Influence of buffer anions in surfactant sensitized metals-dye systems

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Buffer anions: acetate, succinate and phthalate influence the stepwise complex formation in thorium-chrome azurol S-CTAB and indium-bromopyrogallol red-CTAB systems very significantly by participating in the complex formation.

Surfactant sensitized metal-dye systems have been studied mainly with a view to enhancing existing molar absorptivity values of metal-dye systems. Some authors have tried to explain the mode of sensitisation also. But, investigators in this field have generally paid less attention to the study of aspects like optimisation of experimental parameters, influence of ionic strength and buffers used for controlling pH. In the same system studied, by different investigators, different optimum conditions have been reported. In our earlier communication and unpublished work, we have shown the importance of optimisation of dye to surfactant ratio in these studies.

Generally, influence of buffer anions on surfactant sensitized metal-dye systems is not studied. Sometimes, it is concluded from inadequate studies that buffer anions have no influence on the system. This note illustrates the very significant influence of buffer anions on complex formation in thorium-chrome azurol S-CTAB (Th-CAS-CTAB) and indium-bromopyrogallol red-CTAB (In-BPR-CTAB) systems.

**Experimental**

Thorium solution: A 4.0 x 10^{-3}M solution was prepared by dissolving 0.552 g Th(NO_3)_4.4H_2O, supplied by M/s Indian Rare Earths, Bombay, in 1% nitric acid and diluting to 250 ml with the same acid. This solution was standardised with EDTA using pyrocatechol violet indicator. Subsequent dilutions were carried out maintaining a final acidity of 0.25% nitric acid.

Indium solution: A 1.0 x 10^{-2}M solution was prepared by dissolving 0.1150 g of indium metal (purity > 99.9%), obtained from the Chemistry Division, BARC, in 5 ml conc. nitric acid by warming on a water bath and making up the volume to 100 ml with water after cooling. Subsequent dilutions were carried out maintaining 0.25% nitric acid.

Chrome azurol S (CAS) solution: A 2.0 x 10^{-4}M solution was prepared by dissolving 0.012 g CAS (Fluka) in water and making up the volume to 100 ml. This was filtered through a Whatman 540 filter paper before use.

Bromopyrogallol red (BPR) solution: A 2.0 x 10^{-4}M solution was prepared by dissolving 0.011 g BPR (E. Merck, GR grade) in boiling water and making up the volume to 100 ml after cooling. This was freshly prepared before use.

CTAB solution: A 1.0 x 10^{-3}M solution was prepared by dissolving 0.0364 g CTAB (BDH LR grade) in water and making up the volume to 100 ml. All other reagents used were of AR grade.

pH measurements were made using a Beckman expandomatic SS2 pH meter. Spectrophotometric measurements were made using a Beckman DU spectrophotometer with a matched pair of pyrex 1.000 cm cells.

**Results and discussion**

Thorium CAS-CTAB and indium-BPR-CTAB systems

Solutions were prepared with constant concentrations of metal, dye and CTAB at different pH values 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-A curves were constructed at 610 and 630 nm in thorium-CAS-CTAB system (Fig.1) and at 600 and 620 nm in indium-BPR-CTAB system (Fig.2). The pH-A curves in acetate and phthalate media could not be constructed beyond pH 5.0 in the In-BPR-CTAB system due to turbidity. The phthalate concentration was kept at 0.005 M in the In-BPR-CTAB system. At 0.5 M, the solutions at all the pH values were turbid.

pH-A curves furnish information regarding stepwise complex formation in metal-ligand (weak acid or base) systems. These curves, at each wavelength, in a system should be similar, irrespective of the buffer used, provided either there is no influence of buffer anions on complex formation or buffer anions form only binary colourless complexes with metal ions.
In the Th-CAS-CTAB system, formation of two complexes can be seen from Figs. 1a and b in presence of acetate and phthalate. The formation of the higher complex, with $\lambda_{\text{max}}$ at 630 nm (forming at higher pH) is suppressed in the presence of succinate (Fig.1c). It may be mentioned here that the lower complex (forming at lower pH) has $\lambda_{\text{max}}$ at 610 nm.

In In-BPR-CTAB system, formation of two complexes can be seen in presence of acetate and succinate whereas resolution of the two complexes formed in phthalate is poor. It is not even possible to point out presence of a single complex, because $\lambda_{\text{max}}$ of the species, formed throughout the pH range studied, is same, i.e., 620 nm.

It is obvious now that the pH-A curves obtained in the three different buffer media in both the systems are not similar. It is inferred from a close comparison of these curves that buffer anions participate in complex formation and they merely do not compete with metal ion to form colourless binary complexes. This is contrary to the observation reported by Evtimova in Th-CAS-CTAB system, who adjusted required pH of the solution either with acid or alkali and then introduced acetate buffer to control the pH.

When the concentration of acetate was intentionally varied over a wide range, keeping all other parameters constant in the Th-CAS-CTAB system, the high concentration of buffer anion suppressed the formation of the lower complex (forming at lower pH) considerably and increased the formation of the higher complex significantly as shown in Fig.3.

Generally, when two stepwise complexes form in a system, pH-A curves should indicate the
Fig. 3 — pH-A curves of Th-CAS-CTAB system

transformation of one to the other (exhibit two steps only). However, a minimum is observed in pH-A curves in Th-CAS-CTAB system in presence of acetate (Fig.1b) and in In-BPR-CTAB system in presence of acetate (Fig.2a) between the steps expected. It is difficult to offer an explanation for these minima.

References
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