Research Paper

Monitoring the Status of Anionic Surfactants in Various Water Systems in Urban and Rural Areas of Tirupati, Andhra Pradesh, South India

Kanchi S., Niranjan T., K. Babu Naidu, *Naidu Venkatasubba N.
*Department of Chemistry, S.V.University, Tirupati-517 502, A.P.,INDIA.

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Abstract: *Facile, rapid, sensitive and selective spectrophotometric method for the determination of traces anionic surfactants (AS) viz., Sodium lauryl sulfate (SLS), Sodium dodecyl sulfonate (SDS), Sodium hexadecyl sulfonate (SHS) and Sodium dodecyl benzenesulfonate (SDBS) in various water systems collected from Tirupati (urban and rural areas) city with cationic dye such as Azure-A and Azure- was described. The method was based on formation of the ionic pair anionic surfactant-AAandAB in acid medium (pH 3.0 and 4.0) to give colored derivatives with λ_{max} in the range 450 to 513 nm and were stable for more than 10 days at 35 ^{O}C. Beer's law was obeyed for AS-AAandAB in the concentration range of 0.03 –5.4 µg mL^{-1} at the wavelength of maximum absorption. The optimum reaction conditions and other analytical parameters were investigated to enhance the sensitivity of the present method. The detailed study of various interferences made the method more selective. The proposed method was successfully applied to the analysis of Sodium lauryl sulfate (SLS), Sodium dodecyl sulfonate (SDS), Sodium hexadecyl sulfonate (SHS) and Sodium dodecyl benzenesulfonate (SDBS) in various water systems (urbanandrural). The results obtained were agreed with the reported methods at the 95% confidence level. The performance of proposed method was evaluated in terms of Student's 't'-test and Variance ratio 'f'-test which indicates the significance of proposed method(time, easy and accuracy) over standard method (MBAS).*

Keywords: Anionic surfactants (AS), Azure-A(AA), Azure-B(AB), Spectrophotometer, Water systems.

Introduction

Anionic surfactants were reported as pollutants and their permissible limit in drinking water prescribed by the WHO is 1.0 ppm[1]. The main sources of the commonly used anionic surfactant sodium lauryl sulfate (SLS) and others, *viz.*, sodium dodecyl sulfonate (SDS), sodium hexadecyl sulfonate (SHDS) and sodium dodecyl benzenesulfonate (SDBS), in water bodies are household commodities and personal care products, *e.g.* detergents, soaps, shampoos and fabric and cosmetic materials. The level of surfactants in water bodies of densely populated countries such as India is increasing owing to the changes in lifestyle similar to western countries.

Many methods have been reported for the monitoring and analysis of anionic surfactants at trace level, among which the spectrophotometric methods are still

evocative in regular analysis. Almost all of the methods for the spectrophotometric analysis of anionic surfactants depend on the formation of a salt (ion pair associate) when dye cation reacts with anionic surfactants. Fytianos et al.,[2] developed a novel method for the analysis of anionic surfactants in various environmental samples with methylene blue and basic red and also studied the effect of salts on complexation. Acridine Organge was introduced as an analytical ligand for the determination of SDS in different water samples with spectrophotometric technique[3]. A novel spectrophotometric method for the determination of cationic surfactants (CS) by using a new reagent benzothiaxolyl diazoaminoazobenzene (BTDAB) was proposed in 0.06–0.10 M sodium hydroxide in the presence of Triton X-100 to analyze the anionic surfactants in various water systems[4]. Jurado et al.,[5] developed a simplified spectrophotometric method for determining anionic surfactants, based on the formation of

the ionic pair anionic surfactant-methylene blue (AS–MB) and its application to the study of primary biodegradation in aerobic screening tests. Solid-phase extraction (SPE) combined with liquid chromatography electrospray mass spectrometry (LC–(ESI) MS) was used to determine 16 non-ionic and anionic surfactants in different environmental water samples at ng l^{-1} levels[6] .

A new solid phase extraction methodology has been developed for the simultaneous determination of the most frequently used anionic surfactants – linear alkylbenzene sulfonates (LAS), alkyl ethoxysulfates (AES) and alkyl sulfates (AS) – in aqueous and sediment samples[7]. Spectrometric methods for the determination of anionic surfactants (A Surf) in natural and waste water using silica gel (SG) loaded with ion-pair associates of high molecular weight quaternary ammonium salts (QAS) and anionic dyes were developed by Zaporozhets et al.[8]. New automated procedure for preconcentration and analysis of anionic surfactants in water using solid-phase extraction (SPE) in a flow injection (Fl) system together with an UV-vis detection was reported [9].

Simple and specific flow injection analysis (FIA) procedure for the determination of anionic surfactants, *viz.*, sodium lauryl sulfate (SLS), sodium dodecyl sulfonate, sodium hexadecyl sulfonate and sodium dodecyl benzenesulfonate, with cationic dyes, *viz.*, Brilliant Green (BG), Malachite Green, Methylene Blue, Ethyl Violet and Crystal Violet, in water bodies, *viz.*, ponds, tube wells, rivers and municipal wastes, of central India (east Madhya Pradesh) was discussed using spectrophotometer[10]. An analytical method was proposed in order to determine the major nonionic surfactants, octylphenol polyethoxylates (OPEOs), nonylphenolpolyethoxylates (NPEOs) and aliphatic alcoholpolyethoxylates (AEOs), and their metabolites, nonylphenol and octylphenol in wastewater and sludge samples of sewage treatment plants[11].

The above reported methods suffer from poor sensitivity, selectivity, stability of the color derivative[2,3,5] and used highly sophisticated instrumentation[6,8,9] for the monitoring and determination of anionic surfactants in various environmental samples. Water pollution due to anionic surfactants is a matter of serious disquiet in rural areas, because the people in rural areas drink either surface water such as pond or river or openwell or borewell water directly without proper treatment. They wash their clothing etc. directly in the pond water thereby causing surfactant pollution in the surface water. So, it is desirable to develop simple, highly sensitive, reliable and rapid method for the determination of anionic surfactants in various water systems.

In the present study, we reported simple, sensitive, selective and rapid method for the determination of traces of anionic surfactants. The implied reaction was ion pair associated reaction between cationic dyes (AA, AB) and anionic surfactant (SLS, SDS, SHS and SDBS) in acidic medium. The method was successfully employed for the determination of AS in different water samples collected from various parts of Tirupati(urban and rural ares), Andhra Pradesh, South India.

Material and Methods

A HITACHI model U 3400 UV VIS NIR Spectrophotometer with 10 mm stopped glass cells was used. An ELICO model *Li-129* was used for all pH measurements. All chemicals used were of analytical reagent grade and deionised-double distilled water was used to prepare all solutions through out experiments. Cationic dyes, Azure-A and Azure-B were purchased from SD Fine Chemicals (Mumbai, India) and used without further purification. These cationic dyes were dissolved in distilled water to give 0.001 M solutions. Sodium lauryl sulfate (SLS), Sodium dodecyl sulfonate (SDS), Sodium hexadecyl sulfonate (SHS) and Sodium dodecyl benzenesulfonate (SDBS) are the anionic surfactants (SD Fine Chemicals (Mumbai, India) used in the present investigation. Accurately weighed amount of AS (purity 99.5%) was dissolved in distilled water to give 0.00003 M stock solution.

Surface, ground, borewells, openwells and open municipal waste water samples from Tirupati, a famous pilgrim town in South India, situated on the longitude of $79^{o}27$ E, latitude of $13^{o}40'$N and at a height of 500 ft above mean sea level. The city has a population of about 1,800, 000 and more than 10 million pilgrims visit annually this temple town. There are more than 1200 open and borewells which serve as secondary source of drinking water since the water from the municipal supply is inadequate. The sampling points for these samples were rural, urban, semi-urban and industrial areas. The samples were collected in 100 mL polyethylene and filtered with Whatman No. 42 filter-paper and stored in a refrigerator at 4 °C.

General procedure

Sample solution (100 mL) containing anionic surfactants (AS) with concentration (0.00003 M) was transfer into a separating funnel. Cationic dyes, Azure-A, Azure-B and 10 M HCl were added followed by 10 mL of chloroform and adjusting the whole solution pH 3.0 for Azure-A and 4.0 for Azure-B. The content was shaken for 3 min and allowed to settle for 5 min. The aqueous layer was separated and discarded. The organic layer was collected and 2.5 mL of this solution was directly used for absorption measurement in the range of wavelength (λ_{max}) 450 to 513 nm as shown in Scheme 1 against reagent blank.
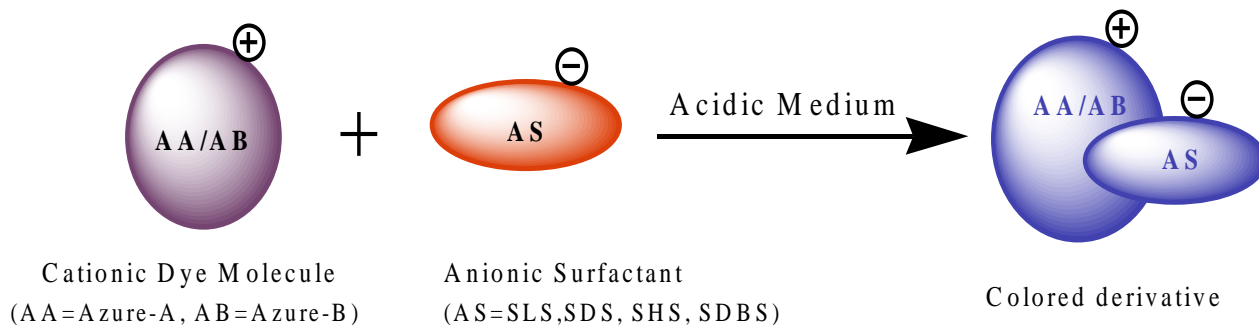
Scheme 1: Ion pair associated reaction of Azure-A and Azure-B with Anionic surfactant (AS) to form a colored derivative

Table 1a
Optical characteristics of ion pair associated mixture (Azure-A -Anionic surfactant) and precision data

Optical characteristics	Anionic surfactants(AS)			
	SLS	SDS	SHS	SDBS
Color	Pale orange	Reddish orange	Red	Orange
λ_{max}[nm]	450	480	510	465
Stability	11 days	10 days	15 days	17 days
Beer's law range [$\mu g\ mL^{-1}$]	0.02-3.4	0.016-3.2	0.022-3.3	0.025-3.9
Molar absorptivity [$L\ mol^{-1}\ cm^{-1}$]	2.95×10^4	2.62×10^4	2.71×10^4	2.84×10^4
Sandell_s sensitivity [$\mu g\ cm^{-2}$]	0.00249	0.00251	0.00230	0.00245
Regression equation (Y^b)				
Slope[a]	0.18600	0.019423	0.16710	0.17298
Intercept[b]	0.0151	0.0164	0.0142	0.0159
Correlation coefficient [r]	0.99981	0.99980	0.99987	0.99980
Relative standard deviation [%][c]	0.8845	0.8642	0.8529	0.8217
Range of error (95% confidence level)	±1.2353	±1.2561	±1.2719	±1.2932
Detection limit [$\mu g\ mL^{-1}$]	0.0171	0.0168	0.0162	0.0170
% Error	0.1225	0.1220	0.1221	0.1228

[a]*Experiments performed under optimized conditions (see text),* [b]*Y = ax + b, where x is the concentration of anionic surfactants(AS) in $\mu g\ mL^{-1}$,* [c] *n = 6.*

Table 1b
Optical characteristics of ion pair associated mixture (Azure-B-Anionic surfactant) and precision data

Optical characteristics	Anionic surfactants(AS)			
	SLS	SDS	SHS	SDBS
Color	Orange	Pale Red	Violet	Purple
λ_{max}[nm]	460	490	505	513
Stability	11 days	10 days	15 days	17 days
Beer's law range [$\mu g\ mL^{-1}$]	0.02-3.0	0.019-3.4	0.020-3.6	0.027-3.7
Molar absorptivity [$L\ mol^{-1}\ cm^{-1}$]	2.91×10^4	2.73×10^4	2.65×10^4	2.80×10^4
Sandell_s sensitivity	0.00252	0.00264	0.00229	0.00235

$[\mu g\ cm^{-2}]$				
Regression equation (Y^b)				
Slope[a]	0.17420	0.018503	0.15035	0.16188
Intercept[b]	0.0160	0.0152	0.0179	0.0144
Correlation coefficient [r]	0.99990	0.99982	0.99980	0.99987
Relative standard deviation [%][c]	0.8871	0.8742	0.8630	0.8842
Range of error (95% confidence level)	±1.2452	±1.2639	±1.2831	±1.2990
Detection limit [$\mu g\ mL^{-1}$]	0.0173	0.0170	0.0175	0.0169
% Error	0.1232	0.1222	0.1241	0.1230

[a]*Experiments performed under optimized conditions (see text),* [b]*$Y = ax + b$, where x is the concentration of anionic surfactants(AS) in $\mu g\ mL^{-1}$,* [c]*n = 6.*

Table 2
Effect of co-existing ions on the determination of anionic surfactants (SLS, SDS, SHS and SDBS)

Co-existing ions	Maximum tolerance limits($\mu g\ L^{-1}$)
NO_3^-	200
As^{5+}	8
Ni^{2+}	10
Fe^{3+}	70
Fe^{2+}	70
Zn^{+2}	15
Cu^{+2}	15
SO_4^-	300
Ca^{2+}	150
As^{3+}	10
Hg^{2+}	15
Cr^{+6}	15
Humic acid	20
Phenol	150
Endosulfan	20

Table 3a
Determination of surfactants using Azure-A(AA) from spiked water samples and compared with standard method

Surfactants	Present method					Standard Method[12]	
	Azure-A						
	Added ($\mu g\ l^{-1}$)	Found ($\mu g\ l^{-1}$)	Recovery(%)[a]	t-test[b]	f-test[c]	Found ($\mu g\ l^{-1}$)	Recovery(%)[a]
Sodium lauryl sulfate	1.0	0.98	98.00	7.75	2.10	0.99	99.00
Sodium dodecyl sulfonate	1.0	0.99	99.00	2.70	0.33	0.98	98.00
Sodium hexadecyl sulfonate	1.0	0.97	97.00	0.95	0.25	0.98	98.00
Sodium dodecyl benzenesulfonate	1.0	0.98	98.00	4.20	1.40	0.98	98.00

[a]n=6, [b]P≥0.000284, [c]P= 0.059.

Table 3b
Determination of surfactants using Azure-B(AB) from spiked water samples and compared with standard method

Surfactants	Present method					Standard Method[12]	
	Azure-A						
	Added (µg l^{-1})	Found (µg l^{-1})	Recovery(%)[a]	t-test[b]	f-test[c]	Found (µg l^{-1})	Recovery(%)[a]
Sodium lauryl sulfate	1.0	0.99	99.00	4.75	0.15	0.98	98.00
Sodium dodecyl sulfonate	1.0	0.98	98.00	5.88	1.00	0.99	99.00
Sodium hexadecyl sulfonate	1.0	0.98	98.00	0.92	0.40	0.99	99.00
Sodium dodecyl benzenesulfonate	1.0	0.97	97.00	2.34	0.38	0.98	98.00

[a]n=6, [b]$P \geq 0.000284$, [c]$P = 0.059$

Table 4
Analytical data for the determination of surfactant in surface and ground water samples collected from Tirupati(urban and rural areas) city, Andhra Pradesh, India

Surfactants	Surface water samples No.	Concentration of surfactants in µg L^{-1}	
		Azure-A	Azure-B
Sodium lauryl sulfate			
SLS1	SWS1	10.00	11.00
SLS2	SWS2	16.00	16.00
SLS3	SWS3	35.00	34.00
SLS4	SWS4	24.00	23.00
Sodium dodecyl sulfonate			
SDS1	SWS5	40.00	38.00
SDS2	SWS6	55.00	54.00
SDS3	SWS7	62.00	62.00
SDS4	SWS8	30.00	30.20
Sodium hexadecyl sulfonate			
SHS1	SWS9	7.00	7.00
SHS2	SWS10	2.00	3.00
SHS3	SWS11	49.00	49.40
SHS4	SWS12	4.00	5.00
Sodium dodecyl benzenesulfonate			
SDBS1	SWS13	22.00	22.49
SDBS2	SWS14	17.00	17.50
SDBS3	SWS15	9.00	9.00
Ground water samples			
Sodium lauryl sulfate			
SLS1	GWS1	19.00	19.20
SLS2	GWS2	4.00	4.100
SLS3	GWS3	10.00	10.00
SLS4	GWS4	42.00	41.00
Sodium dodecyl sulfonate			
SDS1	GWS5	20.00	19.58
SDS2	GWS6	37.00	36.70
SDS3	GWS7	11.00	10.00
SDS4	GWS8	3.00	2.98
Sodium hexadecyl sulfonate			
SHS1	GWS9	33.00	32.47

SHS2	GWS10	25.00	25.90
SHS3	GWS11	27.00	27.00
SHS4	GWS12	6.00	5.50
Sodium dodecyl benzenesulfonate			
SDBS1	GWS13	23.00	23.10
SDBS2	GWS14	18.00	17.90
SDBS3	GWS15	40.00	40.00
SDBS4	GWS16	9.00	8.54

Table 5
Concentration of surfactant in borewell and openwell water samples collected from Tirupati(urban and rural areas) city, Andhra Pradesh, India

Surfactants	Borewell samples No.	Concentration of surfactants in µg L^{-1}	
		Azure-A	**Azure-B**
Sodium lauryl sulfate			
SLS1	BWS1	190.00	190.50
SLS2	BWS2	98.00	98.00
SLS3	BWS3	75.00	74.33
SLS4	BWS4	69.00	68.95
Sodium dodecyl sulfonate			
SDS1	BWS5	31.00	30.00
SDS2	BWS6	74.00	74.30
SDS3	BWS7	69.00	68.54
SDS4	BWS8	70.00	71.00
Sodium hexadecyl sulfonate			
SHS1	BWS9	112.00	112.20
SHS2	BWS10	23.00	24.50
SHS3	BWS11	49.00	48.53
SHS4	BWS12	58.00	57.74
Sodium dodecyl benzenesulfonate			
SDBS1	BWS13	71.00	70.00
SDBS2	BWS14	35.00	34.44
SDBS3	BWS15	46.00	46.00
Openwell water samples			
Sodium lauryl sulfate (SLS)			
SLS1	OWS1	130.00	130.10
SLS2	OWS2	427.00	427.00
SLS3	OWS3	170.00	171.00
SLS4	OWS4	141.00	141.30
Sodium dodecyl sulfonate			
SDS1	OWS5	82.00	81.90
SDS2	OWS6	38.00	38.00
SDS3	OWS7	89.00	88.00
SDS4	OWS8	100.00	101.00
Sodium hexadecyl sulfonate			
SHS1	OWS9	24.00	23.55
SHS2	OWS10	40.00	40.10
SHS3	OWS11	36.00	35.79
SHS4	OWS12	22.00	22.00
Sodium dodecyl benzenesulfonate			
SDBS1	OWS13	49.00	49.05

SDBS2	OWS14	75.00	74.77
SDBS3	OWS15	41.00	40.09
SDBS4	OWS16	28.00	27.03

Table 6
Concentration of surfactant in open municipal drainage waste water samples collected from Tirupati(urban and rural areas) city, Andhra Pradesh, India

Surfactants	Open municipal drainage waste water samples No.	Concentration of surfactants in $\mu g\ L^{-1}$	
		Azure-A	Azure-B
Sodium lauryl sulfate			
SLS1	OMDWWS1	50.00	50.00
SLS2	OMDWWS2	147.00	146.70
SLS3	OMDWWS3	98.00	99.20
SLS4	OMDWWS4	293.00	292.10
Sodium dodecyl sulfonate			
SDS1	OMDWWS5	72.00	72.04
SDS2	OMDWWS6	632.00	631.90
SDS3	OMDWWS7	309.00	308.99
SDS4	OMDWWS8	241.00	240.00
Sodium hexadecyl sulfonate			
SHS1	OMDWWS9	283	283.01
SHS2	OMDWWS10	720.00	720.00
SHS3	OMDWWS11	541.00	541.44
SHS4	OMDWWS12	135.00	135.49
Sodium dodecyl benzenesulfonate			
SDBS1	OMDWWS13	485.00	484.90
SDBS2	OMDWWS14	440.00	440.20
SDBS3	OMDWWS15	664.00	663.71

Results and Discussion

The absorption spectra of the ion associate formed between the SDS and the cationic dyes in chloroform obtained by the aforesaid procedure. The absorption spectra of these ion associates were different from one another and the maximum absorbances of Azure-A(AA) with Sodium lauryl sulfate (SLS), Sodium dodecyl sulfonate (SDS), Sodium hexadecyl sulfonate (SHS) and Sodium dodecyl benzenesulfonate (SDBS) were 450 nm, 480 nm, 510 nm and 465 nm respectively. Similarly Azure-B(AB) associated ion pair complexes gives maximum absorption at 460 nm, 490 nm, 505 nm and 514 nm with Sodium lauryl sulfate (SLS), Sodium dodecyl sulfonate (SDS), Sodium hexadecyl sulfonate (SHS) and Sodium dodecyl benzenesulfonate (SDBS) respectively, where the absorbance of the reagent blank was very small and the calibration graph was constructed as shown in Figures 1a and 1b. Shaking time was a vital parameter to establish a dynamic equilibrium between aqueous and organic phases. In view of this effect of shaking time was considered into the present investigation. The effect of the shaking time was examined by varying the time from 0.5 to 5 min. The absorbances obtained remained constant with shaking for more than 5 min. Therefore, 3 min extraction time was recommended for further studies. In order to establish the optimum conditions necessary for a rapid and quantitative formation of the colored product with maximum stability and sensitivity, the investigators measured the absorbance of a series of solutions by varying one and fixing the other parameters at maximum wavelength. It was found that a 0.001 M solution of Azure-A and Azure-B in the range of 2.0–4.0 mL and 3.0 to 6.0 mL respectively , 0.00003 M solution of SLS, SDS, SHS and SDBS in the range of 5.0–10.0 mL were necessary to achieve the maximum color intensity of the ion pair associated complex (Figures 1a and 1b). The color intensity decreased below the lower limit and above the upper limit, and a red colored product was unstable. Therefore, 3.0 mL of Azure-A and 5.0 mL of Azure-B and 8.0 mL of anionic surfactants (SLS, SDS, SHS and SDBS) solution were recommended for all measurements. The ion pair associated reaction between cationic dyes (AA, AB) and anionic surfactants (SLS, SDS, SHS and SDBS) were found to be instantaneous. However, the effect of temperature on the product was studied at different temperature, it was found that the colored product was stable for more than 10 days in the temperature range of 25–40°C. So, the temperature of 35°C was selected as optimum for maximum color development.
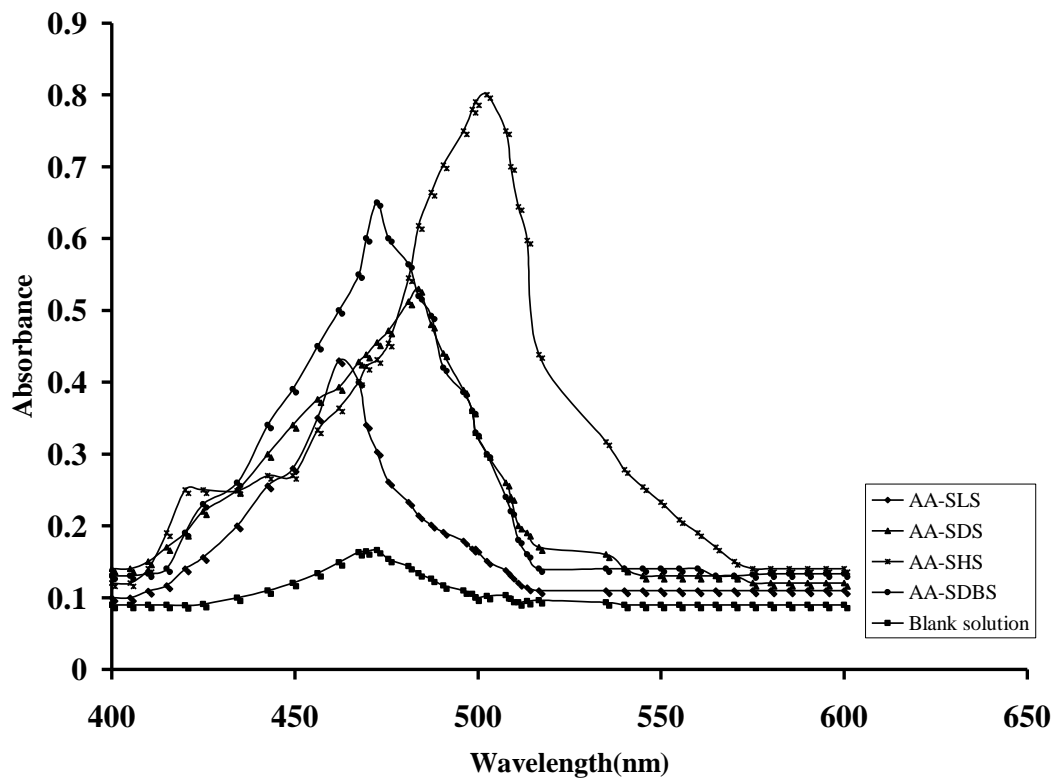
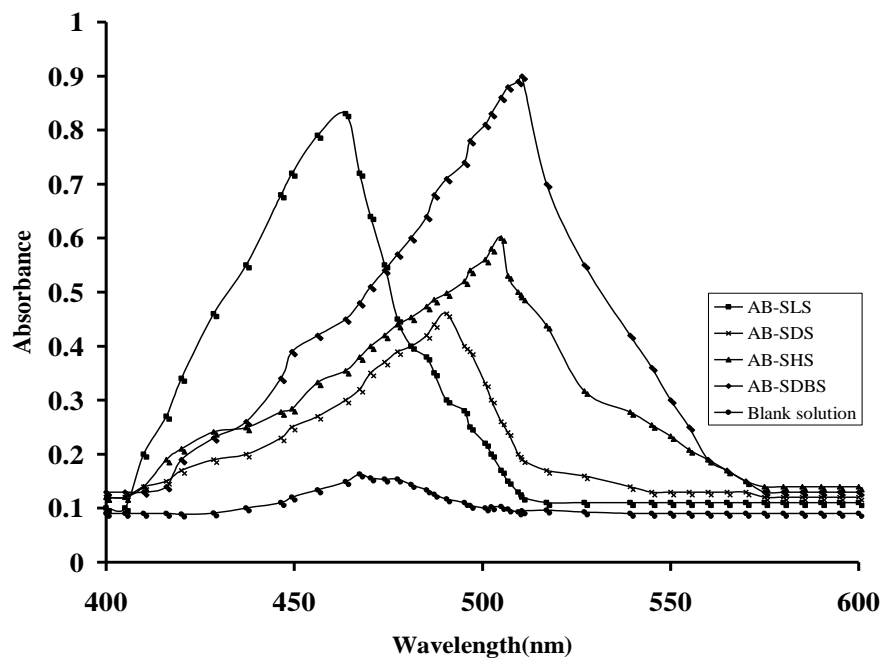**Figure 1a: Absorption spectrum of Azure-A(AA) with anionic surfactants(AS) against reagent blank solution**

Figure 1b: Absorption spectrum of Azure-B(AB) with anionic surfactants(AS) against reagent blank solution
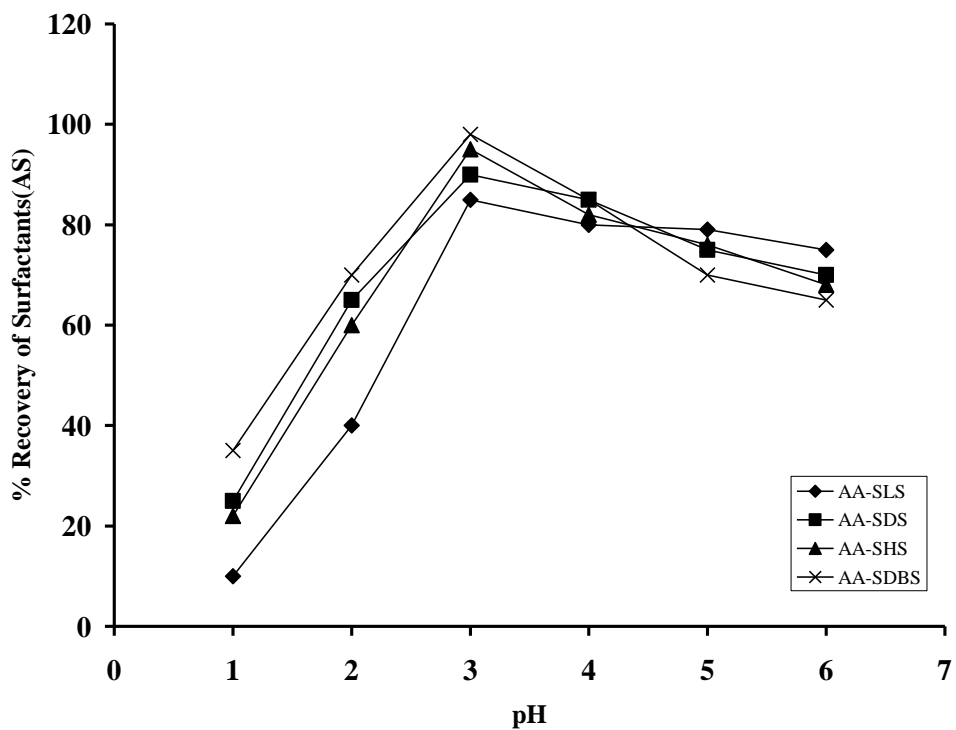
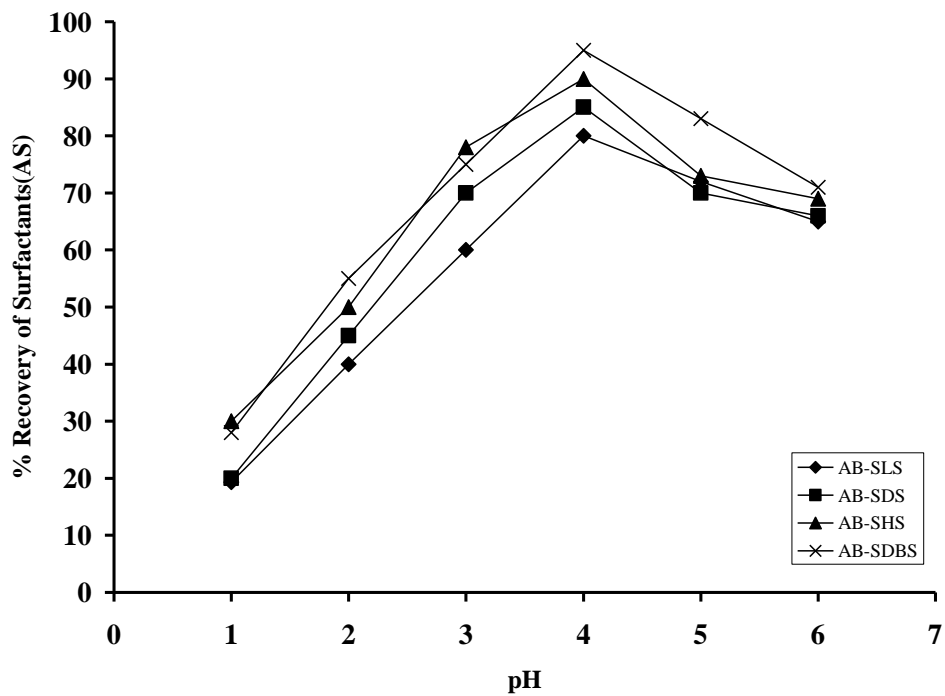**Figure 2a: Effect of pH on recovery of anonic surfactants (AS) with Azure-A (AA)**

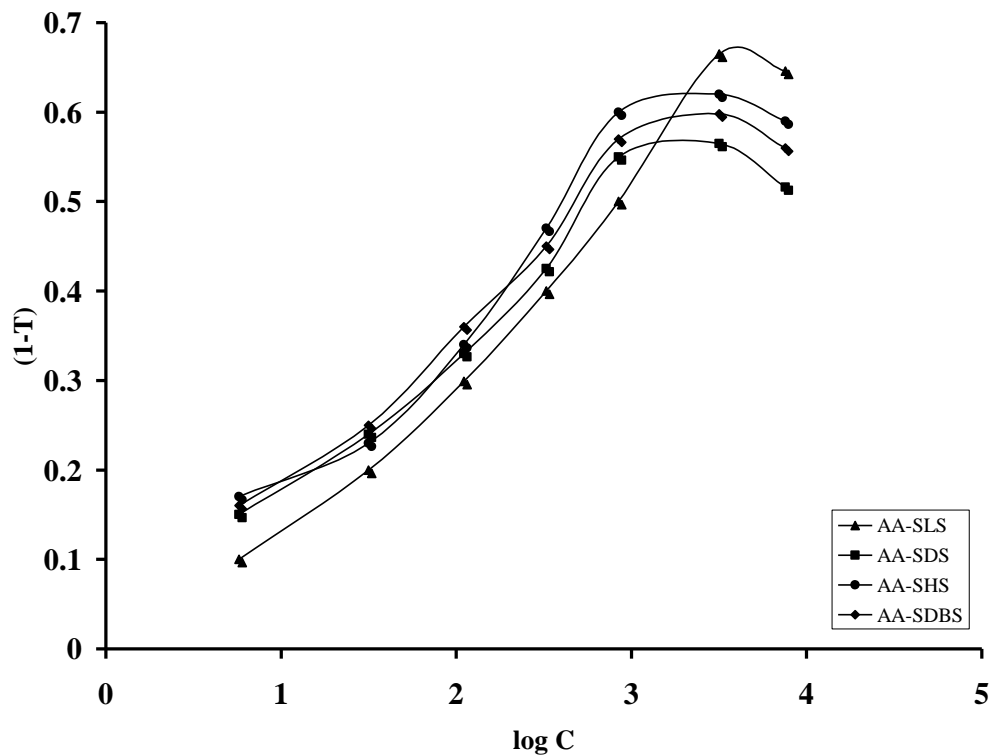**Figure 2b: Effect of pH on recovery of anonic surfactants(AS) with Azure-B(AB)**

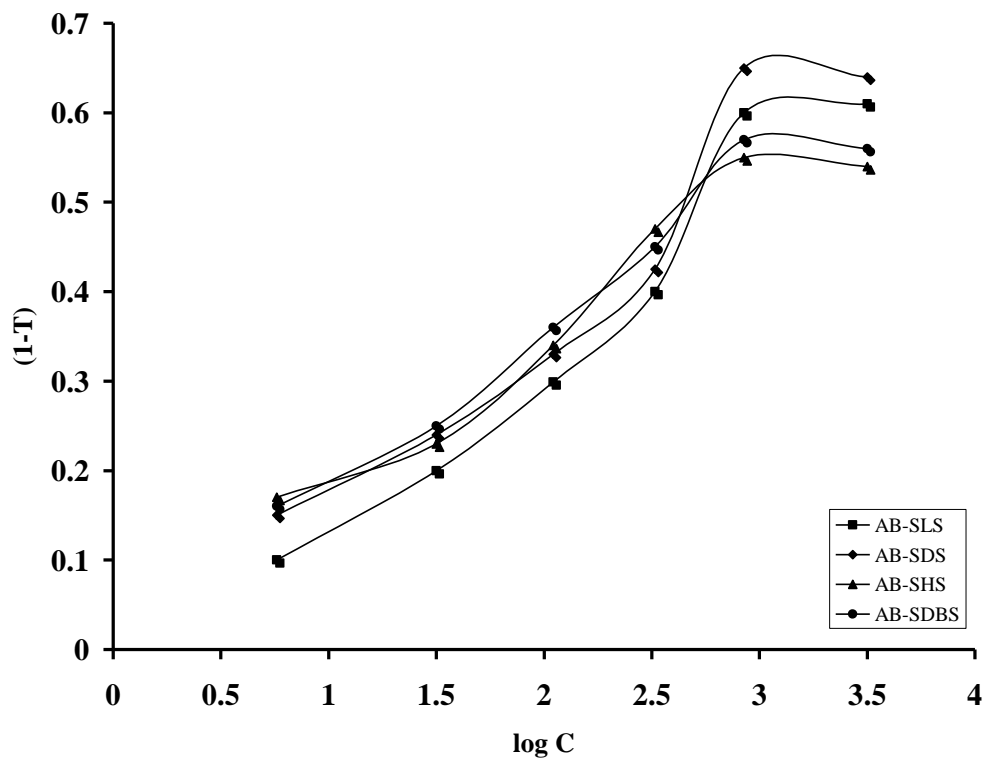**Figure 3a: Ringbom plot for ion pair associated complex of Azure-A(AA) with anonic surfactants(AS)**

Figure 3b: Ringbom plot for ion pair associated complex of Azure-B (AB) with anonic surfactants(AS)
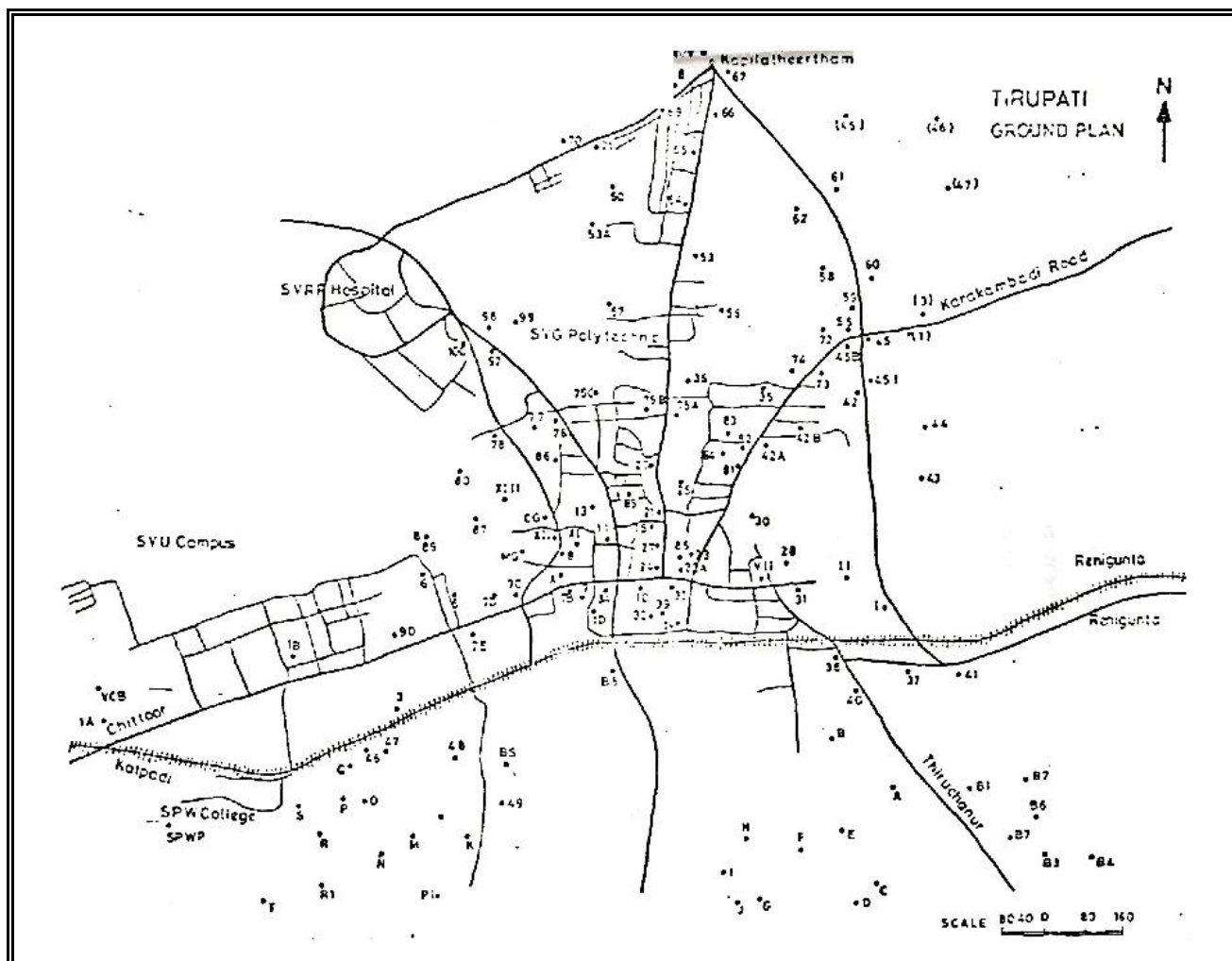
Figure 4: Statistical sampling map of Tirupati, Andhra Pradesh, India

The effect of pH on the ion association of cationic dyes (AA, AB) with anionic surfactants (SLS, SDS, SHS and SDBS) was studied and shown in Figures 2a and 2b. The optimum pH range was between 1.0 and 5.0 for the both cationic dyes (AA and AB). The pH of the solutions was adjusted with hydrochloric acid or sodium hydroxide solution to avoid the interference from anions intermixed. Therefore, a pH 3.0(AA-AS) and 4.0 (AB-AS) was selected for further studies. The effect of 10 M HCl concentration on absorption maximum of colored product was investigated. The maximum intensity was achieved in the range of 2.0–5.0 mL of 10 M HCl. Therefore, 3.0 mL of 10 M HCl was used. Maximum absorbance of the colored derivative was achieved in the range of 2.0–4.0 mL of 10 M HCl. Therefore, 3.0 mL of 10 M HCl was used for better results. Ringbom's plot was the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot was drawn between log C of anionic surfactants and $(1-T)$ (where T is the transmittance). The plot has a sigmoid shape with a linear segment at intermediate absorbance values 0.2–0.7(SLS), 0.1-0.6(SDS), 0.25-0.65(SHS), 0.3-0.7(SDBS) and concentration values 1.25–3.3 µg mL^{-1}(SLS), 1.20-3.6 µg mL^{-1}(SDS), 1.15-2.6 µg mL^{-1}(SHS) and 1.18-3.0 µg mL^{-1}(SDBS) with Azure-A. The slope of Ringbom plot from Figure 3a are 0.3500, 0.3600, 0.3300 and 0.300 for SLS, SDS, SMS and SDBS with Azure-A respectively. Hence, the ratio between the relative error in concentration and photometric errors are 2.50, 2.60, 2.20 and 2.00 for a concentration of 0.0250, 0.0260, 0.0220 and 0.0200 for1 percent photometric error. Figure 3b shows the Ringbom plot of ion pair associated complex between Azure-B(AB) and anionic surfactants(AS). The plot has a sigmoid shape with a linear segment at intermediate absorbance values for SLS (0.18–0.65), SDS(0.15-0.63), SHS(0.27-0.60),SDBS(0.32-0.67) and concentration values were in the range 1.26–3.0 µg mL^{-1} for SLS, 1.22-3.8 µg mL^{-1} for SDS, 1.19-2.7 µg mL^{-1}

for SHS and 1.20-3.4 µg mL^{-1} for SDBS with Azure-B. The slope of Ringbom plot from Figure 3b are 0.3200, 0.3000, 0.3500 and 0.3100 for SLS, SDS, SMS and SDBS with Azure-A respectively. Hence, the ratio between the relative error in concentration and photometric errors are 2.32, 2.00, 2.50 and 2.10 for a concentration of 0.0232, 0.0200, 0.0250 and 0.0210 for1 percent photometric error. Beer's law range, molar absorptivity, Sandell's sensitivity, and other parameters of the ion pair associated colored derivatives were given in Tables 1a and 1b. The precision and accuracy of the method was studied by analyzing the coupling solution containing known amounts of the cited reagents within Beer's law limit. The low values of the standard deviation (%) and the percentages of error indicated the high accuracy of the present investigation.

To test the best efficiency of chloroform for the quantitative recovery of the ion pair associated complex in the present method, a study has been performed using different volumes of chloroform keeping the volume of water constant. The water: chloroform(v/v) ratio was varied from 1 : 1 to 1 : 0.1. It was observed that water:chloroform(v/v) 1:1 to 1:0.5 shows complete recovery of the complex. Therefore, water:chloroform(v/v) 1:0.5 was used for the further study. Each time 5 mL of chloroform was added to the water solution during the extraction of the complex. It was important to see whether after extraction and collection also, the volume remains same or not. After the contents are shaken for 1 min and are settled for 5 min, the chloroform layer containing the complex was colleted and the volume was measured. For six such individual experiments, it was noticed that five experiments the volume of chloroform was 5. 0 mL and for one experiment it was 4.9 mL. This indicates that there was no much change in the volume of chloroform before and after extraction. The absorbance measurements are thus performed directly with the chloroform layer. The effect of co-existing ions was also investigated. The limiting concentrations of the constitutents those do not interfere in the determination of AS (SLS, SDS, SHS and SDBS) as shown in Table 2. The ions are added as their salts into the AS solution of 20 µg L^{-1}. Absorbance variation up to 3 % which was considered as tolerance limit. The applicability of the method for a practical sample of doubly distilled deionized water has been tested. For that purpose the doubly distilled deionized water (100 mL) has been spiked with known amounts of AS and the concentration was determined using aforesaid procedure and the obtained results were presented in Tables 3a and 3b. The obtained results were compared with the standard method [12] in terms of Student's '*t*'-test and Variance ratio '*f*'-test. The analytical data summarized in Tables 3 to 6 suggest that the percentage of AS recovery from various water systems collected from urban and rural areas of Tirupati ranges from 97.0% to

99.00%, which was more reliable and sensitive than the other methods.

The concentration of surfactant in water samples collected from surface, ground, borewells, openwells and open municipal drainage waste waters of Tirupati city (urban and rural areas) were reported in Tables 4 to 6. These results show that the levels of surfactants in surface and ground water system are ranging from 2 to 62 µg L^{-1} which was in considerable limits. The range becomes 22 to 427 µg L^{-1} for borewells and open wells. The levels of surfactant present in open municipal drainage waste water samples ranges from 50 to 720 µg L^{-1}. A critical study of data presented in Tables and the location of sampling sites in Figure 4 reveal that surfactants are presented in high concentrations both in open wells and bore wells that are located in the surrounding area of open municipal waste water drainage canals. This shows that surfactants which enter drains and ponds from domestic effluents are percolating through soil into ground water which is one of the important sources of drinking water. This further demonstrates the ability of their movement through red sandy and gravel aquifer which is the soil type in Tirupati city. The recovery percentage of AS under study represented in Tables 4 to 6 indicates that their orders in various environmental systems under study are as follows:
Open municipal drainage waste waster > Borewell and Openwell water,
Borewell and Openwell water >Surface and Ground water,
Open municipal drainage waste waster > Surface and Ground water.

Conclusion
A new-fangled and facile spectrophotometric method for the determination of anionic surfactants by using the new reagents Azure-A and Azure-B was recognized. An ion pair associated complex was formed between cationic dyes (AA and AB) and anionic surfactants (SLS, SDS, SHS, SDBS) and extracted into chloroform. The colored derivative was stable for more than 10 days. The method has the advantage of being trustworthy, reproducible, choosy and more perceptive than many reported methods. It was well suited for the determination of trace AS in industrial various water systems collected from urban and rural areas of Tirupati city, Andhra Pradesh, India. The method has been compared with standard MBAS method[12].

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