Spectrophotometric Studies on the Chelates of Zinc, Cadmium and Mercury with Bromopyrogallol Red in the Presence of Cetyltrimethylammonium Bromide

OM PRAKASH, R. C. GUPTA & S. P. MUSHARAN
Chemical Laboratories, University of Allahabad, Allahabad

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Bromopyrogallol red forms binary chelates with zinc ($\lambda_{\text{max}}$ 550 nm), cadmium (564 nm) and mercury (400 nm). In the presence of cetyltrimethylammonium bromide (CTAB) green ternary chelates ($\lambda_{\text{max}}$ 600 and 630 nm) are formed. Compositions of binary and ternary chelates have been determined by the continuous variation and mole ratio methods. For photometric measurements using 1 sq. cm quartz cells. All absorbance values were recorded against distilled water blank.

The metal solutions were prepared by dissolving zinc oxide in hot dil. HCl and cadmium sulphate and mercuric chloride in redistilled water and standardised gravimetrically. Solutions of desired concentrations were obtained by suitable dilutions. BPGR solution was prepared in 20% (v/v) ethanol-water medium. Solutions of CTAB were prepared by dissolving calculated amounts in 20% methanol and standardised by argentometric determination of the bromide ion content.

A series of trial experiments were carried out in order to find out optimum conditions for the study. The experiments were performed at a fixed pH maintained by acetate or phosphate buffer solution. Total volume of the mixtures was kept at 25 ml. All the experiments were carried out at room temperature (25°C).

The colour formation in the case of zinc and cadmium binary systems was immediate and no significant change in absorbance value was noticed up to 2 hr. Temperature had no effect on the colour intensity up to 30°C. However, above this temperature slight change in absorbance was noticed. In Hg(II)-BPGR system yellow colour was developed by heating the mixture on a water bath for 20 min. Absorbance of yellow solutions remained unchanged up to 40 hr.

In the presence of CTAB, blue-green ternary chelates were formed with each metal. Maximum absorbance value was attained within few minutes

![Absorption spectra of binary and ternary systems](image)
and no change was observed for at least 3 hr. Absorbances of mixtures were therefore, recorded within 1 hr. No significant change in absorbances of ternary chelate solutions was observed up to 30°C but above this temperature ternary chelates were unstable.

Several mixtures containing BPGR and ten-fold excess CTAB were prepared over pH range of 3 to 7 and their spectra recorded. It was observed that λ\text{\text{max}} of BPGR (570 nm) shifted to 590 nm. Absorption spectra of BPGR in the presence of different amounts of CTAB were also recorded at pH 7.6. Absorption maxima gradually shifted to 590 nm, for which at least four-fold excess of CTAB was required. Absorbance values of these mixtures at 590 nm were plotted against the amount of CTAB and critical micelle concentration value calculated.

Fig. 1 shows absorption spectra of the binary and ternary chelates investigated. Binary chelates, Zn(II)-BPGR and Cd(II)-BPGR are stable in the pH range 6.0-8.0 and 4.5-6.5 respectively. Absorption maxima are shifted to 550 nm and 564 nm respectively. A yellow color Hg(II)-BPGR chelate (λ\text{\text{max}} 400 nm) is formed in the pH range of 4.5-6.5 by heating the mixtures for 20 min on a water-bath. These metals formed blue-green ternary chelates in the pH range of 6.0-8.5 with BPGR in presence of CTAB as indicated by pronounced bathochromic shifts in the maximum absorptions (600 to 630 nm).

The continuous variation and mole ratio methods were applied to establish the composition of binary chelates and M : BPGR ratio in ternary chelates in the presence of suitable excess amount of CTAB. The results are given in Table 1. The number of CTA⁺ in the ternary chelate was determined by measuring absorbances of the mixtures containing metal and BPGR in the stoichiometric ratio and varying amounts of CTAB. Absorbance values were then plotted against the amount of CTAB and the inflections in the curve gave the number of CTA⁺/mol of ternary chelate.

For binary systems, calibration curves were prepared by the standard procedure. Calibration curves for ternary systems were prepared as follows: To mixtures containing constant amount of CTAB and BPGR, were added varying amounts of the metal solution. pH and BPGR, was of the mixtures was maintained with acetate and phosphate buffer solutions keeping total volume at 25 ml. Absorbance values of these mixtures were recorded at 640 nm and plotted against the amount of metal. Beer’s law range, Sandell’s sensitivity and molar absorbity values determined for each system are given in Table 1.

On the basis of the experimental results (Table 1), it can be concluded that the bathochromic shift of the absorption spectra due to formation of ternary chelates in the presence of CTAB is the basis of a more sensitive and selective spectrophotometric method. In the presence of CTAB, molar absorbity and sensitivity is increased and Beer’s law is followed over wider range of concentrations of metal ions. The method is simple and precise. Small amounts of the other transitional metals do not interfere, but, when present in higher amounts these ions disturb the determination by forming competing binary or ternary chelates.

References