Sensitization of indium-bromopyrogallol red system with cetyltrimethyl-ammonium bromide

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Indium-bromopyrogallol red (In-BPR) system is sensitized with cetyltrimethylammonium bromide (CTAB) and the buffers used for controlling the pH influence the system. A calibration curve, at 610 nm, is non-linear in the entire metal concentration range studied. However, the curve, at 620 nm, is linear for 0-23.2 µg In in 25 ml. Molar absorptivity of the complex, at 620 nm, is 4.0×10^4 $mol^{-1}dm^3cm^{-1}$.

An attempt is made to sensitize indium-bromopyrogallol red (In-BPR) system with cetyltrimethylammonium bromide (CTAB), in place of NH_4^+ ions[1,2], to obtain higher sensitivity following the methodology used by us in the Nb-BPR-EDTA-CTAB system[3]. We have shown here that one can come across calibration curves with different slopes in different metal concentration ranges in surfactant sensitized metal-dye systems inspite of optimization of experimental parameters to obtain a single complex. We have also tried to explain this non-ideal behaviour.

Experimental

Indium solution $(1.0 \times 10^{-2} M)$ was prepared by dissolving indium metal (0.115 g; purity > 99.99%) in nitric acid (5 ml) by warming and diluting with distilled water (100 ml). Subsequent dilutions were carried out maintaining 0.01% nitric acid.

Bromopyrogallol red (BPR) solution $(2.0 \times 10^{-4} M)$ was prepared by dissolving BPR (0.011g; E Merck, GR) in boiling water and diluted to 100 ml with distilled water. This was freshly prepared before use.

Cetyltrimethylammonium bromide (CTAB) solution $(1.0 \times 10^3 M)$ was prepared by dissolving CTAB (0.0364 g; BDH, LR) in water and diluting to 100 ml.

All other reagents used were of AR grade. Spectrophotometric measurements were made using Beckman DU spectrophotometer with a matched pair of pyrex cells of 1.00 cm path length.

Results and discussion

pH-absorbance curves

Solutions containing fixed concentrations of In, BPR and CTAB at different pH values were prepared in acetate, phthalate and succinate media. The spectra were scanned between 350 and 650 nm after keeping the solutions overnight. From the spectral data pH-absorbance curves were constructed at 600 and 620 nm (Fig. 1). Such curves in acetate and phthalate media could not be constructed beyond pH 5.0 due to turbidity. The phthalate concentration was kept at 0.005 M. The solutions at all the pH values were turbid at 0.5 M phthalate concentration. Formation of two complexes can be seen in the presence of acetate and succinate; whereas resolution of the two complexes formed in phthalate was poor. Further, in the phthalate medium it was not even possible to detect the presence of a single complex as λ_{max} of the species, formed throughout the pH range studied, was the same, i.e., 620 nm. No single complex was saturated to a greater extent in acetate and phthalate media irrespective of the ratio of CTAB to BPR employed (Figs
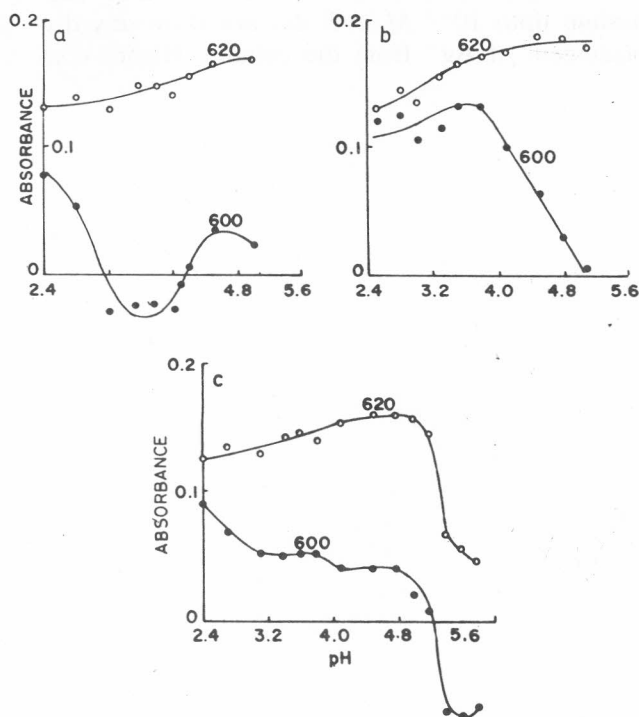

Fig. 1—pH-Absorbance curves of indium-BPR-CTAB systems (a) Acetate (0.08M); (b) Phthalate (0.005 M); and (c) succinate (0.04M) [$C_{In} = 4.0 \times 10^{-6} M$; $C_{BPR} = 4.0 \times 10^{-5} M$; $C_{CTAB} = 2.0 \times 10^{-4} M$]

2a, b); whereas the lower (forming at lower pH) or the higher complex was saturated, depending on the CTAB to BPR ratio employed in the succinate medium (Fig. 2c). Hence further experiments were carried in the succinate medium. At fixed BPR concentration, the pH of formation of the higher complex shifted towards more acidic side when CTAB to BPR ratio was increased.

Effect of varying CTAB/BPR/succinate concentrations

Absorbance values at pH 4.5 were constant at CTAB to BPR ratios of 4.0 and 6.0 and a ratio of 5.0 was utilised for the construction of a colour saturation curve. Absorbance values were constant between 2.0 and $8.0 \times 10^{-5} M$ BPR. Succinate concentration, between 8.0×10^{-3} and $8.0 \times 10^{-2} M$, did not have any influence on the absorbance values.

Calibration curves

Calibration curves were constructed following the procedure described below. The calibration curves at λ_{max}, i.e. at 620 nm and at 650 nm were linear and passed through origin; however the one constructed at 610 nm was nonlinear in the entire metal concentration range studied.

Indium (2.9 to 23.2 μg) was taken in 10 ml of 0.01% HNO_3. To this was added 0.011% BPR (2 ml) and 5% succinic acid (2.5 ml; pH 4.5 adjusted with NaOH), followed by 0.0364% CTAB (4.0 ml). The mixture was diluted to 25 ml with distilled water and its absorbance measured at 620 nm after keeping the solution overnight.

Though a single complex is saturated to a greater extent in this system, the calibration curve at 610 nm is not linear over wide range of In concentration. This is due to presence of atleast two species existing in solu-
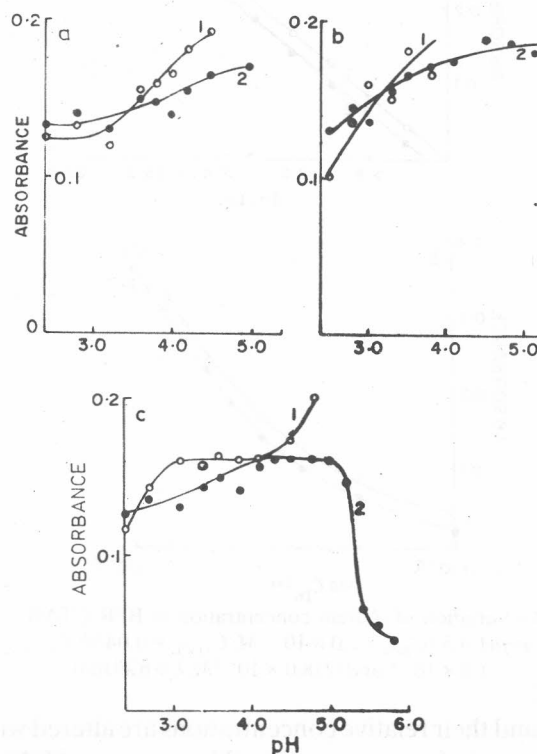
Fig. 2—pH-Absorbance curves of **In-BPR-CTAB** system in presence of different buffers (a) Acetate (0.08 M); (b) Phthalate (0.005 M); and (c) succinate (0.04 M) [$C_{In} = 4.0 \times 10^{-6} M$; $C_{BPR} = 4.0 \times 10^{-5} M$; $C_{CTAB} = 1.0 \times 10^{-4} M$; and (2) $2.0 \times 10^{-4} M$; $\lambda = 620$ nm]
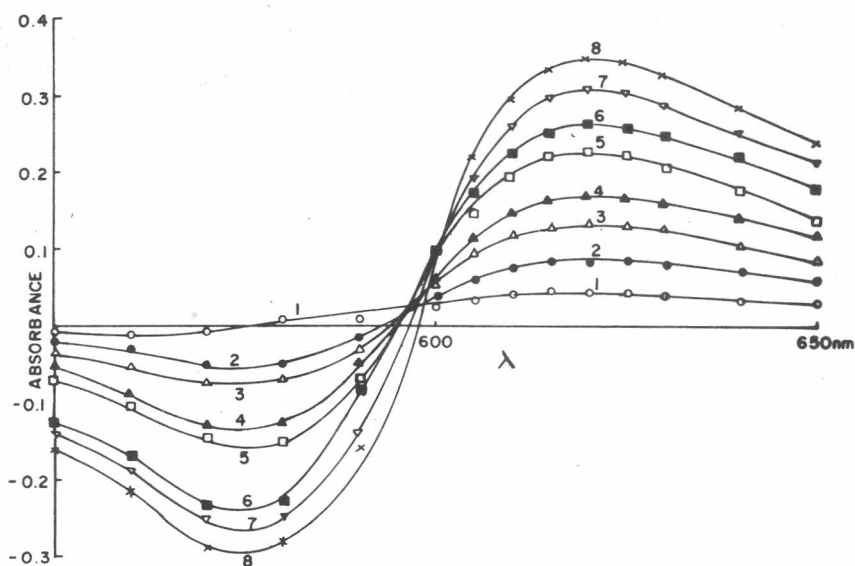
Fig. 3—Spectra of calibration curve solutions of In-BPR-CTAB system at pH 4.5 [$C_{BPR} = 3.2 \times 10^{-6} M$; $C_{CTAB} = 1.6 \times 10^{-5} M$; and $C_{SUCC} = 0.04 M$]
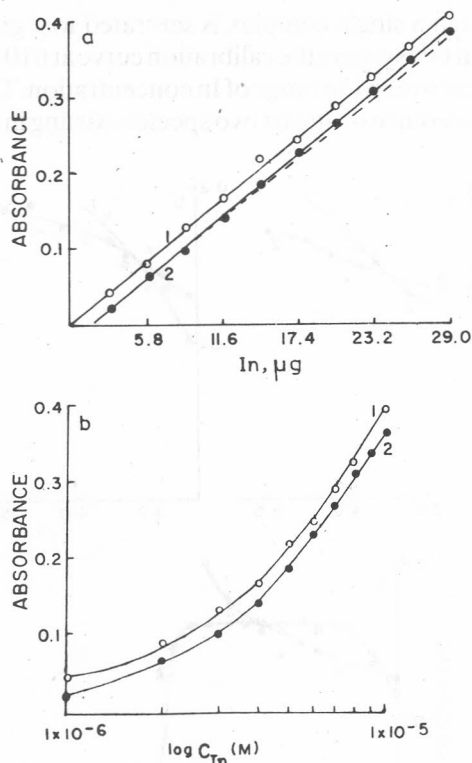
Fig. 4—Variation of indium concentration in BPR-CTAB mixtures at pH 4.5 [$C_{BPR} = 2.0 \times 10^{-5}M$, $C_{SUCC} = 0.04M$; C_{CTAB}: (1) 1.0×10^{-4}; and (2) $8.0 \times 10^{-4}M$; $\lambda = 620$ nm]

tion and their relative concentrations are altered with a change in In concentration. The presence of these species was inferred from different isosbestic points observed in the spectra of the solutions used for construction of the calibration curves (Fig. 3). The existence of these species could be seen even in CTAB micelles (Fig. 4a). The calibration curve at 620 nm is ideal, however, this does not indicate that a single species is present in the solutions employed for constructing the calibration curves. In the plot of absorbance values as a function of log In concentration (Fig. 4b) the existence of two species is clearly noticed. Generally, surfactant micelles block chelating centres of the dye and consequently affect degree of formation of metal-dye-surfactant complex. This effect is noticed also in this system (comparison of the curves 1 and 2 in Fig. 4), however, it is not as severe as observed in metal-chromeazrol S-surfactant systems[4]. This may probably be due to the structure of the dye in question or functional groups present in the dye molecule.

Molar absorptivity of the complex at 620 nm is $4.0 \times 10^4 mol^{-1}dm^3cm^{-1}$ and it is higher than the molar absorptivity of the 1:2 complex ($5.7 \times 10^3 mol^{-1}dm^3cm^{-1}$), formed in aqueous solution in the presence of NH_4^+ ions,[1,2] at 610 nm.

References

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