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Acidity Constants Determination of Triazine Dye Derivative in the presence of some Surfactants by Multiwavelength Spectrophotometric and Spectrofluorimetric

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In this work, acidity constants protonated form of 4.4'-bis astilbene-2,2'-disulfonic-disodium salts (TRIAZ) have been determined spectrophotometrically and spectrofluorimetrically at 25°C and ionic strength of 0.1M KNO_3. A program based on MCR-ALS applied for determination of acidity constants. The results show that the peak values of dye are influenced by the presence of anionic, cationic, and nonionic surfactants. The effects of sodium dodecyl sulfate (SDS), Triton X-100 (TX-100) and cetyl trimethyl ammonium bromide (CTAB) as a surface-active agent on the acidic and basic forms, and the spectral properties of dye were studied. Also, we determined the critical micelle concentration (CMC) for these surfactants by spectrophotometric and spectrofluorimetric triazine dye probes. In addition, by using of evolving factor analysis (EFA) and multivariate curve resolution alternative least squares (MCR-ALS) methods, acidity constants were acquired.

1. Introduction

For several years now surfactant molecules and their effects have been increasingly used in analytical techniques, in part as new solvent systems and in part to provide a very particular environment able to alter the analytes' properties and their reactivity. As a consequence of such surfactant-analyte interactions, new determination methods, new analytes' properties and new chemical processes have been developed and established which also find interesting applications in other important areas such as biotechnology and pollution control. So it is important that their physico-chemical properties, the quantitative description of solute-surfactant interactions and the effects of such interactions on chemical equilibria such as acid-base equilibria and reactivity must be carefully considered. In most cases surfactant-modified procedures allow an improvement in the sensitivity, the selectivity and other indexes of methods such as spectroscopic pK_a determinations, Commonly

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performed in homogeneous solutions because their biochemical applications. Integration of this benefits with chemometrics data analysis methods such as MCR-ALS will multiply these advantages.

It is important to study the physical and chemical properties of dyes. Among these properties, the acidity constant is very important especially in the presence of surfactants. The interactions between surfactants and dyes have been investigated numerously[1-6]. The study of the acid–base behavior in micelles, reverse micelles (RMs) water-in oil micro emulsions etc., has attracted and interests. These compartmentalized systems have many applications in the fields of chemistry, biotechnology and biochemistry[5, 7]. The apparent pK_a of dyes in water-in-oil micro emulsions depends on the charge of the acid and base forms.

Accurate determination of acidity constants of various data analysis methods is important due to its immense importance in different chemical and biochemical areas. A chemometrics method such as extended principal component analysis and combination of this method with multiple linear regressions allow the determination of the apparent pK_a and pure spectral profiles of the acid and base forms of the dye precisely[8-11]. So the acidity constant values must be determinate accurately[12, 13].

It is important that we have a proper understanding of the distribution, binding to receptors, transport behavior and mechanism of action of certain compounds[14, 15]. The acidity and basicity form of dyes play a very fundamental role in many analytical procedures such as acid–base titration, solvent extraction and complex formation. Different methodologies have been proposed for the experimental determination of the acid dissociation constants including ^1H NMR spectroscopy, capillary electrophoresis, FT-IR spectrometry, UV–Vis absorption and fluorescence spectrophotometry and potentiometry[16-20]. Among these techniques, potentiometry and spectrophotometry are the methods of choice due to their simplicity, low cost, ease of application, and so on. For many systems, particularly those with similar components of dye form, this is not easy, and these have been difficult to analyze. Therefore, we want to unravel this problem, with employing the chemometrics methods. We can analyze whole spectra by using chemometrics methods; thereby we can acquire all spectral information in order to calculate triazine dye pK_a. Fig. 1. The approach is superior to any single-point measurement since several hundred data point per spectrum can be treated simultaneously[21-24].

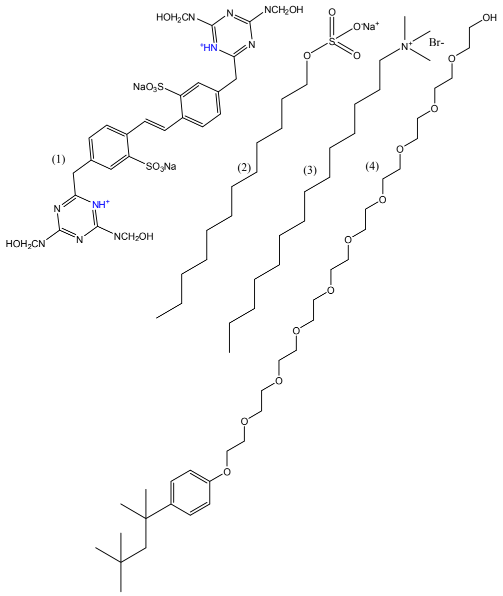

Fig. 1. Schematic representation of TRIAZ dye (1), SDS (2), CTAB (3) and TX-100 (4)

Triazine dyes have interacted with some drugs, DNA and biological compounds. Industrial applications of them as brightener and removal those from waste water are very important. The knowing exact amount of acidity constant of dye in this process is very important and crucial. Hydroxyl, amino and sulfonic group of this triazine dye can be protonated at pH<2. A nitrogen atom of the *s*-triazine ring are protonated in aqueous solution at low pH because the ring nitrogen is more basic than the amino group on the side chain of the *s*-triazine ring[3, 25]. The pKa values and some selected characteristics of *s*-triazine studied, which include five chloro, three methoxy and five alkylthio-*s*-triazine[25-33]. The pK_a values of chloro-, methoxy-, and alkylthio-*s*- triazine reported in the literature are in the range of 1.3–2.0, 4.0–4.4, and 3.1–4.4, respectively [25-28, 31, 34].

In this work, we report pK_a values of protonated triazine, concentration distribution diagrams and pure spectra of species involved for triazine dye. For this purpose, we used evolving factor analysis (EFA) and multivariate curve resolution alternative least squares (MCR-ALS) methods. We investigate three surfactant effects on pK_a. Also, we report critical micelle concentration (CMC) of SDS, CTAB and TX-100 in the presence of this dye as spectrophotometric and spectrofluorimetric probe (Table 1).

Table1. The acquired critical micelle concentration (CMC Mol. L^{-1}) at three pH and I=0.1 M KNO_3

Surfactant		In pH=3. 00	In pH=7. 50	In pH=9. 00
SDS	Spectrophotometric	0.74×10^{-3}	0.55×10^{-3}	0.57×10^{-3}
	Spectrofluorimetric (Ex)	0.62×10^{-3}	1.42×10^{-3}	1.42×10^{-3}
	Spectrofluorimetric (Em)	0.64×10^{-3}	1.05×10^{-3}	1.42×10^{-3}
CTAB	Spectrophotometric	1.32×10^{-3}	1.00×10^{-3}	1.34×10^{-3}
	Spectrofluorimetric (Ex)	0.35×10^{-3}	0.62×10^{-3}	0.75×10^{-3}
	Spectrofluorimetric (Em)	0.51×10^{-3}	0.35×10^{-3}	1.52×10^{-3}
TX-100	Spectrophotometric	3.51×10^{-3}	1.08×10^{-3}	0.51×10^{-3}
	Spectrofluorimetric (Ex)	1.82×10^{-3}	0.63×10^{-3}	0.38×10^{-3}
	Spectrofluorimetric (Em)	1.44×10^{-3}	0.77×10^{-3}	1.24×10^{-3}

2. Results and Discussion

The absorption spectra of TRIAZ in 250–450 mm intervals and a fluorescence spectrum (excitation at 250-340nm, emission in 350-600nm intervals) in pure water at several of pH value were recorded. In order to determine the influence of the non-ionic surfactant (TX-100) and the anionic surfactant (SDS) and cationic surfactant (CTAB) and binary mixtures of solvent ethanol-water on acidity constants, a series of experiments were run at different TX-100, CTAB and SDS concentrations, above and below the critical micelle concentration (CMC) value of each surfactant. In this work the CMC values were obtained and presented at Table 1.

The principal component analysis of all absorption and fluorescence data matrices obtained at various pH value shows at least three significant factors that are also supported by the statistical indicators of Elbergali and et al [33]. These factors could be attributed to the two dissociations equilibria of a diprotic acid such as TRIAZ. Acidity constants of TRIAZ in several mixtures were evaluated the MATLAB environment using appropriate commands, singular value decomposition (svd command) using the corresponding spectral absorption-pH and fluorescence-pH data from inspection of the experimental spectra. The number of species involved guessing is hard. The three calculated most significant projection vectors with clear spectral features (as compared to the noise) reveal the presence of three spectroscopically and spectrofluorimetrically distinguishable components. From the output of the program 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 can be acquired and determined. The obtained pK_a values are listed in Table 2.

Table2. The Effect of surfactant concentration on pK_{a1} and pK_{a2} of TRIAZ at 25°C and I=0.1 M KNO_3 by two methods

Surfactants	[Surfactant]×10^{-4}(M)	pK_{a1}		pK_{a2}	
		UV	Em	UV	Em
None	---	2.71±0.13	2.93±0.14	5.04±0.25	5.07±0.32
SDS	0.20	3.55±0.17	3.54±0.22	5.42±0.21	5.43±0.27
SDS	1.2	3.53±0.14	3.53±0.15	6.03±0.24	6.21±0.31
SDS	5.1	3.84±0.19	3.65±0.21	6.36±0.31	6.44±0.35
SDS	10.5	4.98±0.24	3.76±0.18	6.53±0.13	6.31±0.31
SDS	31.0	5.91±0.29	5.13±0.25	8.41±0.47	8.55±0.43
CTAB	0.20	4.63±0.23	3.95±0.18	7.61±0.38	7.57±0.37
CTAB	1.2	4.37±0.22	3.59±0.17	7.47±0.21	7.27±0.36
CTAB	5.1	4.11±0.20	3.32±0.15	7.08±0.35	6.65±0.24
CTAB	10.5	3.75±0.18	3.08±0.21	6.31±0.31	5.97±0.29
CTAB	31.0	3.29±0.16	2.95±0.14	5.26±0.28	5.02±0.25
TX-100	0.2	4.32±0.22	3.92±0.19	8.38±0.41	8.34±0.28
TX-100	1.2	4.37±0.21	3.83±0.29	7.68±0.38	8.22±0.41
TX-100	5.1	3.86±0.19	3.87±0.28	7.45±0.37	8.49±0.32
TX-100	10.5	3.64±0.18	3.72±0.24	7.25±0.36	8.24±0.41
TX-100	31.0	3.92±0.19	3.44±0.17	7.45±0.37	8.59±0.43

Also in this work, we have determined the CMC value of surfactants by spectrophotometric and spectrofluorimetric methods. From the measurements of absorbance and fluorescence intensity of the dye solution; 2.5×10^{-5} M at different concentrations of surfactants in three buffer solutions (pH = 3.00, 7.50 and 9.00) at 25^{o}C and ionic strength of 0.1M KNO_3, the CMC values were obtained by drawing the absorbance and fluorescence intensity in the presence of different concentration surfactant at the maximum wavelength (e.g. emission at 420nm for SDS). The slope change in absorbance and fluorescence intensity above the CMC is also indicated the formation of larger units, i.e. micelles in solution. For all measurements, solutions were kept at 25 ± 0.1^{o}C using a thermostated cell Fig. 2. Results are shown in table one that has agreed with previous studies[35]. Also, the effect of surfactant concentrations (CTAB, SDS and TX-100) on pK_a of H_2L^{2+} were investigated at 25 (C and an ionic strength of 0.1 M KNO_3 spectrophotometrically and spectrofluorimetrically.

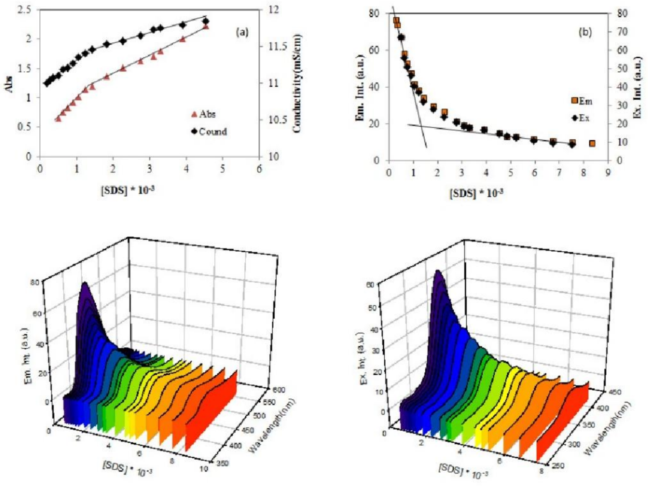

Fig. 2. Determination of CMC value by spectroscopically and spectrofluorimetrically for SDS in pH=7. 50, 0.1M KNO_3 and dye 2.5×10^{-5} M

2.1 Effect of SDS

An interesting property of SDS solutions is the interaction between dye and surfactant below and above the critical micelle concentration (CMC). Acidity constant values (pK_a) in five different concentrations of SDS are calculated and shown in table 1. The absorption and fluorescence emission spectra of solution containing 2.5×10^{-5} M relative to SDS and dye at different pH are shown in figure 3a and 3b respectively. Distribution diagram for solution containing 1.0×10^{-3} M SDS and 2.5×10^{-5} M TRIAZ dye is shown in Fig. 4.

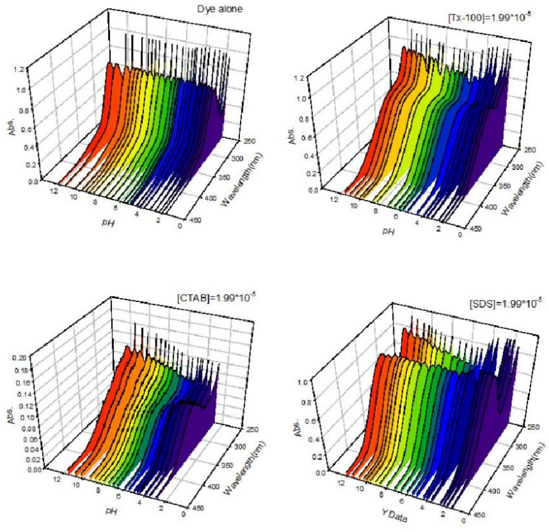

Fig. 3. pH effect on Absorbance of TRIAZ (2.5×10^{-5}M) in the absence and presence of three surfactants (1.99×10^{-5}M)

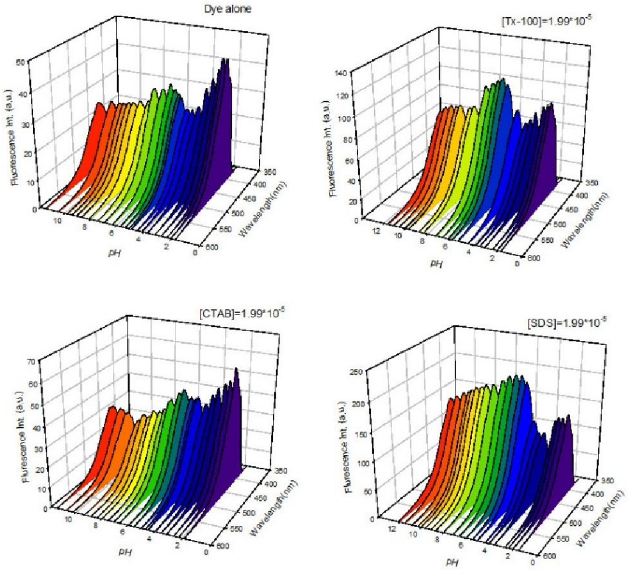

Fig. 4. pH effect on the fluorescence emission intensity of TRIAZ (2.5×10^{-5}M) in the absence and presence of three surfactants (1.99×10^{-5}M)

In addition, three pure spectra of three major species acquired from MCR-ALS are shown in figure 5. The results shown in table two clearly illustrate a relationship between the pK_a of two dissociation steps (first and second steps) increases with increasing concentration of SDS (Fig. 6a). There are electrostatic interactions between dye and surfactant. These interactions are attractions force so acidity constants of protonated form of TRIAZ (H_2L^{2+}) for first and second dissociation steps (pK_{a1}, pK_{a2}) with increasing the concentration of SDS, increases. This can be attributed to the attractive electrostatic interactions between the negatively charged species of SDS and positive protonated form of TRIAZ [36].

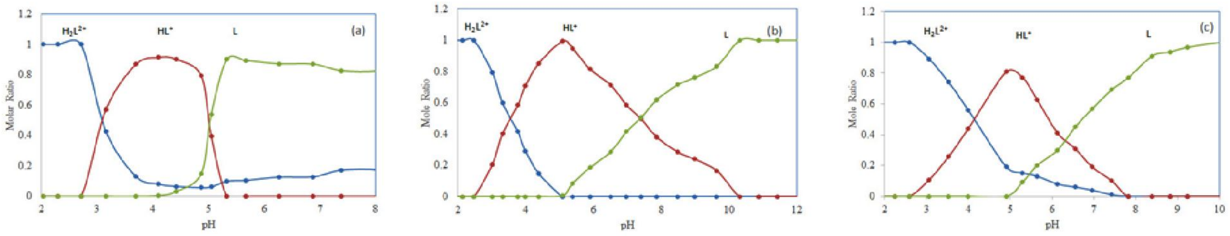

Fig. 5. Distribution diagrams of different species of TRIAZ, H_2L^{2+}(circle line), HL^+ (square line) and L(triangles line): a) fluorescence (em) of the TRIAZ (2.5×10^{-5}M), b) Absorption of TRIAZ (2.5×10^{-5}M) in the presence of CTAB(1×10^{-3}M), c) Absorption of TRIAZ (2.5×10^{-5}M) in the presence of SDS(2×10^{-5}M)

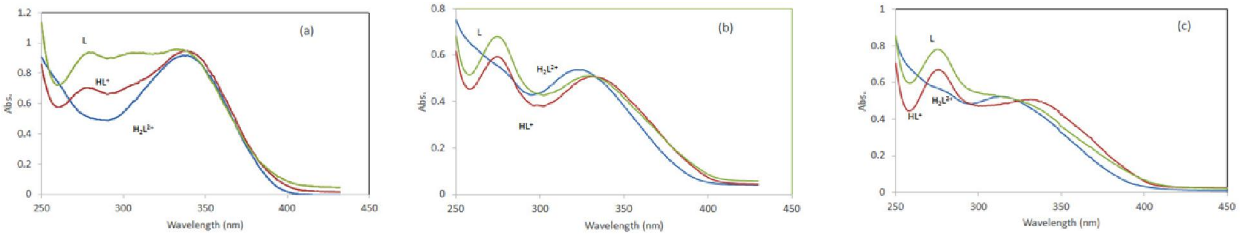

Fig. 6. Pure Spectra of TRIAZ species: a) Absorption of TRIAZ (2.5×10^{-5}M) in the presence of CTAB (1×10^{-3}M), b) Absorption of TRIAZ (2.5×10^{-5}M) in the presence of SDS (2×10^{-5}M), c) Absorption of TRIAZ (2.5×10^{-5}M) in the presence of TX-100 (2×10^{-5}M) spectra

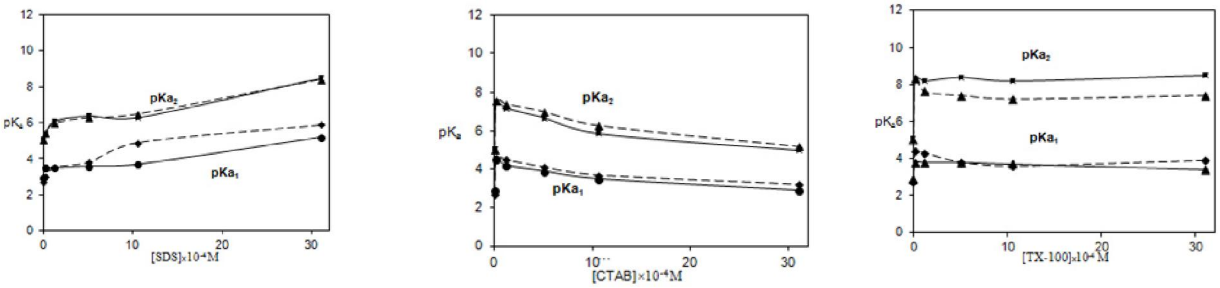

Fig. 7. Variation of acidity constant values of TRIAZ with different percentages of (a) SDS, (b) CTAB, (c) TX-100, were acquired spectrophotometrically(dash line) and spectrofluorimetrically(solid line)

2.2 Effect of CTAB

Acidity constant values (pK_a) were obtained in five different concentrations of CTAB. Results are presented in table tow and shown that with increasing of CTAB concentrations, pK_{a1} and pK_{a2} decreases (Fig 6b). This is due to electrostatic interactions (repulsion force) between H_2L^{2+}, HL^+ and CTAB. So pK_{a1} and pK_{a2} decreases with increasing CTAB concentrations.

2.3 Effect of TX-100

Acidity constant values (pK_a) obtained in five different concentrations of TX-100 are shown in table 2. TX-100 is a nonionic surfactant there are no electrostatic interactions between H_2L^{2+}, HL^+ and TX-100. The results clearly illustrate the TX-100 has no more effect on the dissociation equilibriums (Fig 6c).

3. Conclusion

In this work, we investigate the behavior of acidity constant one of the triazine derivative (TRIAZ), in pure water, water–TX-100, water–SDS and water–CTAB systems at 25 °C and an ionic strength of 0.1M KNO_3. This was carried by spectrophotometric and spectrofluorimetric methods. The effect of added common salt on the pK_a in the presence of surfactant was described. So we used constant concentration of common salt in all experiment (I=0.1 M KNO_3). We used the dilute dye solution, 2.5×10^{-5} M at different concentrations of surfactants, so we don't have dye aggregation. This is shown in Figure 2 that has no change in λ_{max} absorbance and florescence of dye at different concentration of surfactants. The pKa shifts have been attributed to the binding of the acid-base interaction with micellar, due to both electrostatic and hydrophobic interactions. The results shows that the variation of pK_a as a function of the concentration of surfactant depended on the hydrophobic transfer constant of the weak acid. This is shown that cationic amino group being stabilized through the formation of an ion-pair with an anionic sulphate head group. The results suggest that most acid-base equilibria which involve the protonation of a heterocyclic nitrogen group within the interfacial microenvironment of a SDS micelle are affected by specific molecular interactions between the anionic sulphate head groups and the cationic protonated nitrogen moieties. Depending on the sign of the micellar charge, shifts are positive or negative and are more noticeable as the hydrophobicity increases. Maxima or minima appear very close the cmc. The screening of the micellar charge leads to a decrease of pK_a, shifts. The experimental measurements for pK_a as a function of cationic, anionic and nonionic surfactants well accord and also been predicted with reported mechanism and model.[37, 38]

The chemometrics method with good reliability was applied for determination of dissociation constants and concentration and spectral profiles of the components from the experimental data. In this work we use for first time fluorescence excitation spectrum data to acquire acidity constant that were shown good correspondence with pK_a obtained from emission spectrum Uv-Vis spectrophotometric data. All results have good correspondence with together and previous investigations and can be used for improved investigations about triazine dye derivatives.

4. Experimental

4.1 Materials

TX-100, SDS, CTAB, hydrochloric acid, potassium hydroxide and potassium nitrate were analytical reagent grade purity (all from Merck). The Triazine dye derivative was synthesized and purified in laboratories of the research group of organic chemistry in Mazandaran University [39]. These reagents were used without further purification. Standard stock solution of 2.5×10^{-5}M of TRIAZ was prepared by dissolving appropriate amounts of TRIAZ in water. The stock solutions of surfactants were prepared by dissolving weighted amounts of substances in appropriate amounts of water. All the solutions were prepared in double distillated water.

4.2 Apparatus

A Carry300 (Varian) spectrophotometer and an Eclipse Varian spectrofluorimeter controlled by a computer and equipped with a one cm path length quartz cell were used for UV–Vis spectra, emission and excitation spectra acquisition respectively. A Metrohm720 pH-meter furnished with a combined glass-saturated calomel electrode which calibrated by three buffer solutions at pH 4.00, 7.00, and 9.00 respectively.

4.3 Computer Hardware and Software

All absorption spectra were digitized at one data point per nanometer in the wavelength 250-450 nm and excitation and emission spectra were obtained in 200-340 and 350-600 nm with excitation and emission slit is 2.5 nm respectively. The data transferred (in ASCII format) to a PC with Intel 5400 as CPU using XP operating system for subsequent analysis by MATLAB software, ver. 7.5 (The Math Works).

4.4 Spectrophotometric and Spectrofluorimetric Titration Methods

For a 2.5×10^{-5} M solution of TRIAZ absorption and fluorescence spectra were measured and titration setup controlled with a compute. All measurements were performed in pure water, water-TX-100, water-SDS, and water-CTAB. After each pH adjustment, the solution is transferred into the cavity and the absorption and fluorescence spectra are recorded. Ionic strength was maintained at 0.1M by adding appropriate amounts of KNO_3. All measurements were carried out at the temperature (25±0.5 ◦C).

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