl. All solutions were prepared with doubly distilled water. Chemicals used were of analytical grade and were purchased from E. Merck.

3.2. Apparatus

UV-Visible absorbance digitized spectra were collected on a UV-VIS GBC 916 spectrophotometer, using a 1 cm quartz cell. Spectra were acquired between 350-750 nm and transferred (in ASCII format) to a computer for subsequent analysis by MATLAB software, version 7.04. Measurements of pH were made with a Metrohm 780 pH-meter using a combined glass electrode.

3.3. Procedure

For the Bromothymol blue ($39 \mu\text{mol L}^{-1}$, in 1% ethanol), bromophenol blue ($37.3 \mu\text{mol L}^{-1}$ in 1% ethanol) and bromocresol green ($40 \mu\text{mol L}^{-1}$ in 1% ethanol) in water, water-TX-100, water-SDS and water-CTAB mixtures, absorption spectra were measured at different pH. Solutions were kept at 25 °C using a thermostated cell.

4. Results and Discussion

The absorption spectra of BTB, BCG and BPB in 1% ethanol solution at various pH values are shown in Fig. 1. The absorption spectrums show absorption bands which have absorption maximum at 432, 440 and 435 for BTB, BCG and BPB, respectively. These absorption bands are attributed to the acidic form of BTB, BCG and BPB, respectively. With the increasing of pH, the absorptions for acidic form gradually decrease whereas the absorption about 616, 610 and 590 nm increase for BTB, BCG and BPB, respectively. An isobestic point is observed in Fig. 1 for each of dyes. The PCA of absorption data matrices obtained at various pH values shows two significant factors. These factors can be attributed to the two species in an acid-base equilibrium.

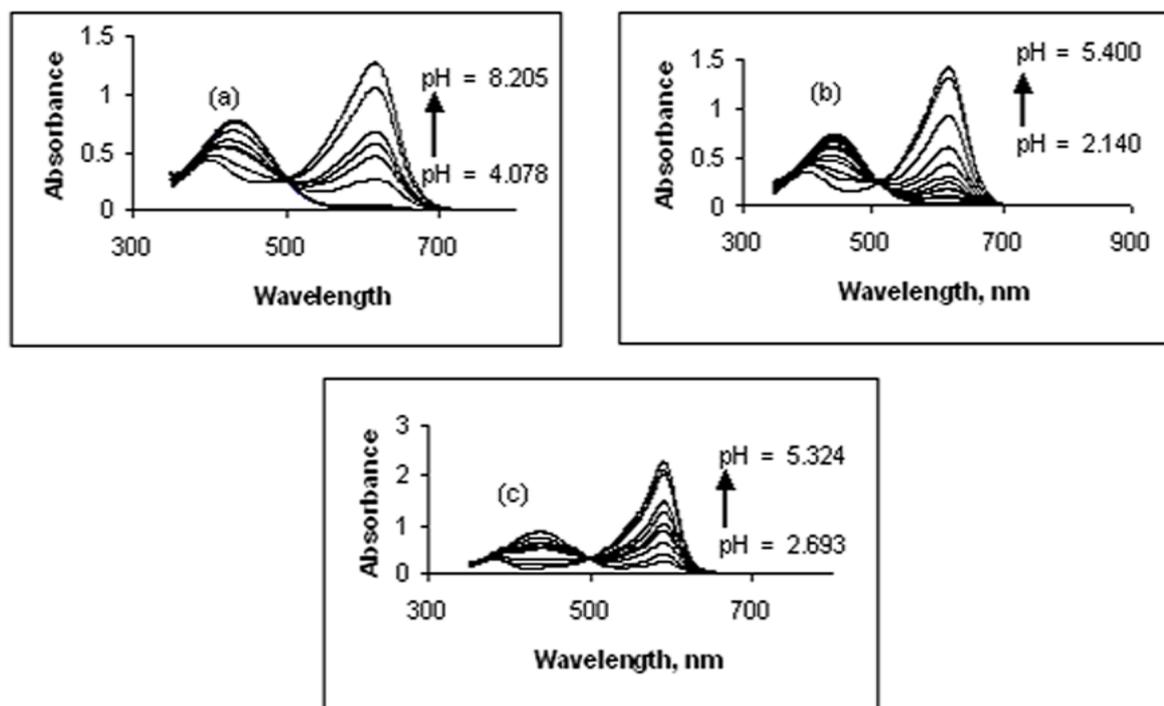
The acidity constant values of these indicators were investigated spectrophotometrically without any surfactant at 25 °C and an ionic strength of 0.1 mol L⁻¹. The pK_a of three sulfonephthalein dyes were obtained by RAFA method and relationships between R.S.D. and pK_a values for these dyes were shown in Fig. 2.

Table 1 show the obtained pK_a values and also previous reported values [35], as can be seen in this table, there is a good agreement between previous reported values and obtained values by RAFA.

Table 1. pK_a values of BPB, BCG and BTB at 25 °C and constant ionic strength of 0.1 mol L⁻¹

Indicator	*pK _a (RAFA)	pK _a (35)
BPB	3.91	3.85
BCG	4.62	4.66
BTB	7.19	7.19

* in 1% ethanol solution

**Fig. 1** Absorption spectra for Bromothymol blue (3.9×10^{-5} mol L⁻¹) (a) , Bromophenol Blue (3.9×10^{-5} mol L⁻¹) (b) and Bromocresol Green (4.0×10^{-5} mol L⁻¹) (c) in water.

4.1. The effect of TX-100 concentration on the acidity constant of BTB, BCG and BPB

In order to investigate the influence of the nonionic surfactant (Triton X-100), on acidity constant, a series of experiments were run at different surfactant concentrations (8.0×10^{-5} – 1.6×10^{-3} mol L⁻¹). The variations of pK_a values with TX-100 concentrations were shown in Fig. 3.

As it can be seen, pK_a values increases by increasing of TX-100 concentration and then they become smooth and reach constants. It seems these variations are attributed to stronger hydrophobic attraction of the monoionic form (BH⁻) than the doubly ionic form (B²⁻) with the micelle. Though both the acid and the base form of the dye associate with the nonionic micelles, but the association of the dianionic base form is much less than the other [36]. Preferential incorporation of the BH⁻ form into the micelles causes an imbalance between the two forms of the dye and some of the B²⁻ form of dye converts into the BH⁻ form. Therefore the K_a value decrease and then pK_a value increase.

The strength of the interaction of the dyes with TX-100 varies in the order BPB < BCG < BTB which is in the order of increasing hydrophobicity of the dyes (Fig. 4).

In addition to the above-mentioned points the effect of CMC (critical micelle concentration) amount effect must be considered. The CMC for TX-100 in presence of BTB in ionic strength of 0.01 mol L⁻¹ and temperature of 313 K was reported as 2.5×10^{-4} [36].

However CMC amount depend on temperature, pH and ionic strength, but as the results show at below this concentration which it seems the micelle has not been formed yet, the slope of variations of pK_a is lower than the higher concentrations (Fig. 3a) up to 4.0×10^{-4} and after that it is nearly constant. Therefore it is possible that interaction of dyes with micelle form is being very major than monomeric form of surfactant.

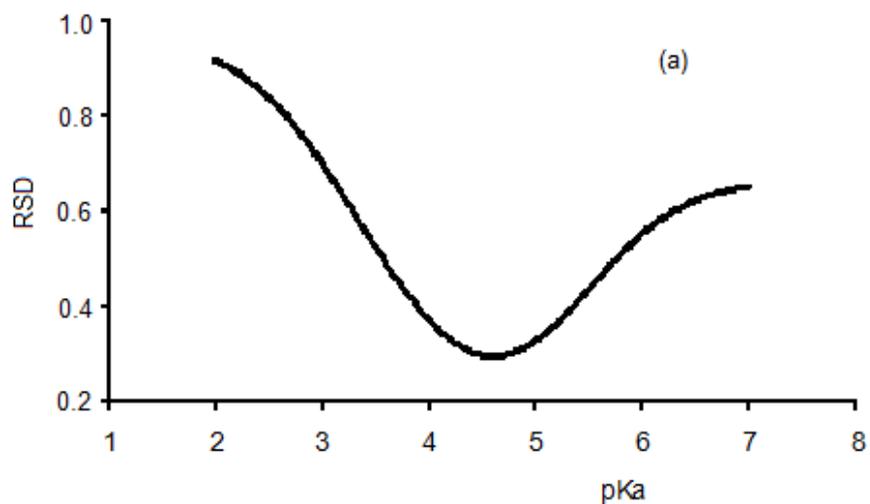


Fig. 2 (a) Relationship between R.S.D. and pK_a values for 3.9×10^{-5} mol L⁻¹ Bromothymol blue, without any surfactant at different pH values.

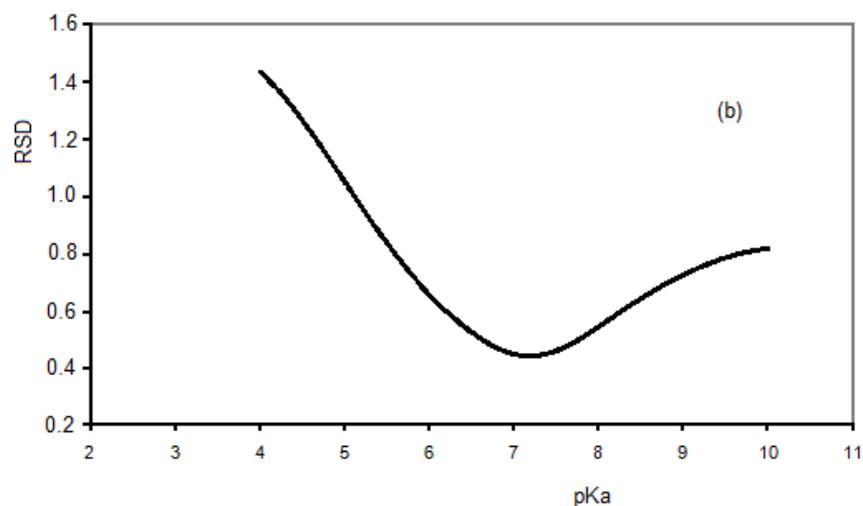


Fig. 2 (b) Relationship between R.S.D. and pK_a values for 3.9×10^{-5} mol L⁻¹ Bromophenol Blue without any surfactant at different pH values.

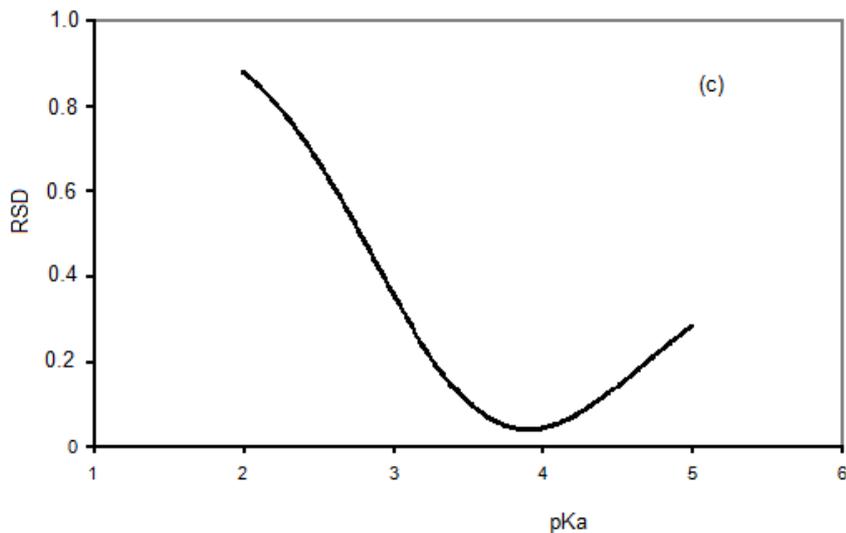


Fig. 2 (c) Relationship between R.S.D. and pKa values for 4.0×10^{-5} mol L⁻¹ Bromocresol Green without any surfactant at different pH values.

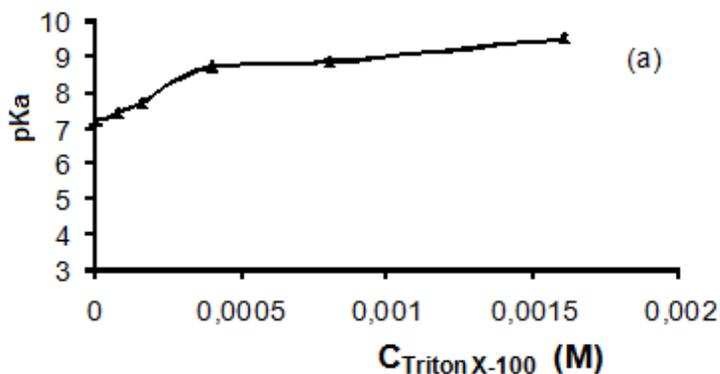


Fig. 3 (a) The variations of pK_a for Bromothymol blue in the presence of different amount of Triton X-100.

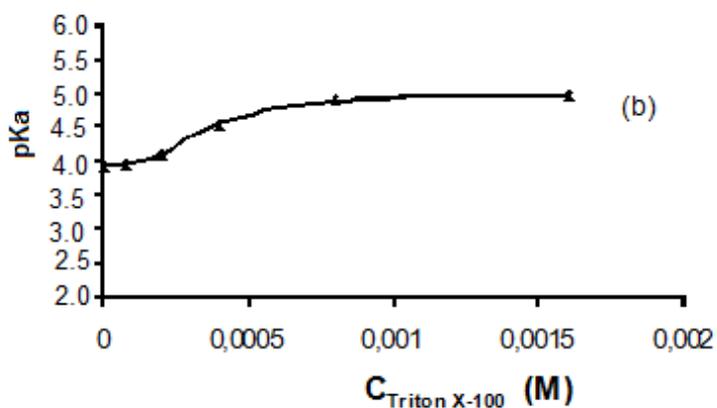


Fig. 3 (b) The variations of pK_a for Bromophenol blue in the presence of different amount of Triton X-100.

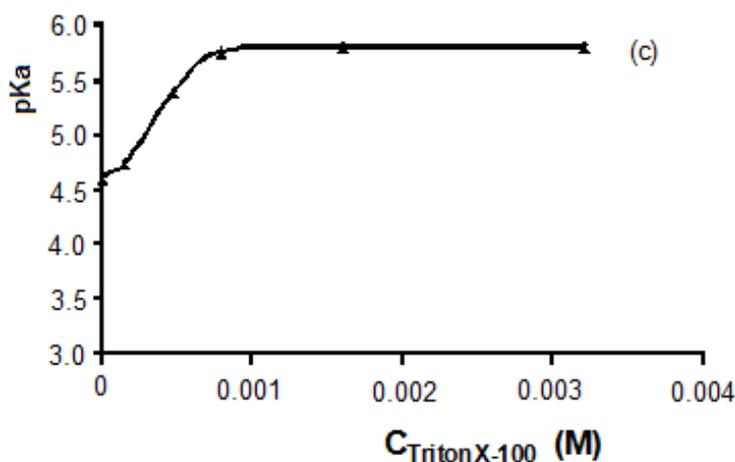


Fig. 3 (c) The variations of pK_a for Bromocresol green in the presence of different amount of Triton X-100.

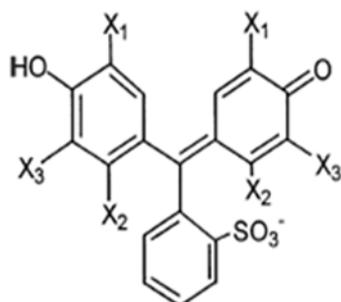


Fig. 4. Structure of the BH^- forms of the chosen Indicators.

4.2. The effect of SDS concentration on the acidity constant of BTB, BCG and BPB

Similar trends have been observed for variation in pK_a with varying SDS concentration ($5.0 \times 10^{-5} \text{ mol L}^{-1}$ - 5.0×10^{-4}) as an anionic surfactant (Fig. 5). But the variations with SDS are lower than TX-100 surfactant, because about SDS, as an anionic surfactant, in addition to hydrophobicity effects (that with hydrophobic attraction of the monoionic form (BH^-) with surfactant lead to increasing of pK_a value), there is an electrostatic effect. It seems this electrostatic effect is a repulsion force between anionic surfactant and both of two anionic forms of dyes that it prevents hydrophobic attraction of the monoionic form (BH^-) with surfactant. In other words, these two effects are against each other. Again, the variations in pK_a are largest amount for BTB with high hydrophobicity among three dyes and these variations are lowest amount for BPB with low hydrophobicity. The variations in pK_a of BCG place between two other dyes.

The effect of CMC amount for SDS is also similar to TX-100. As Fig. 5a shows at lower concentration than $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SDS, the slope of variations of pK_a in the range of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ - $2.5 \times 10^{-3} \text{ mol L}^{-1}$ of SDS is very higher than lower concentration than $1.0 \times 10^{-3} \text{ mol L}^{-1}$ SDS. It seems this amount is near to its CMC. The amount of CMC for SDS in presence of BTB at ionic strength of 0.01 mol L^{-1} has been reported as $1.7 \times 10^{-3} \text{ mol L}^{-1}$ [37]. Again it must be mentioned that CMC amount is related to pH, temperature and ionic strength.

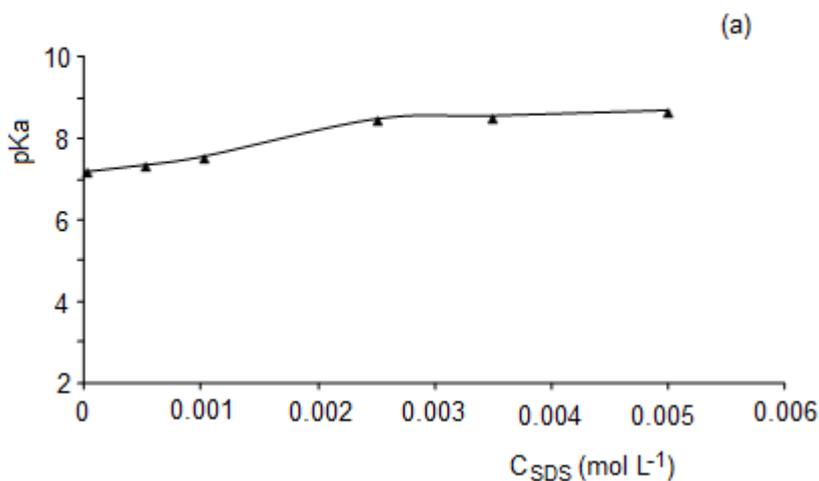


Fig. 5 (a) The variations of pK_a Bromothymol blue, in the presence of different amount of SDS.

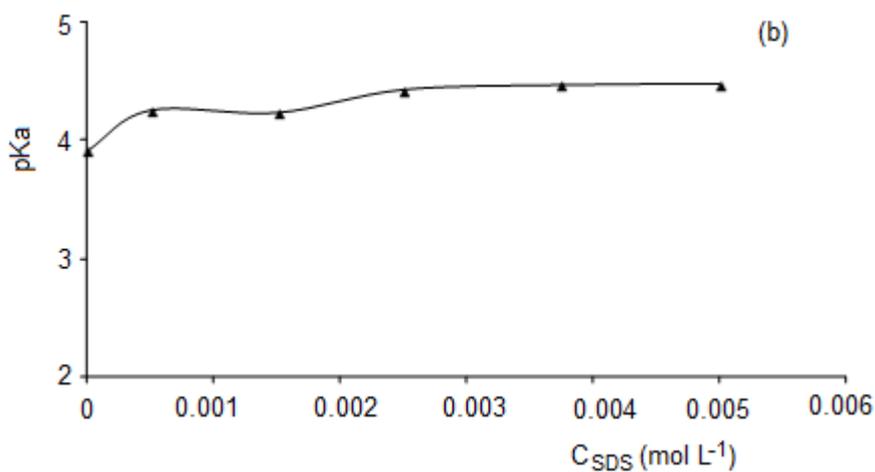


Fig. 5 (b) The variations of pK_a : Bromophenol blue in the presence of different amount of SDS.

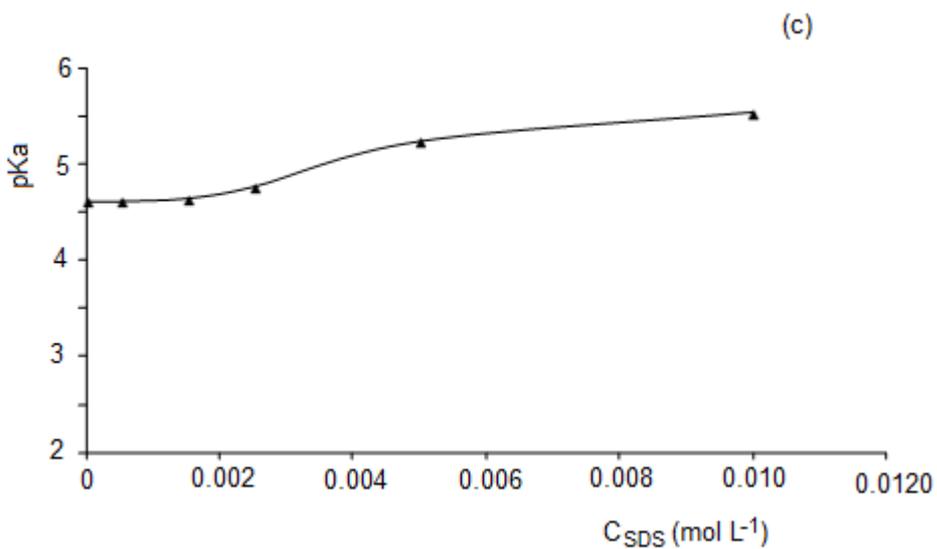


Fig. 5 (c) The variations of pK_a : Bromocresol green in the presence of different amount of SDS.

4.3. The effect of CTAB concentration on the acidity constant of BTB, BCG and BPB

The effect of CTAB on the observed dissociation constant of BTB, BCG and BPB are different from each other.

The variations of pK_a values in CTAB surfactant concentrations (5.0×10^{-6} - 5.0×10^{-5} mol L⁻¹) can be attributed to two different interactions with two different effects. In addition to hydrophobicity effect that can lead to increasing of pK_a value, it seems there is an electrostatic attraction between cationic surfactant and dianionic form of dyes. This effect can shifts dissociation reaction (Eq.1) to the right and then lead to increasing of K_a value or decreasing of pK_a value.

As it can be seen from Fig. 6, the effect of hydrophobicity overcome about BTB with high hydrophobicity and pK_a values are increased with increasing of CTAB concentration to 1.5×10^{-5} mol L⁻¹ and then they are nearly constant. Similar results are observed for BCG with lower hydrophobicity than BTB, as pK_a values are increased with increasing of CTAB concentration to 5.0×10^{-6} mol L⁻¹ and then they are nearly constant, but this increasing is lower than BTB with higher hydrophobicity. Whereas pK_a values about BPB initially are increased to 1.5×10^{-5} mol L⁻¹ CTAB concentration and then decreased, gradually. This decreasing seems conclusion of electrostatic attraction effect that overcomes about BPB with low hydrophobicity after 1.5×10^{-5} mol L⁻¹ CTAB concentration.

All of the calculated pK_a amounts together with standard deviation of them were given in Table 2.

Table 2. pK_a values of BPB, BCG and BTB at different concentrations of surfactants at 25 °C and constant ionic strength of 0.1 mol L⁻¹ (n=3)

Indicator	[TX-100] x 10 ⁴ mol L ⁻¹	pKa	[SDS] x 10 ³ mol L ⁻¹	pKa	[CTAB] x 10 ⁵ mol L ⁻¹	pKa
BPB	0.8	3.97±0.03	0.5	4.25±0.03	0.5	4.41±0.04
	2.0	4.09±0.03	1.5	4.23±0.03	1.5	4.53±0.05
	4.0	4.54±0.04	2.5	4.42±0.04	2.5	4.42±0.05
	8.0	4.89±0.04	3.7	4.46±0.04	3.7	4.27±0.04
	16.0	4.96±0.04	5.0	4.47±0.04	5.0	3.94±0.04
BTB	0.8	7.38±0.06	0.5	7.35±0.06	0.5	7.87±0.08
	1.6	7.70±0.06	1.0	7.55±0.06	1.5	8.02±0.08
	4.0	8.71±0.07	2.5	8.46±0.07	2.5	8.13±0.07
	8.0	8.87±0.07	3.5	8.54±0.07	3.7	8.19±0.07
	16.0	9.51±0.08	5.0	8.67±0.07	5.0	8.07±0.07
BCG	1.6	4.73±0.03	0.5	4.61±0.04	0.5	4.81±0.04
	4.8	5.38±0.04	1.5	4.64±0.04	1.5	4.94±0.04
	8.0	5.76±0.04	2.5	4.76±0.05	2.5	4.95±0.05
	16.0	5.80±0.04	3.2	5.23±0.05	3.7	4.89±0.05
	32.0	5.80±0.05	5.0	5.53±0.05	5.0	4.81±0.05

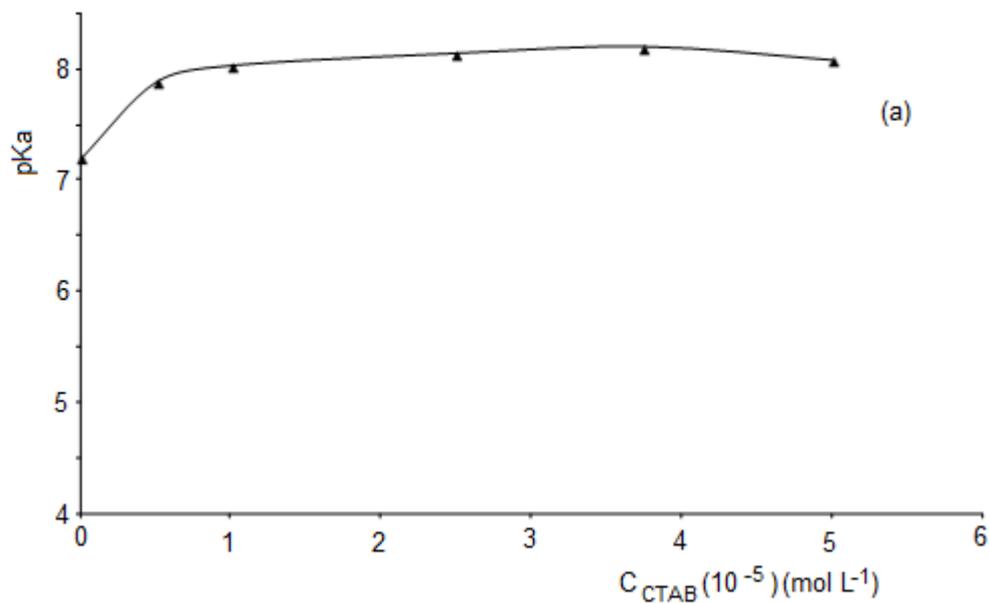


Fig. 6 (a) The variations of pK_a for Bromothymol blue in the presence of different amount of CTAB.

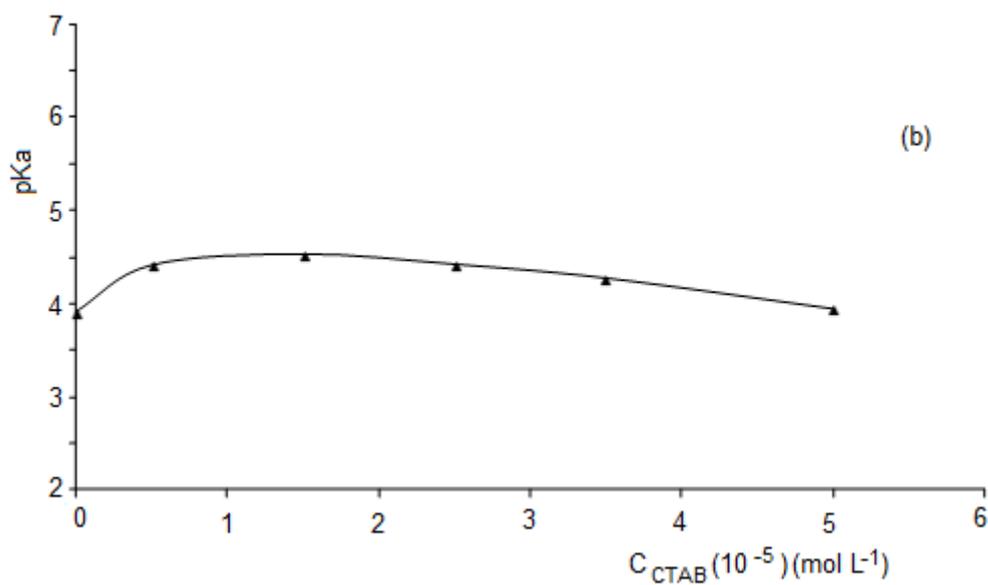


Fig. 6 (b) The variations of pK_a for Bromophenol blue in the presence of different amount of CTAB.

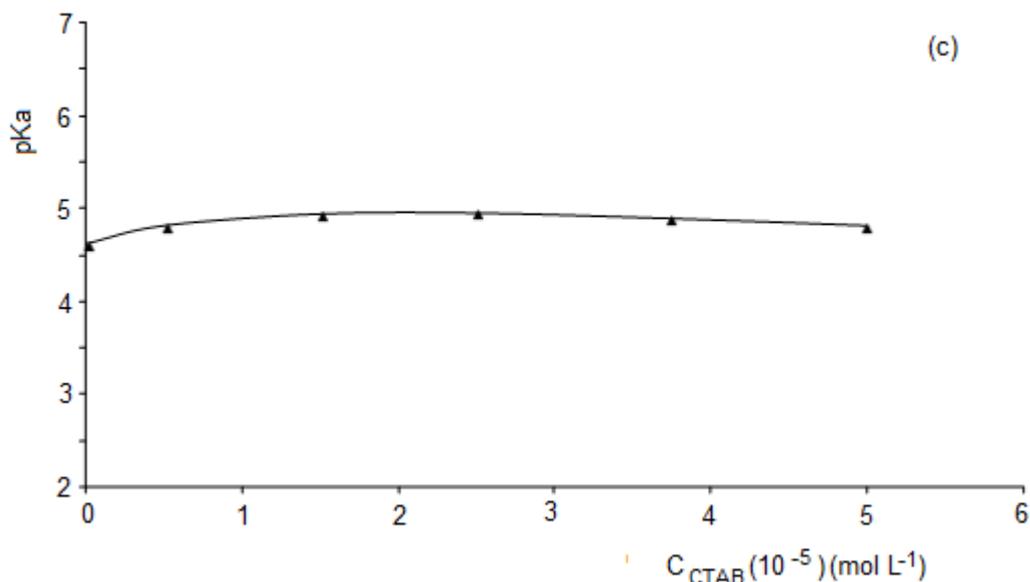


Fig. 6 (c) The variations of pK_a for Bromocresol green in the presence of different amount of CTAB.

5. Conclusion

In this work, the behavior of acidity constant of some sulfonephthalein dyes (BTB, BCG and BPB) was investigated in water, water-TX-100, water-SDS and water-CTAB systems at 25 °C and an ionic strength of 0.1 mol L⁻¹ by spectrophometric methods. RAFA method as useful chemometrics algorithm was applied for analysis of acid-base equilibrium systems. In conclusion, interaction with surfactants induces significant pK_a shifts, which can be rationalized in terms of hydrophobicity and electrostatic interactions.

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