Spectrophotometric Study of Lead & Mercury Complexes with Xylenol Orange Analogue

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Separation of xylenol orange analogue (XOA) from semixylenol orange analogue (SXOA) has been accomplished by partition extraction at <60°. Lead forms a 1:1 complex with XOA at pH 5-6 with $A_{M583} = 41,000$ litre mol^{-1} cm^{-1}, and mercury forms a 1:2 complex at pH 10-10.1 with $A_{M590} = 74,500$ litre mol^{-1} cm^{-1}. These are mixed colour complexes hence the difficulty in attaining the sensitivity of augmented absorption. A concept of using attenuation of absorption of the ligand for correct evaluation of physicochemical characteristics of the two complexes has been suggested.

The better efficacy of xylenol orange analogue, 3,3'-bis[bis(carboxymethyl)nitrilo]methyl-*o*-cresol-sulphamphthalein (XOA) in the complexometric determination of lead over that of mercury was earlier explained in terms of difference in molar colour discrimination values of these complexes[1] (even though the molar absorbancy index of the latter was twice that of the former). In this note we describe the spectrophotometric determination of practical formation constants of the complexes of XOA with Pb(II) and Hg(II); some remarks about their determination are also given. Some pertinent observations on synthesis of XOA starting from *o*-cresolsulphamphthalein[2] are briefly mentioned.

The XOA was prepared by the condensation of *o*-cresolsulphamphthalein with disodium salt of iminodiacetic acid below 60°C in a manner similar to that used for the preparation of xylenol orange from *o*-cresolsulphonephthalein. At higher temperatures, semi-XOA (SXOA) was formed in larger proportion. The product as a fine powder was obtained by pouring the condensation product in ethanol, filtered, washed with ethanol and ether, and dried *in vacuo*; yield 85%. The alumina and silica column chromatography being unsuitable, purification of XOA was carried out by partition extraction of its 5×10^{-3} M solution in 10% acetic acid saturated with butanol in a multipurpose solvent extractor[3] at reduced pressure and below 60° with butanol saturated with 10% acetic acid. The XOA was left in the aqueous extract after 15 extractions.

The absorption curves of XOA and SXOA differ only at a Hammett acidity, $H_o = -1.2$. At this acidity XOA exhibits maximum absorption at 510 nm (A_M = 4,860 litre mol^{-1} cm^{-1}), whereas SXOA exhibits it at 435 nm ($A_M = 11,250$ litre mol^{-1} cm^{-1}). This difference was utilised to monitor the progress of separation of XOA from SXOA. The purified XOA indicator gave a single spot on a paper chromatogram (Found: N, 5.51; S, 4.24. Reqd.: N, 5.53; S, 4.21%).

The solution of XOA (2.5×10^{-3} M) was prepared in doubly distilled water. A 2.5×10^{-3} M solution of lead nitrate (BDH, AnalaR) was prepared in doubly distilled water containing a few drops of nitric acid (AnalaR). The mercury solution (0.05 M) was prepared by dissolving mercury metal (BDH, AnalaR: 5.015 g) in conc. HNO$_3$ (10 ml), evaporating the resulting solution to complete dryness, treating the residual mass with a few drops of perchloric acid and dissolving in doubly distilled water; the final volume was made to 500 ml. Working solutions of lead and mercury were prepared by appropriate dilutions of the stock solutions.

Hilger-Watt Uvispek spectrophotometer, model H.700,308 was used for absorbance measurements. Bechman Expandomatic pH meter, model 76005 was used for pH measurements.

Absorption characteristics of lead-XOA complex

Hexamine solution (10%) was used as a buffer for preparing the lead complex. The lead-XOA complex exhibits maximum absorption at 583 nm (A_M = 41,000 litre mol^{-1} cm^{-1}) in the pH range 5-6. The maximum augmented absorption occurs at 580 nm with measured $A_{M580aug}$ = 38,000 litre mol^{-1} cm^{-1}. At wavelength <480 nm the absorbance of lead-XOA complex is less than that of the ligand used as blank, but its maximum value is attained at 430 nm which has been designated as the wavelength of maximum attenuation with $A_{M430 attn}$ = 14,000 litre mol^{-1} cm^{-1}. This value has been utilised in the determination of the formation constant.

The complex obeys Beer's law in lead concentration range of 2.5×10^{-3} M to 15×10^{-5} M. The absorbance remains constant for about 18 hr. The alkali and alkaline earth metals in 200 molar excess do not interfere in the determination of lead while Sn^{2+}, Fe^{3+} and Al^{3+} interfere. The anions F$^-$, Cl$^-$, Br$^-$, HCO$_3^-$, BrO$_3^-$, SO$_4^{2-}$, NO$_3^-$, ClO$_3^-$, CNS$^-$, H$_2$PO$_2^-$, in 200 molar excess do not interfere, but NO$_2^-$, S^{2-}, SO$_3^{2-}$, S$_2$O$_3^{2-}$, S$_2$O$_8^{2-}$, BO$_4^{3-}$, oxalate, citrate, tartrate, phthalate and EDTA interfere.

Practical formation constant of lead-XOA complex

(i) *Job's method*[4,5]—Two curves each were drawn showing the variation of absorbances of maximum

augmented absorption (580 nm) and maximum attenuation (430 nm) with [M]/[M]+[L] (Fig. 1), keeping the total concentrations of lead and XOA as 2 $\times 10^{-5}$ M and 5×10^{-5} M respectively and varying the concentrations of lead and XOA in the ratios of 1:9 to 9:1. The pH was maintained at 5.5 using hexamine solution as buffer. The results presented in Fig. 1 reveal the formation of 1:1 lead-XOA complex.

The formation constant of the complex was calculated using Eq. (1) and

$$K_f = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)} \qquad \dots (1)$$

K_f was found to be 12.5×10^5 by substitution in Eq. (1) the value of x given by Eq. (2)

$$x = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)} \qquad \dots (2)$$

In Eq. (2), x is the amount of Pb-XOA complex formed and a and b are the initial concentrations of lead and XOA, respectively.

It may be noted that the augmented absorption has been measured at 580 nm using indicator solution as blank. This requires to be corrected for the small absorption due to indicator consumed in the formation of the lead complex. This is apparent from the small negative intercept on the ordinate of the curve (Fig. 1). A corrected curve, therefore, needs to be employed for calcul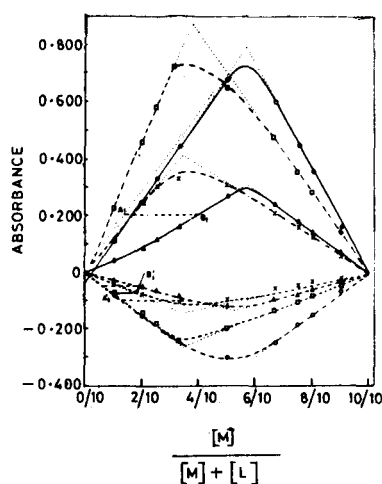ating the formation constant. This correction is not needed if curves are drawn between absorbance at wavelength of maximum attenuation (430 nm) and [M]/[M]+[L].

(ii) Mole ratio method[6]—In these experiments the concentration of lead was kept constant at 2.5 $\times 10^{-5}$ M, while that of XOA was increased from 2.5 $\times 10^{-6}$ M to 12.5×10^{-5} M, the solutions being buffered at pH 5.5 using hexamine. The formation of 1:1 Pb-XOA is also supported by the mole ratio method. The augmented absorbance at 580 nm and attenuated absorbance at 430 nm reached maximum values at Pb:XOA ratio of greater than 1:1 (Fig. 2). The formation constant of the complex was found to be 15×10^5 from the values at points close to the saturation where the effect of excess of reactants is minimal, and the degree of dissociation (α) is equal to $(E_m - E_s)/E_m$ (E_m and E_s are the values of maximum absorption at complete transformation of metal present to the complex and the absorption of the solution, respectively).

Absorption characteristics of mercury-XOA complex

Sodium bicarbonate solution (10^{-1} M) was used as a buffer for preparing mercury complex. The mercury-XOA complex exhibits maximum absorption at 590 nm ($A_M = 74,500$ litre mol^{-1} cm^{-1}) in the pH range 10.0 to 10.1. The complex shows maximum augmented absorption at 600 nm ($A_M = 17,000$ litre mol^{-1} cm^{-1}). At wavelengths <580 nm the complex has lesser absorbance than the XOA used as blank. The wavelength of maximum attenuation in this case is 460 nm ($A_M = 6,500$ litre mol^{-1} cm^{-1}).

Beer's law is obeyed for Hg(II) concentration up to 5 $\times 10^{-5}$ M. The absorbance remains constant for 18 hr. The cations Na$^+$ and K$^+$ do not interfere if present in 200 molar excess, but Li$^+$, Ca^{2+}, Ba^{2+}, Mg^{2+}, Sr^{2+} and Al^{3+} interfere. The anions, namely, F$^-$, NO$_3^-$, oxalate, tartrate, BO$_3^-$ and HPO$_4^{2-}$ do not interfere when present in 200 molar excess while Cl$^-$, Br$^-$, I$^-$, CO$_3^{2-}$, NO$_2^-$, BrO$_3^-$, citrate, CNS$^-$, S$_2$O$_3^{2-}$, S$_2$O$_8^{2-}$, SO$_3^{2-}$, H$_2$PO$_4^-$ and EDTA interfere.

Practical formation constant of mercury-XOA complex

(i) Job's method—Two sets of solutions of pH 10, using 0.1 M sodium bicarbonate buffer and total concentrations of mercury and XOA as 5×10^{-5} M and 10×10^{-5} M respectively, were prepared for the determination of formation constant of mercury-XOA complex. The results revealed the formation of a 1:2 Hg-XOA complex. From the points of equal absorption of the complex in the two relevant curves of Fig. 1 the formation constant, K_f was calculated using Eq. (3)

$$K_f = \frac{x}{(a_1 - x)(b_1 - 2x)^2} = \frac{x}{(a_2 - x)(b_2 - 2x)^2} \qquad \dots (3)$$

Fig. 1—Job's curves for formation of lead-XOA complex at pH 5.5 and of mercury-XOA complex at pH 10. [Augmented absorption of solution containing XOA and lead (5×10^{-5} M, O—O) and (2 $\times 10^{-5}$ M, $\triangle$—$\triangle$) at 580 nm; and XOA and mercury (10×10^{-5} M, $\square$—$\square$) and (5×10^{-5} M, ×---×) at 600 nm]. A$_1$ and B$_1$ are the points of equal absorption on the corrected absorption of Pb-XOA complex—attenuated absorption of the solution mixture of XOA with lead complex at 430 nm and with mercury complex at 460 nm (same indices below zero ordinate)]
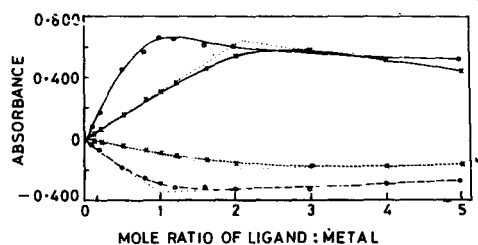
Fig. 2—Mole ratio method of determining the formation constant of lead and mercury complexes of XOA [Lead-XOA complex; O—O, the augmented absorption at 580 nm, and O---O, the attenuated absorption at 430 nm at pH 5.5. Mercury-XOA complex; × —— ×, the augmented absorption at 600 nm, and × --- ×, the attenuated absorption at 460 nm at pH 10].

where $x = $ [mercury-XOA complex]; $a = $ initial conc. of mercury and $b = $ that of XOA. From the curves (Fig. 1) the value of x could be calculated by solving the quadratic equation. By substituting the value of x in Eq. (3) the value of formation constant (K_f) of the mercury-XOA complex was found to be 18.6×10^{10} at room temperature (about 34°C).

(ii) Mole ratio method—In this method the concentration of mercury was kept constant $(2.5 \times 10^{-5} M)$ and that of XOA was varied from $2.5 \times 10^{-6} M$ to $12.5 \times 10^{-5} M$ at pH 10 (Fig. 2). This method also revealed the formation of a 1:2 Hg-XOA complex with $K_f = 18.6 \times 10^{10}$.

In the case of highly coloured ligands forming highly coloured complexes, whether the absorption maxima of the complex and the ligand occur at widely different wavelengths or at the same positions, the augmented or the attenuated absorption can be usefully employed for the evaluation of practical formation constant. In the case of augmented absorption, a correction factor is necessary to get the true values of absorption of the complex, as in the blank the equivalent amount of consumed ligand is present and absorption due to it can cause error in the calculation of formation constant. Such correction is reported[4,5] and it has been employed in the present study also. The absorption maxima of lead and mercury complexes of XOA undergo only a small bathochromic or hypsochromic shift as compared to that of the free ligand. In the case of mercury complex, the varying values of measured maximum absorption around 600 nm is caused due to the steep slopes of two absorption curves at this wavelength. The varying values of the formation constant of mercury complex of XOA accordingly have been reported[7-9]. Removal of this difficulty as well as the use of purified XOA has ensured more reliable results in the present investigation.

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