PRELIMINARY INVESTIGATION OF DYE-ION-SURFACTANT SYSTEMS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF TRACE METALS.

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ABSTRACT

The procedure for establishing promising combinations of dye-ion-surfactant systems for study in the spectrophotometric determination of trace metals using surfactants is described. The spectral characteristics of dye-ion and dye-ion-surfactant systems in acidic and alkaline media were studied for Bromopyrogallol Red (BPR) and Pyrogallol Red (PR) dyes, Cetyltrimethylammonium bromide (CTAB), Hexadecyltrimethylammonium Chloride (HDTAC), Benzyldimethylhexammonium Chloride (BDHAC), Benzyldimethylcetylammonium Chloride (BDCAC) surfactants and ions of Mn, Mo, Zn, Cd, Cr, Al, Ni, Mg, Pb, Ag, Ba, Te, In, K, Na, Ca, No_3, SO_4 and CO_3. The systems

BPR HDTAC-Zn, Cu (pH 10.5)
BPR-CTAB-Cu (pH 10.5)
BPR-BDCAC-Cu, Zn (pH 10.5)
PR-BDHAC-Ni, Zn (pH 10)
BPR-HDTAC-Mo (pH 2.2)
BPR-BDHAC-Cu (pH 10.5)
PR-HDTAC-Zn (pH 10)
PR-BDHAC-Zn (pH 10)
BPR- CTAB-Mo (pH 10.5)
BPR-BDHAC-Mo, Al (pH 2.2)
PR-HDTAC-Cu, Pb (pH 2.2)
PR-BDHAC-Cu (pH 2.2)

were found to be promising while the systems BPR - CTAB - Mo and BPR - CTAB - Cu were found to be highly promising.

INTRODUCTION

In recent time the trend in ultraviolet and visible absorption spectrophotometry has been to employ surfactants and micellar systems in the attempt to improve the sensitivity of its trace metal analysis[1-4]. This is because surfactants form ternary or mixed complexes with metal ions and chelorometric indicators or dyes. These ternary complexes are more sensitive in metal analysis than the conventional binary complexes of metal indicators[5].

The addition of a surfactant to a dye-metal system at a suitable pH results in a marked bathochromic shift in the wavelength of maximum absorbance of the complex with an attendant increase in the molar absorptivity and colour intensity of the complex[6,7].

Dyes that go well with surfactants are usually those having vicinal (-0H) adjacent to (-COOH) or (-SOH) in a chromophoric framework[8]. The dyes form complexes with colours distinctively different from those of the dyes[9]. These dyes include triphenylmethane reagents like catechol violet and bromopyrogallol red and those containing the iminodiacetic acid group such as xylenol orange.

One very essential condition for the formation of the ternary complex involving the surfactant and the dye is that neither of them alone forms a coordination saturated complex with the metal ion. So it requires specific combinations of surfactants and dyes to sensitise the spectrophotometric determination of any particular trace metal.

The present work is to establish and document suitable surfactant-dye-metal combinations with potentials for spectrophotometric analysis of trace metals.

EXPERIMENTAL

Materials

All chemicals used were of analytical reagent grade. The dyes from BDH were purified by column chromatography on cellulose. The surfactants were obtained from BDH and used without further purification. Distilled deionized water was used to prepare stock solutions including 1 x 10^{-3}M of each of the surfactants and each of the dyes, 1 x 10^{-1}M sodium hydroxide and 1 x 10^{-1}M hydrochloric acid and 5ppm of each ion listed for study. Acid buffers, HCl/KCl[10], and alkaline buffers, $NaHCO_3$/NaOH[11] were also prepared.

Apparatus

Absorbance measurements were made with a double beam Unicam UV spectrophotometer model 1750B using 10mm matched silica cells. pH determinations were made with a W.G. Pye model 290 pH meter with glass electrode.

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Determination of optimum pH for using dye solutions

The potentiometric trirations of each dye separately with 1 x 10^{-1}M HCl and 1 x 10^{-1}M NaOH were carried out. From the results, the pH ranges within which a dye was well buffered and therefore should contain stable ionic forms were identified. Then acid buffers[10] and alkaline buffers[11] of appropriate pH values were prepared for use with each dye. A typical potentiometric titration result for a dye is shown in Fig. 1 for bromopyrogallol red while the dependence of its absorbance on pH is shown in Fig. 2. Stable pH values for the listed dyes are indicated in Table 1.

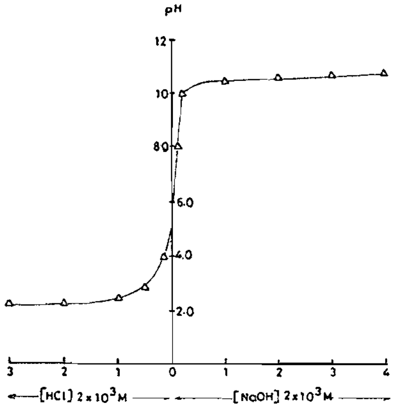

Fig-1: Potentiometric titration of [BPR] 2x10^{-5} M at pH 4.6

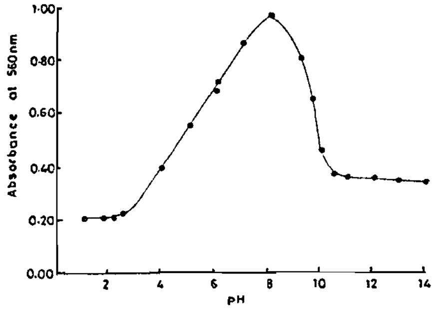

Fig.2: Variation of the absorbance of BPR with pH at 560nm [BPR] = 2 x 10^{-5} M

Table 1: A summary of the study to select suitable dye-M^{n+}- surfactant system for further and detailed study.

Dye	Surfactant	Stable pH for dyes systems	M^{n+} suitable for Dye-ion-surfactant system	Remarks
BPR	HDTAC	10.6	Zn, Cu, Cd	Promising
BPR	HDTAC	2.2	Mo	Promising
BPR	BDHAC	10.6	Cu, Cd	Promising
BPR	BDHAC	2.2	Mo, Al	Promising
BPR	CTAB	10.6	Cu	Very Promising
BPR	CTAB	2.2	Mo	Very Promising
BPR	BDCAC	10.6	Cu, Zn	Promising
BPR	BDCAC	2 2	Mo	Promising
PR	CTAB	10	-	Not Promising
PR	CTAB	2.2	-	Not Promising
PR	HDTAC	10	Zn	Promising
PR	HDTAC	2.2	Cu, Pb	Promising
PR	BDHAC	10	Zn, Cs, Ni	Promising
PR	BDHAC	2.2	Cu	Promising
PR	BDHAC	10	Zn	Promising
PR	BDCAC	2.2	-	Not Promising

Investigations on the various systems at alkaline pH range

1cm³ of the 1 x 10^{-3}M dye solution, 15cm³ of the buffer solution of pH 10.5 and 5cm³ of the 5ppm metal stock solution were transferred into a 50cm³ volumetric flask and the mixture made up to mark with distilled deionized water. This experimental solution was prepared for every dye with each of the ions listed for study. The absorption of each solution in the wavelength range 400-670nm was then measured on the spectrophotometer against a reagent blank prepared in the same manner as the sample solution but without the ion, recording the wavelength of maximum absorption (λ_{max}) and the corresponding maximum absorbance (A_{max}) of each solution. A typical result for dye-ion systems is shown for BPR-Cu in Fig. 3B.

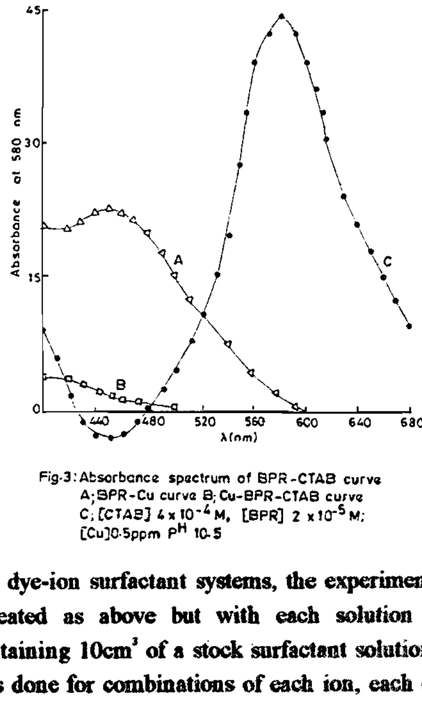

Fig-3: Absorbance spectrum of BPR-CTAB curve A; BPR-Cu curve B; Cu-BPR-CTAB curve C; [CTAB] 4 x 10^{-4} M, [BPR] 2 x 10^{-5} M; [Cu] 0.5ppm pH 10.5

For dye-ion surfactant systems, the experiments were repeated as above but with each solution studied containing 10cm³ of a stock surfactant solution. This was done for combinations of each ion, each dye and each surfactant listed for study. A typical result for dye-ion-surfactant system at alkaline pH range is shown for BPR-Cu-CTAB at pH 10.5 in Fig. 3C and BPR-ion-CTAB for the listed ions in Table 2.

Investigation on the various systems at acidic pH range

For dye-ion systems at acidic pH range, 1cm³ of the 1 x 10^{-3}M dye solutions, 30cm³ of the appropriate acidic buffer solution and 5cm³ of a 5ppm ion stock solution were transferred into a 50cm³ volumetric flask. The solution mixture was made up to mark with distilled

Table 2: Absorbance between 410 nm and 670 nm of various ions in a BPR-ion-CTAB system at pH 10.5

(nm)	Ba^{2+}	Mo^{6+}	Cd^{2+}	Na^{+}	K^{+}	Cu^{2+}	Cr^{3+}	$Cr_2O_7^{2-}$	Pb^{2+}	Ni^{2+}	Mn^{2+}	Al^{3+}	Zn^{2+}	Fe^{3+}	Co^{2+}
410	-0.020	N	-0.010	-0.010	0.012	0.040	N	N	N	N	N	N	N	N	N
420	-0.010	N	0.010	-0.010	N	N	N	N	N	N	N	N	N	N	N
430	-0.020	N	-0.020	N	N	-0.030	N	N	N	N	N	N	N	N	N
440	-0.020	N	-0.020	N	N	-0.050	N	N	N	N	N	N	N	N	N
450	-0.010	N	-0.020	N	N	-0.050	N	N	N	N	N	N	N	N	N
460	-0.010	N	-0.020	N	N	-0.040	N	N	N	N	N	N	N	N	N
470	N	N	-0.010	N	N	-0.030	N	N	N	N	N	N	N	N	N
480	N	N	-0.010	N	N	-0.020	N	N	N	N	N	N	N	N	N
490	N	N	-0.010	N	N	N	N	N	N	N	N	N	N	N	N
500	N	N	N	N	N	0.030	N	N	N	N	N	N	N	N	N
510	N	N	N	N	N	0.070	N	N	N	N	N	N	N	N	N
520	N	N	N	N	N	0.110	N	N	N	N	N	N	N	N	N
530	N	N	N	N	N	0.150	N	N	N	N	N	N	N	N	N
540	N	N	N	N	N	0.240	N	N	N	N	N	N	N	N	N
550	N	N	N	N	N	0.300	N	N	N	N	N	N	N	N	N
560	N	N	N	N	N	0.390	N	N	N	N	N	N	N	N	N
570	N	N	N	N	N	0.400	N	N	N	N	N	N	N	N	N
580	N	N	N	N	N	0.420	N	N	N	N	N	N	N	N	N
590	N	N	N	N	N	0.400	N	N	N	N	N	N	N	N	N
600	N	N	N	N	N	0.380	N	N	N	N	N	N	N	N	N
610	N	N	N	N	N	0.350	N	N	N	N	N	N	N	N	N
620	N	N	N	N	N	0.250	N	N	N	N	N	N	N	N	N
630	N	N	N	N	N	0.200	N	N	N	N	N	N	N	N	N
640	N	N	N	N	N	0.170	N	N	N	N	N	N	N	N	N
650	N	N	N	N	N	0.140	N	N	N	N	N	N	N	N	N
660	N	N	N	N	N	0.110	N	N	N	N	N	N	N	N	N
670	N	N	N	N	N	0.006	N	N	N	N	N	N	N	N	N

(N = no absorbance)

Table 3: Absorbance at 400-670 nm of the various ions in a BPR-CTAB-ION system at pH 2.2.

(nm)	Fe^{3+}	Al^{3+}	Co^{2+}	Ni^{2+}	Cd^{2+}	Cr^{3+}	Ba^{2+}	Pb^{2+}	Zn^{2+}	Mn^{2+}	Cu^{2+}	K^{+}	Na^{+}	Mo^{6+}	Ca^{2+}	$Cr_2O_7^{2-}$
400	0.030	0.106	N	N	N	N	N	N	N	0.030	0.060	N	N	0.030	N	N
410	0.020	0.020	N	N	N	N	N	N	N	0.040	0.040	N	N	0.040	N	N
420	0.020	0.010	N	N	N	N	N	N	N	0.050	0.090	N	N	0.030	N	N
430	0.020	-0.030	N	N	N	N	N	N	N	0.050	0.020	N	N	0.020	N	N
440	0.010	-0.040	N	N	N	N	N	N	N	0.040	0.040	N	N	0.010	N	N
450	0.010	0.040	N	N	N	N	N	N	N	0.040	N	N	N	0.010	N	N
460	0.010	-0.040	N	N	N	N	N	N	N	0.040	N	N	N	0.020	N	N
470	0.010	-0.030	N	N	N	N	N	N	N	0.030	N	N	N	0.010	N	N
480	0.010	-0.020	N	N	N	N	N	N	N	0.020	0.010	N	N	0.020	N	N
490	N	-0.020	N	N	0.010	N	N	N	N	0.010	-0.010	N	N	0.020	N	N
500	N	-0.020	N	N	N	N	N	N	N	N	-0.020	N	N	0.010	N	0.010
510	N	-0.020	N	N	N	N	N	N	N	-0.010	-0.040	0.010	N	N	N	0.010
520	N	-0.020	0.010	0.010	N	N	N	N	N	-0.030	-0.070	0.020	0.010	-0.020	N	0.010
540	-0.020	-0.100	0.040	0.030	N	N	0.010	-0.010	0.040	-0.080	-0.180	0.020	N	-0.090	N	0.020
550	-0.030	-0.130	0.050	0.040	N	N	0.020	-0.030	0.050	-0.100	-0.210	0.020	N	-0.090	0.001	-0.030
560	-0.040	-0.180	0.060	0.050	N	N	N	-0.040	0.060	-0.120	-0.240	N	N	-0.100	N	0.040
570	-0.050	-0.250	0.070	0.050	N	N	N	-0.050	0.060	-0.140	-0.280	-0.020	-0.020	-0.230	N	-0.060
580	-0.020	-0.270	0.080	0.030	N	N	N	-0.060	0.070	-0.140	-0.300	-0.030	-0.020	-0.110	N	-0.060
590	-0.010	-0.200	0.050	0.010	N	N	N	-0.040	0.040	-0.130	-0.220	N	-0.010	0.030	N	-0.050
600	-0.010	-0.040	0.010	N	N	N	N	-0.010	0.020	-0.080	-0.060	N	N	0.250	N	0.040
610	N	0.040	N	N	N	N	N	N	N	-0.040	0.040	N	N	0.440	N	0.060
620	N	0.100	-0.020	0.010	N	N	N	N	N	-0.020	0.001	N	N	0.445	N	0.060
630	N	0.100	-0.020	0.010	N	N	N	N	N	0.010	0.120	N	N	0.275	N	0.100
640	N	0.080	-0.020	N	N	N	N	N	N	N	0.120	N	N	0.150	N	0.060
650	N	0.060	0.020	-0.010	N	N	N	N	N	N	0.110	N	N	0.070	N	0.040
660	N	0.050	0.020	-0.010	N	N	N	0.010	N	N	0.090	N	N	0.030	N	0.040
670	N	0.030	-0.020	0.010	N	N	N	0.010	N	N	0.070	N	N	N	N	0.040

(N = no absorbance)

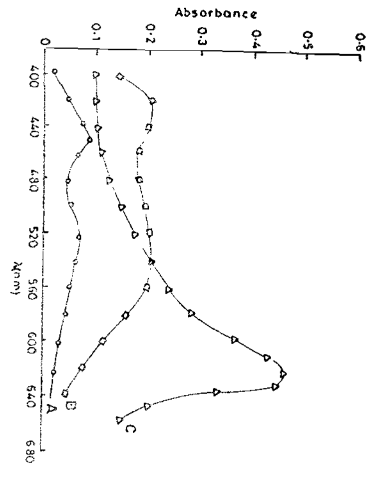

Fig-4:Absorbance sppectra of CTAB-BPR at pH 2·2 curve A, BPR-Mo curve B and Mo-BPR-CTAB curve C, [CTAB] =2 x 10^{-4}M; [BPR] = 2 x10^{-5}M [Mo] =.5ppm.

deionized water. This experimental solution was prepared for each dye against each ion listed for study. The absorbance of each solution was then measured on the spectrophotometer using a reagent blank prepared as the experimental solution but without the ion solution. The wavelength of maximum absorbance and the corresponding maximum absorbance for each experimental solution were recorded. A typical result for dye-ion systems is shown for BPR-Mo in Fig. 4B. For dye-ion-surfactant systems, the above experiments were repeated but with each experimental solution studied containing, in addition, 10cm^3 of a stock surfactant solution. This was done for each dye against each ion and against each surfactant listed for study. A typical result is shown in Table 3 for BPR-ion-CTAB system and BPR-Mo-CTAB in Fig. 4C.

Reagent combinations investigated.

The systems studied included combinations of bromopyrogallol red (BPR) and Pyrogallol red (PR) dyes with Cetyltrimethylammonium bromide (CTAB), Hexadecyltrimethylammonium Chloride (HDTAC), Benxyldimethylhexammonium Chloride (BDHAC), Benxyldimethylcetylammonium Chlo-ride (BDCAC) surfactants and ions of Mn, Mo, Zn, Cd, Cr, Al, Ni, Mg, Pb, Ag, Ba, Te, In, K, Na, Ca, NO_3, SO_4 and CO_3.

RESULTS AND DISCUSSION

The potentiometric titration of the dyes showed that each has stable ionic forms at a very low pH range and at a very high pH range as indicated in Table 1. The specific values were pH 2.2 for both dyes and pH 10 and pH 10.5 for PR and BPR respectively.

The systems BPR-BDCAC-Cu, Zn (pH 10.5); BPR-BDHAC-Mo, Al (pH 2.2); BPR-BDHAC-Cu (pH 10.5); BPR-CTAB-Cu (pH 10.5); BPR-CTAB-Mo (pH 2.2); BPR-HDTAC-Mo (pH 2.2); BPR-HDTAC-Zn, Cu (pH 10.5); PR-BDHAC-Cu (pH 2.2); PR-BDHAC-Zn (pH 10); PR-BDHAC-Ni, Zn (pH 10); PR- HDTAC-Cu, Pb (pH 2.2); PR-HDTAC-Zn (pH 10) are found to be promising and deserve further studies.

A system is said to be promising and so deserve further study when the surfactant causes a reasonable bathochromic shift in the λ_{max} of the dye-ion system, does not produce any reasonable absorbance for other ions or species at the λ_{max} of the dye-ion-surfactant system and shows a large difference between the spectral characteristics of the dye-ion system and those of the dye-ion- surfactant system.

Typical absorbance spectra of systems at both acidic and alkaline pH ranges are shown for BPR- CTAB-ion in Tables 2 and 3 respectively. BPR-CTAB seems to be very specific for Mo at acidic pH range (Table 3) and Cu at alkaline pH range (Table 2). Table 3 shows that the absorbance of Mo is much higher than those of the other ions in BPR-CTAB-ion systems. It also shows that the absorbance of other BPR-CTAB-ion systems at the wavelength of maximum absorbance of BPR-CTAB-Mo, 626nm, is negligible. This implies that the Mo system will encounter negligible interference from other ions or species. This is also applicable to the BPR-CTAB-Cu system at alkaline pH (Table 2). Under the conditions of pH 2.2 and pH 10.5, the dye BPR is well buffered against pH changes (Fig. 1) and the absorbance is not only constant but also relatively smaller than around neutral pH. This implies little or no interferences from excess dye in the sample solutions during absorbance measurement.

The presence of CTAB in the BPR-CTAB-Mo system causes a marked increase in the absorbance and a bathochromic shift of 82nm in the molybdenum system changing from about 0.2 absorbance at 540nm to about 0.46 at 626nm (Fig. 4). Fig. 4 also shows the large difference between the spectral characteristics of the sample solution BPR-CTAB-Mo and that of the reference solution BPR-CTAB. The nearly zero absorbance of the reference BPR-CTAB solution at the λ max (626nm) of the sample solution means that any excess reagent in the reference solution will not significantly affect the absorbance at λ max of the test solution, implying a high specificity for this method of molybdenum determination. Fig. 3 highlights the effect of CTAB on the BPR-Cu system. There is over 1.000% increase in absorbance from 0.02 to about 0.29 with concommitant bathochromic shift of 170nm from 410nm for BPR-Cu to 580nm for BPR-CTAB-Cu.

In both cases, the large bathochromic shift allows the metal determinations to be conducted at wavelengths away from the absorption maxima of reagent species in the analytical solution. Interference in the determination by these concommitant species is avoided. The degree to which this is achieved is determined by the size of bathochromic shift. The degree was high enough in these cases.

Another analytically significant result is the near zero absorbance of the reference BPR-CTAB solution at the λmax of the sample (BPR-CTAB-Cu) solution.

CONCLUSION

The combinations of dyes, surfactants and metals selected as promising are suitable for investigation as systems for metal determinations. The dyes usually form complexes with colours distinctively different from those of the dyes. The systems suffer negligible interference from concommitant metal ions. The high selectivity attainable is amply illustrated for Zn, Mo and Cu in various combinations with appropriate dyes and surfactants.

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