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Cloud Point Extraction and Spectrophotometric Studies for the Extraction of Nigrosin and Aniline Blue Dyes using Mixed Micelles of TBAB and Triton X-114

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The extractions of two anionic dyes *viz.* nigrosin and aniline blue by cloud point extraction method using mixed micelles of tetrabutylammonium bromide (TBAB) and Triton X-114 were conducted. To get the greatest extraction efficiency, pH of the solution, surfactant concentration, concentration of electrolyte, equilibrium temperature and time were optimized. A linear calibration curve in the range of 0.567-9.07 mg/L (nigrosin) and 0.982-19.645 mg/L (aniline blue) was obtained. Limit of detection were found to be 2.45 ng/L and 2.008 ng/L for nigrosin and aniline blue dyes, respectively. Thermodynamic parameters were also calculated to establish the feasibility of the process. This method was then used to determine the dyes in tap and sea water samples. The extraction efficiency was explained in terms of dye surfactant interaction as shown by observed spectral changes between anionic dye and cationic surfactant followed by solubilization of the complex in non-ionic surfactant.

Keywords: Mixed micelles, Tetrabutylammonium bromide, Nigrosin, Aniline blue, Triton X-114.

INTRODUCTION

The long term exposure of toxic dyes leads to the acute and chronic effects on the human organisms. The sunlight that enters the water absorbs and prevents photosynthesis in aquatic plants [1]. The concentration of toxic dyes in the industrial effluents must therefore be monitored and an appropriate method of removing these toxic dyes should be adopted. Cloud point extraction (CPE) procedure is widely applied in the environmental analysis for the determination of dyes [2], metals [3] and other organic substances [4]. CPE utilizes low amounts of less toxic, non-volatile and non-flammable surfactants, unlike the other extraction techniques which involve highly toxic and volatile organic solvents [5]. In CPE, the surfactant goes through a phase separation into surfactant rich phase and aqueous phase, at a temperature greater than its critical temperature, called cloud point temperature. Consequently, the analytes are separated with high preconcentration factor into the surfactant rich phase.

To get maximum efficiency in separation and determination of the analyte, mixed micelles are used in CPE instead of single surfactant. The mixed micelle extraction involves the formation of ion-pair between the dye and oppositely charged surfactant and subsequent solubilization of the ion-pair in the micelles of non-ionic surfactant. Pourreza *et al*. [6] studied the determination of allura red and orange II in food samples using Triton X-114 and CTAB mixed micelles. The simultaneous extraction of erythrosine and tartrazine in food samples was reported using mixed micelles of TX-114 and CTAB [7].

In present work, cloud point extraction using mixed micelles of tetrabutylammonium bromide (TBAB) and Triton X-114 was applied to the preconcentration and spectrophotometric determination of two anionic dyes *viz.* nigrosin and aniline blue in aqueous solutions. The optimum conditions of pH, temperature, concentration and time of surfactants and salt on the extraction of dyes were established. The change in the thermodynamic parameters during CPE process, such as enthalpy, entropy and Gibbs free energy has also been determined. In addition, interactions of the dye molecules with cationic and non-ionic surfactant were also studied to reveal the ion-pair/dye-surfactant complex formation process between the anionic nigrosin, aniline blue dyes and cationic surfactant, TBAB using spectrophotometry.

EXPERIMENTAL

All the chemicals used were of analytical grade and the solutions were prepared by using double-distilled water. Stock solutions of 5×10^{-4} mol L^{-1} of nigrosin dye (Merck, India, *m.w.* 453.5) and 5×10^{-3} mol L^{-1} aniline blue dye (Merck, India, *m.w.* 799.8) were prepared. Aliquot solutions were obtained by appropriate dilutions of the stock solution; 10% w/v TX-114 (polyethylene glycol *tert*-octylphenyl ether, Sigma-Aldrich, USA); 10% w/v TBAB (tetrabutylammonium bromide, Merck, India); 30% w/v sodium chloride and sodium sulphate (Merck, India); acetate buffer solution of pH 4.8 and citrate buffer solution of pH 3.2 were prepared.

All absorbance measurements and spectra of nigrosin and aniline blue dyes were recorded using Shimadzu 1800 UV-Vis spectrophotometer. The pH meter 335 was used to measure the pH and centrifugation of the samples was done using Remi R-24 centrifugation. Thermostat was used to maintain the desired temperature. All the experiments were carried out in 15 mL calibrated centrifuge tubes.

Dye-surfactant interactions: Some of the forces that existed between dye molecules and surfactant aggregates are hydrophobic interactions, electrostatic interactions, hydrogen bonds, π-stacking and van der Waals forces [8-10]. Due to which there is a change in position and intensity of absorption spectra of the dye in the presence micellar system [11,12]. The interactions between the anionic dyes (nigrosin and aniline blue) with the cationic and non-ionic surfactants were studied by recording the spectra at different concentrations of surfactant while keeping the dye concentration constant. The concentration of cationic surfactant, TBAB was varied between 9.4×10^{-3} M to 992×10^{-3} M (CMC -250×10^{-3} mol L^{-1}) (Fig. 1) and the concentration of non-ionic surfactant, Triton X-114 was varied between 0.05×10^{-3} M to 0.4×10^{-3} M (CMC -0.2×10^{-3} mol L^{-1}) (Fig. 2).

The intensity of nigrosin and aniline blue dyes in TBAB was lower than in aqueous solution and as the concentration of TBAB increased the absorbance of nigrosin and aniline blue decreased in both pre-micellar and post-micellar region associated with a bathochromic shift in λ_{max} value. These changes in the absorption spectra of nigrosin and aniline blue in the presence of oppositely charged surfactant, TBAB suggests that

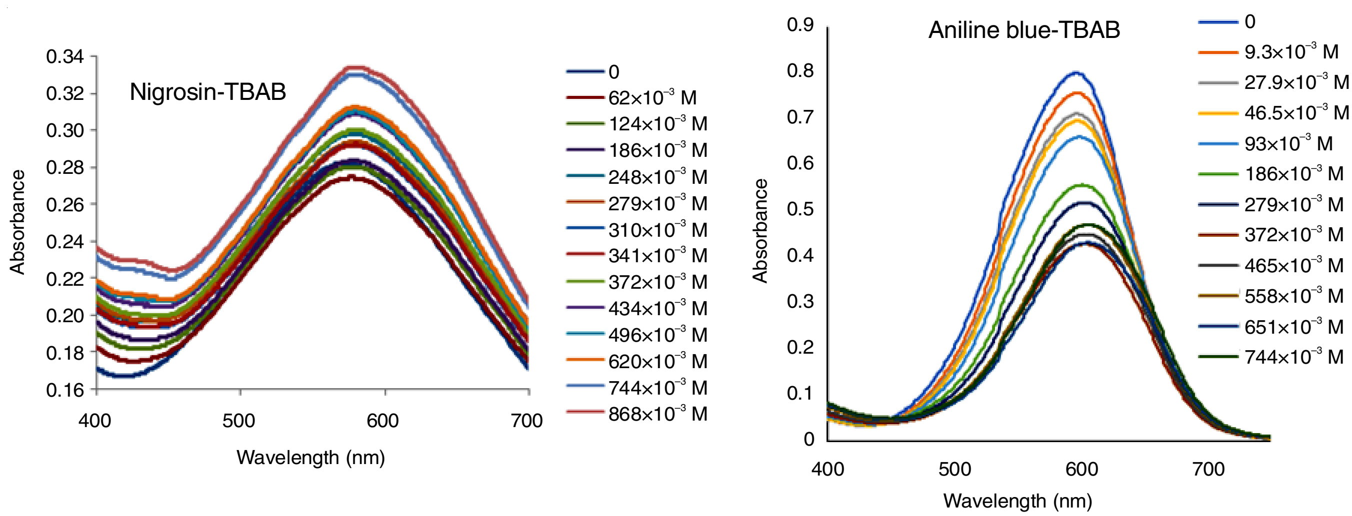

Fig. 1. Spectra of nigrosin and aniline blue dyes in different concentrations of TBAB

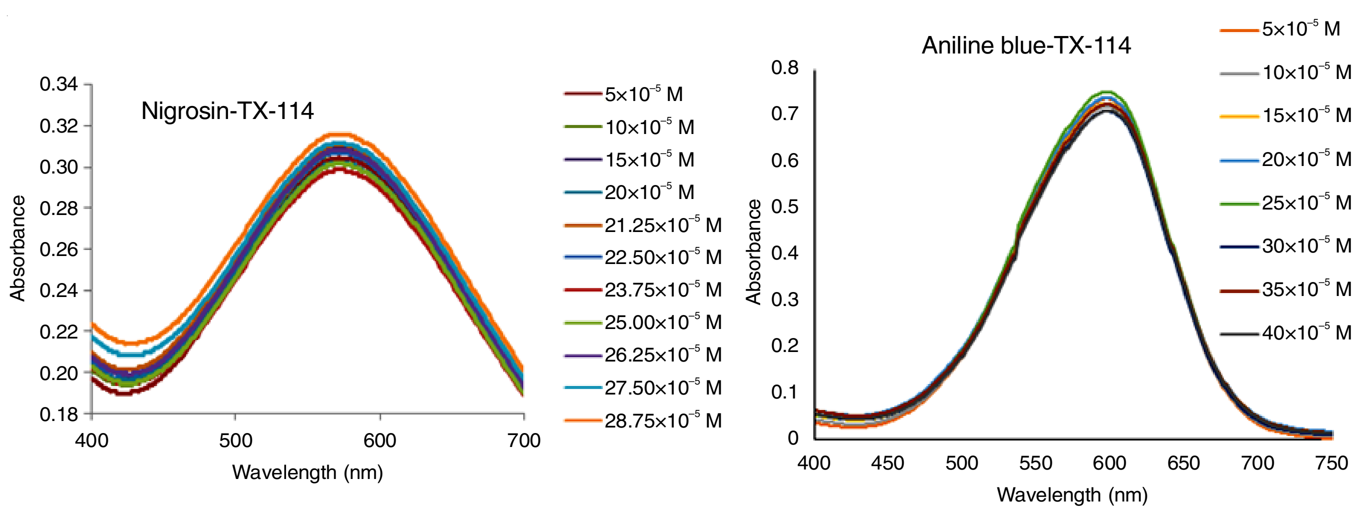

Fig. 2. Spectra of nigrosin and aniline blue dyes in different concentrations of Triton X-114

the aggregate species between dye and surfactant are either insoluble salts or less absorbing species. This indicates form atom of dye-surfactant complex between the dye and oppositely charged surfactant [13]. An increase in the λ_{max} values for both dyes also indicates dye surfactant complex formation.

Cloud point extraction: In a 15 mL tube, acetate buffer at pH 4.8, citrate buffer at pH 3.2 and corresponding concentrations of the dye standards (0.0 to 9.07 µg mL^{-1} of nigrosin dye and 0.0 to 19.645 µg mL^{-1} of aniline blue) were added. To this 10% w/v TBAB, 10% w/v TX-114, 30 % w/v Na_2SO_4 and NaCl double-distilled water have been added to set the solution to 10 mL and heated for 15 min, resulting into two-phase separation of the solution. Post-centric separation was then completed, followed by cooling in an ice bath for 15 min. The aqueous phase, which is the top layer, was decanted and the surfactant rich phase (SRP) dissolved in 20% methanol and the homogenized SRP was analyzed by UV-1800 spectrophotometer at a wavelength of 574 nm for nigrosin dye and 598 nm for aniline blue dyes to determine the amount of extracted dye. The analytical characteristics of nigrosin and aniline blue dyes are shown in Table-1.

TABLE-1
ANALYTICAL CHARACTERISTICS OF
NIGROSIN AND ANILINE BLUE DYE

Parameter	Nigrosin	Aniline blue
λ_{max} (nm)	574	598
Linear range (µg mL^{-1})	0.0-9.07	0.0-19.645
Slope	0.095	0.0581
Intercept	0.0	0.0
Correlation coefficient (R^2)	0.994	0.996
LOD (ng mL^{-1})	2.45	2.008
Pre-concentration factor	10.0	20.0
Phase volume ratio	0.11	0.05
Extraction efficiency (%)	96	80

RESULTS AND DISCUSSION

Nigrosin and aniline blue are anionic dyes, which are highly soluble in water. Aqueous solution of nigrosin and aniline blue show maximum absorbance at 574 and 598 nm in the visible region, respectively. To get the maximum extraction, the parameters which effect the extraction such as pH, concentration of surfactant, salt, temperature and time were optimized. Determination of nigrosin and aniline blue were performed at 574 and 598 nm, respectively spectrophotometrically.

Variation of pH: The impact of pH on the absorbance of nigrosin and aniline blue from the aqueous solution was studied in the pH range 3.0-5.6 using suitable buffers. Maximum absorbance was obtained at pH 3.2 for aniline blue and pH 4.8 for nigrosin dyes, respectively. Therefore, the extraction of nigrosin and aniline blue were carried out at this optimum pH for all the subsequent experiments (Fig. 3).

Variation of surfactant concentration (Triton X-114 and TBAB): Surfactant concentration plays an important role in phase separation. At low concentrations, the separation may be incomplete and at high concentrations, the surfactant rich phase becomes too viscous that leads to difficulty in measuring absorbance of the dye. Also increase in volume of micellar phase decreases the phase volume ratio which undesirable. The concentration of TX-114 was varied from 0.2% w/v to 3% w/v and the recoveries of the dye were recorded. Maximum recovery was obtained at 2.2% w/v (NG) and 2.5% w/v (AB) of TX-114 (Fig. 4a-b).

The absorbance spectra indicate the percentage formation of ion-pair complex, but anionic and cationic surfactant which might increase the efficiency of the process. These ion-pairs get extracted into the non-ionic surfactant, TX-114. The concentration of cationic surfactant, the optimization of TBAB range was thus between 0.04% w/v and 1.0% w/v, while maintaining constant TX-114 concentrations. In case of nigrosin dye and aniline blue dye w/v of TBAB, the regeneration also increased to 0.28 and 0.5% w/v as the concentrations increased gradually. Therefore, the optimal TBAB concentration was chosen for 0.28% w/v (aniline blue) and 0.5% w/v (nigrosin dye) (Fig. 4c-d).

Variation of salt: The effect of electrolytes were studied using various salts like, NaCl, Na_2SO_4, $NaNO_3$ and KBr. The electrolyte NaCl was choosen for nigrosin dye and Na_2SO_4 was choosen for aniline blue and found that the concentrations of NaCl and Na_2SO_4 were optimized in the range from 0.0 to 6.0% w/v. The recoveries of the dye increased as a function of NaCl and Na_2SO_4 concentration until 0.8% w/v and 1.2% w/v and then the recoveries were almost constant. Thus, the optimum concentrations of NaCl and Na_2SO_4 were found to be 0.8% w/v and 1.2% w/v, respectively (Fig. 5).

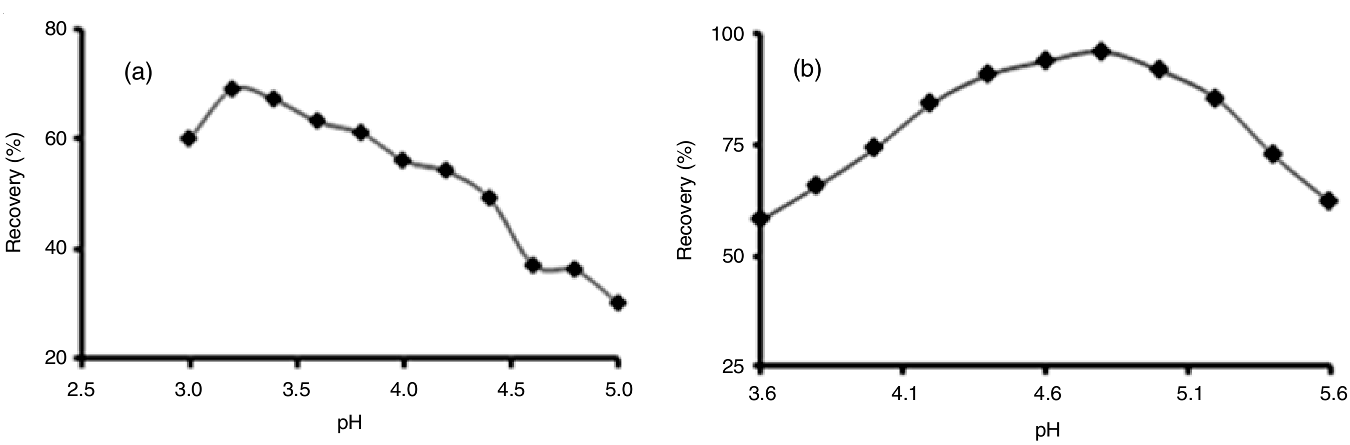

Fig. 3. Effect of pH on the recovery of aniline blue (a) and nigrosin dye (b)

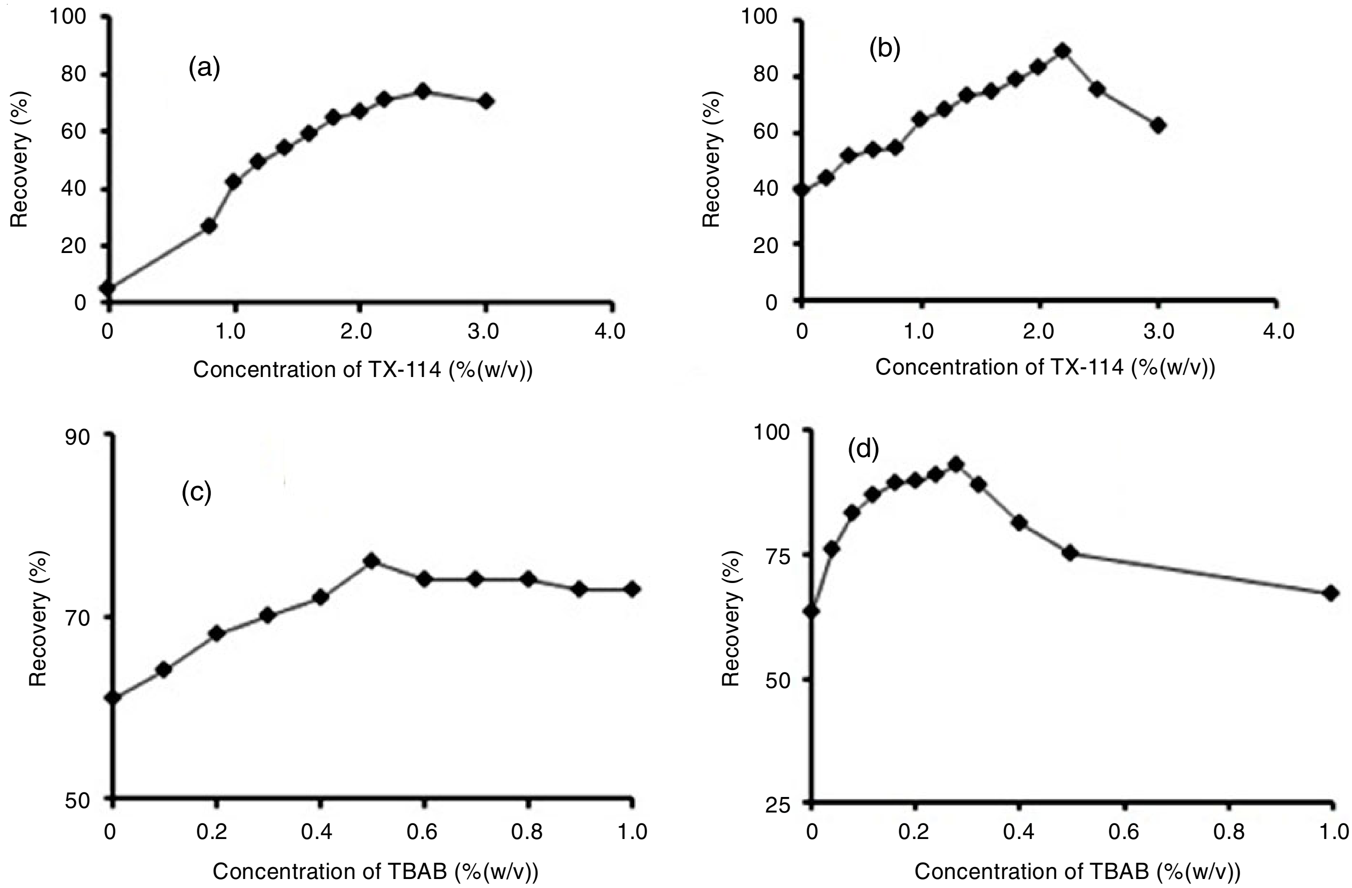

Fig. 4. (a) Effect of TX-114 on the recovery of the Aniline blue, (b) Effect of TX-114 on the recovery of the Nigrosin, (c) Effect of TBAB on the recovery of the Aniline blue, (d) Effect of TBAB on the recovery of Nigrosin

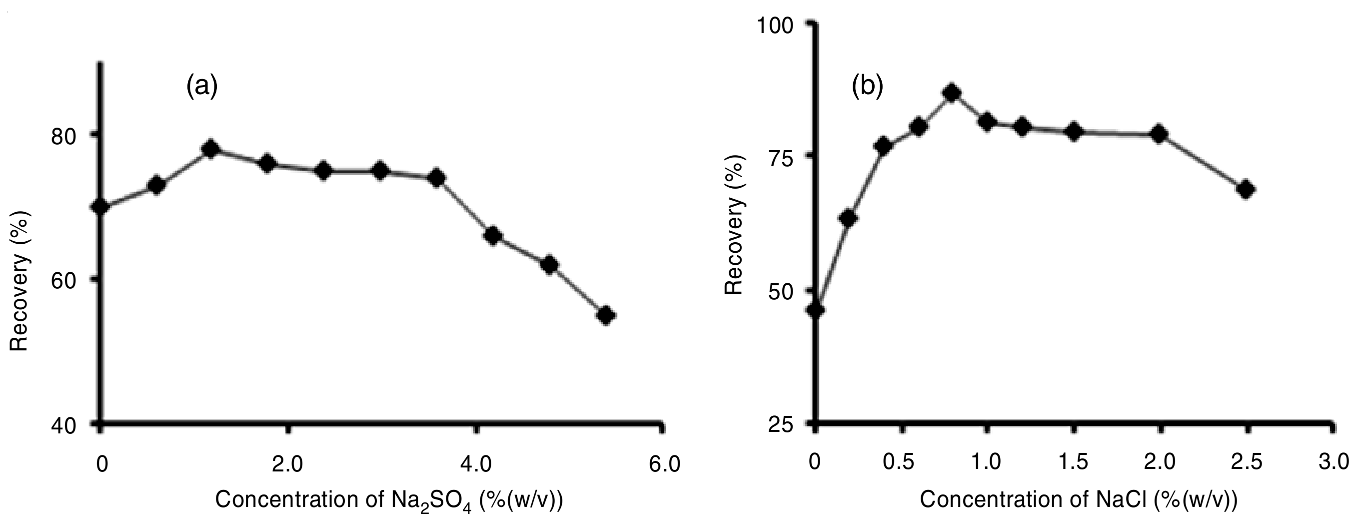

Fig. 5. Effect of Na_2SO_4 salt on the recovery of aniline blue (a) and NaCl salt on the recovery of nigrosin dye (b)

Variation of temperature and time: The optimization of the incubation temperature and time is necessary to obtain the easy separation of phases. The lowest incubation time possible and the shortest incubation time are desirable. The temperature effect was studied at a temperature range of 30-100 ºC and found that the extraction of such dyes is adequate for 70 ºC (nigrosin) and 60 ºC (aniline blue). The influence of incubation time in the range 5-60 min was also studied and a maximum recovery of 15 min was achieved.

Validation of the method: The developed mixed cloud-point extraction method was used to determine the level of nigrosin and aniline blue dyes in tap and marine water samples. It was found that the maximum recovery rate was 99% (Table-2).

Thermodynamic studies: The solubilization process for the extraction of nigrosin and aniline blue dyes was studied in the temperatures range of 303 to 343 K to evaluate the thermodynamic parameters like Gibb′s free energy (ΔG), enthalpy of

TABLE-2
DETERMINATION AND RECOVERY OF NIGROSIN AND ANILINE BLUE DYES IN THE ACTUAL SPECIMENS OF THE PRESENT METHOD

Dyes	Tap water			Sea water		
	Spiked (µg mL^{-1})	Detected (µg mL^{-1})	Recovery (%)	Spiked (µg mL^{-1})	Detected (µg mL^{-1})	Recovery (%)
Nigrosin	–	Not detected	–	–	Not detected	–
	3.40	3.23	95.0	3.40	3.36	98.8
	5.66	3.50	61.8	5.66	5.54	97.9
Aniline Blue	–	Not detected	–	–	Not detected	–
	3.93	3.72	94.6	3.93	3.91	99.5
	7.85	6.43	81.9	7.85	7.19	91.6

solubilization (ΔH), and entropy of solubilization (ΔS) using the following equations [14]:

$$\Delta G = \Delta H - T \times \Delta S$$

$$\log\left(\frac{q}{C_e}\right) = \frac{\Delta S}{2.303R} + \left(-\frac{\Delta H}{2.303RT}\right)$$

where q is the amount of dye solubilized per mole of surfactant

$$= \frac{C_m}{C_s} = \frac{C_o V_o - C_d V_d}{V_o C_s}$$

where C_m is the concentration of dye in surfactant rich phase (SRP); C_s is the surfactant concentration in SRP; C_o is the initial concentration of dye; V_o is the initial volume of the solution; C_d is the concentration of dye after phase separation; V_d is the volume of diluted SRP; C_e is the dilute phase equilibrium concentration of the dye (mol L^{-1}); q/C_e is the solubilization affinity; T and R have the usual meaning of temperature in Kelvin and gas constant in J K^{-1} mol^{-1}.

The ΔH and ΔS values were calculated from the slope and intercept of the line obtained from the plot of log (q/C_e) *versus* 1/T. The ΔG values at different temperatures were then calculated using these plots (Fig. 6). The nigrosin and aniline blue dyes value of ΔH and ΔS were 41.04 J, 26.52 J and 167.41 J/mol, 115.56 J/mol, respectively and -ΔG values obtained at temperatures 40, 50, 60 and 70 ºC were 52.36 & 35.04; 54.03 & 36.2; 55.71 & 37.35; 57.38 & 38.5 J mol^{-1} K^{-1}, respectively (Table-3). The positive enthalpy, the positive entropy and negative values of ΔG indicates that the process is spontaneous and thermodynamically favourable.

Conclusion

The cloud point extraction method using mixed micelles of TBAB and TX-114 for the determination of the anionic nigrosin and aniline blue dyes in different water samples was successfully developed to get maximum extraction efficiency of 96%. The increase in negative values of ΔG with increase in temperature indicates that the process was spontaneous and thermodynamically favourable for cloud point extraction (CPE). Changes in the absorption spectra of nigrosin and aniline blue dyes in cationic and non-ionic surfactants revealed the formation of dye-surfactant due to short range electrostatic interactions and subsequent solubilization of the complex in non-ionic surfactant due to long range hydrophobic interactions.

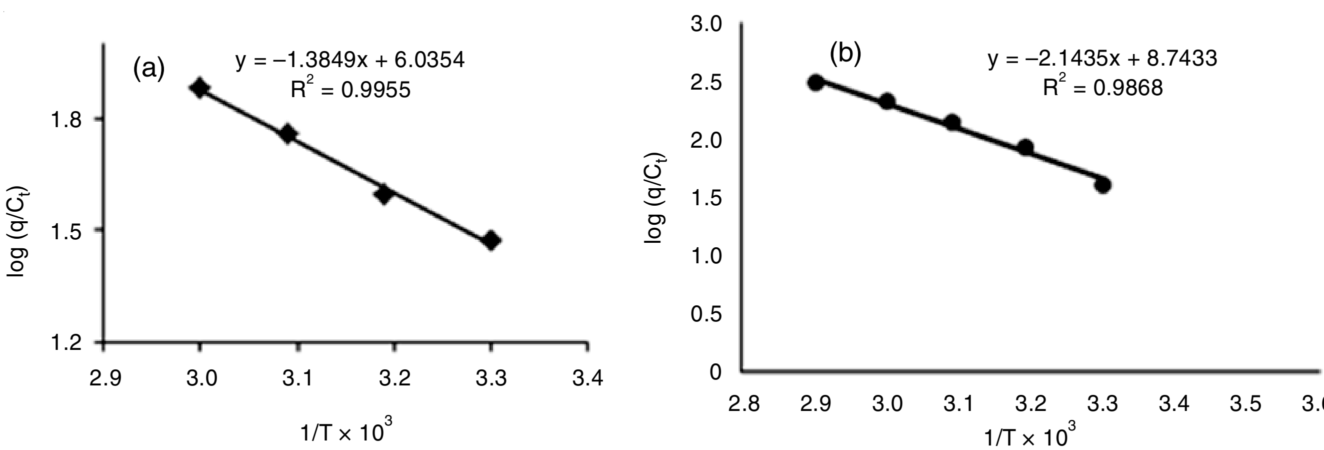

Fig. 6. A plot of log (q/C_e) *versus* 1/T for aniline blue dye (a) and for nigrosin dye (b)

TABLE-3
THERMODYNAMIC PARAMETERS OF NIGROSIN AND ANILINE BLUE DYES

Temp. (°C)	–ΔG (KJ/mol/K)		ΔH (J)		ΔS (J/mol)	
	Nigrosin	Aniline blue	Nigrosin	Aniline blue	Nigrosin	Aniline blue
40 ± 0.1	52.36	35.04	41.04	26.52	167.41	115.56
50 ± 0.1	54.03	36.2				
60 ± 0.1	55.71	37.35				
70 ± 0.1	57.38	38.5				

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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