Synergic Extraction of Lead with 2-Thenoyltrifluoroacetone and Tribenzylamine by Atomic Absorption Spectrophotometry

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Summary: Synergic extraction studies of lead with HTTA-TBA in chloroform is carried out employing atomic absorption spectrometry. Quantitative extraction is observed at pH 3.0, ionic strength 0.1M(H^+, ClO_4^-) with an equimolar concentration of 0.5M for both extractants. The stoichiometry of the adducts and reaction mechanism have been suggested at different pH conditions. Equilibrium constants (log $K_{2,0}$ and log $K_{2,1}$) are found to be - 7.27 and - 4.12 respectively and the stability constant (log $\beta_{2,1}$) is 3.15 at pH 3.

Introduction

Solvent extraction of metal ions with acidic chelating agents and neutral ligands has been extensively investigated [1-3]. Acidic chelating agents with lower pK value form a stable adduct with neutral ligands and are useful for the extraction of metal ions from acidic media [4]. A representative example of such an extraction pair is 2-Thenoyltrifluoroacetone (HTTA) and Tribenzylamine (TBA). The extraction of Fe(III), Mn(II) and Ni(II) with HTTA has shown considerable increase in extractability with the addition of TBA due to the formation of synergic adducts [5-7]. The marked synergic enhancement is mainly due to the increase in the coordination number of the central metal ion.

The information on the extraction of lead with HTTA and its mechanism is scanty [8]. Present communication deals with the synergic extraction of Pb(II) with HTTA and TBA in chloroform from perchlorate media at different pHs using atomic absorption spectrophotometry.

Results and Discussion

Fig. 1 depicts the effect of pH on the extraction of lead(II) with 0.5M HTTA and 0.5M TBA separately or in their mixture. WSith HTTA, the extraction increases gradually with an increase in pH and reaches around 60% at pH 5.5 then starts decreasing sharply probably due to the hydrolysis [9] of lead. The distribution coefficient of lead(II) with TBA is negligibly small (<0.01) in the entire pH range studied. However, synergism is observed in the mixture and maximum extraction is noted between pH 3 to 5.5 having a distribution coefficient of the order of 10^3.

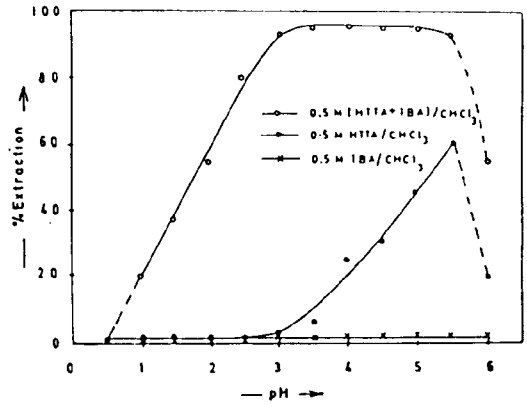

Fig. 1: pH dependence of the percentage extraction of Pb(II).

Fig. 2(a) shows the effect of shaking time on the extraction of lead with an equimolar (0.5M)

mixture of HTTA and TBA at pH 3 whereas Fig. 2(b) indicates the effect of equimolar concentration of the mixture of both extractants in the range from 0.1 to 0.5M. For fig. 2(b), 10 minutes an optimum shaking time, as evident from fig. 2(a), was employed. The extraction increases with an increase in equimolar concentration of mixture. A further increase beyond 0.5M is not possible due to low solubility of TBA in chloroform.

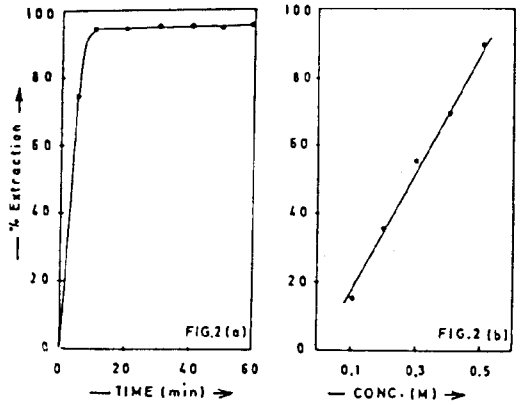

Fig. 2: Percentage extraction as a function of (a) shaking time and (b) equimolar concentration of HTTA-TBA in chloroform, at pH 3, ionic strength 0.1M(H^+, ClO_4^-).

Under the optimal conditions of shaking time, pH and synergic extractants concentration, the loading capacity is also determined to be 50 μg/ml. The distribution coefficient is randomly checked by measuring lead in aqueous phase after its subsequent back-extraction into 1.5M nitric acid solution and found to be within the experimental error of $\pm$ 3-4%.

The following equations have been used to ascertain the stoichiometric compositions, equilibrium contants ($K_{m,n}$ and $K_{m,o}$) and stability constant ($\beta_{m,n}$):-

$$M^{+m} + m\,HTTA \underset{}{\overset{K_{m,o}}{\rightleftharpoons}} M(TTA)_m + mH^+ \quad (1)$$

$$\log K_{m,o} = \log D_o - mpH - m \log [TTA] \quad (2)$$

$$M^{+m} + m\,HTTA + n\,TBA \overset{K_{m,n}}{\rightleftharpoons} M(TTA)\,M^{+m}\,TBA + mH^+ \quad (3)$$

$$\log K_{m,o} = \log D_{syn} - mpH - m \log [HTTA] - n \log [TBA] \quad (4)$$

$$M(TTA)_m + n\,TBA \overset{\beta_{m,n}}{\rightleftharpoons} M(TTA)_m, n\,TBA \quad (5)$$

$$\log \beta_{m,n} = \log K_{m,n} - \log K_{m,o} \quad (6)$$

Where $D_{syn} = D\text{-}D_o$ and D and D_o are the distribution coefficients in the presence and absence of TBA respectively.

Fig.3(a) shows that at constant TBA concentrations (0.4 M and 0.25 M) the slope of the curve is two at higher and one at lower concentration of HTTA at pH 3. This indicates the number of HTTA molecules attached to Pb(II) at its higher and lower concentration respectively.

The slope analysis at pH 5.5 has been carried out using equations (2) and (4) at constant TBA concentration of 0.4 M and 0.25 M. Similar curve (curve C in fig 3 (b) having a slope of two is exhibited irrespective of its concentration. However, in the absence of TBA (curve D in fig. 3 (b)), the slope of the curve is one over the entire range of HTTA.

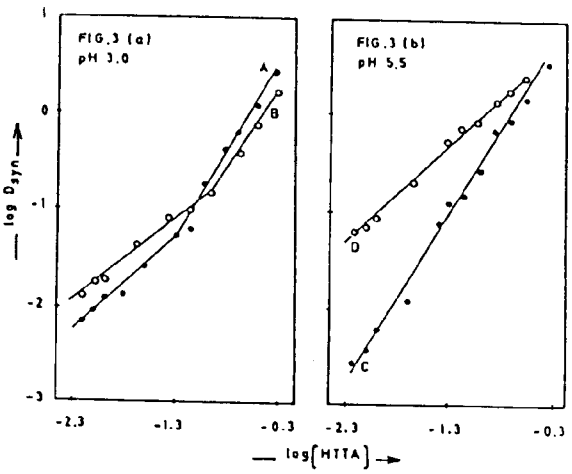

Fig. 3: Variation of distribution coefficient as a function of HTTA at constant TBA concentration in chloroform. A = 0.4M TBA; B = 0.25M TBA; C = 0.4M TBA and 0.25 M TBA; D = 0.00M TBA.

Fig. 4 shows the variation of D_{syn} with respect of TBA concentration at pH 3 at constant HTTA concentration of 0.4M and 0.25M (curve A and B) respectively, indicating that only one TBA molecule is attached to the metal in the synergic adduct. Moreover, at pH 5.5 and at similar constant HTTA concentration the slope of the curve C in fig. 4 is zero indicating no attachment of TBA molecule to central metal ion.

The data indicates that at pH 3, two possible species i.e. $Pb(TTA_2.TBA$ or $PB(TTA)^+.TBA$ are formed depending upon HTTA concentration. The

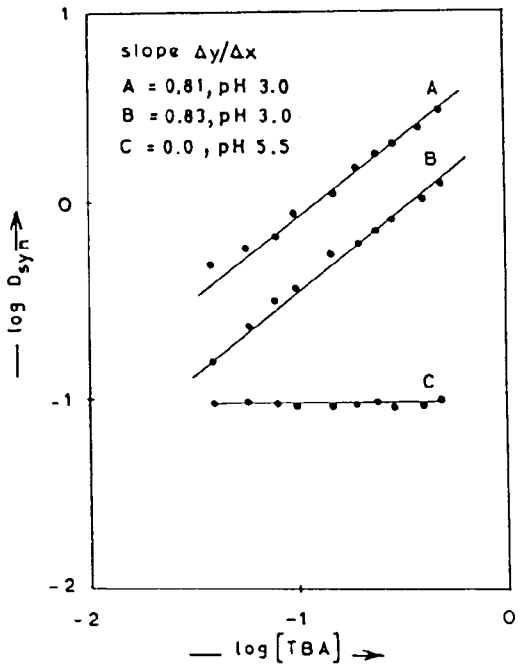

Fig.4: The influence of TBA on the distribution of Pb(II) at fixed HTTA concentration in chloroform, ionic strength 0.1M(H^+, ClO_4^-) A = 0.4M HTTA, pH 3; B = 0.25M HTTA pH 3; C = 0.4M and 0.25M HTTA, pH 5.5.

first species $Pb(TTA)_2$.. TBA is neutral and quantitatively extractable ($D_{syn} > 10^3$), whereas second species [Pb(TTA).TBA]ClO_4 has least extractibility ($D_{syn} < 0.1$). The possible mechanism for adduct formation of the first species from Figs. 3(a) and 4 (curve A and B) may be as follow:

$$Pb^{2+} + \overline{HTTA} \rightleftharpoons \overline{Pb(TTA)} + H^+ \quad (7)$$

$$\overline{Pb(TTA)^+} + TBA \rightleftharpoons \overline{Pb(TTA)^+.TBA} \quad (8)$$

$$\overline{Pb(TTA)^+TBA} + HTTA \rightleftharpoons \overline{Pb(TTA)_2.TBA} + H^+ \quad (9)$$

where bar indicates the organic phase.

The results at pH 5.5 show that in the presence of TBA, the number of HTTA molecules attached to Pb(II) is two indicating the following reaction:

$$Pb^{+2} + \overline{2HTTA} \xrightarrow[(TBA)]{K_2} \overline{Pb(TTA)_2} + 2H^+ \quad (10)$$

Where TBA may act as a catalyst. However, in the absence of TBA, the number of HTTA molecules attached to the Pb(II) is one, showing the following pathways:

$$Pb((OH)^+ + \overline{HTTA} \rightleftharpoons \overline{Pb(TTA).(OH)} + H^+ \quad (11)$$

or

$$Pb^{+2} + \overline{HTTA} \xrightleftharpoons{K_1} \overline{Pb(TTA)^+} + H^+ \quad (12)$$

$$\overline{Pb(TTA)^+} + ClO_4^- \rightleftharpoons \overline{Pb(TTA).ClO_4} \quad (13)$$

In view of the low percentage of hydrolyzed species $Pb(OH)^+$ (<1%) [9-10] the possibility of reaction (11) is ruled out. Therefore, extraction of lead at pH 5.5 proceeds via equations (12) and (13). It can be concluded from Fig. 1 that the species Pb(TTA).ClO_4 has lower extractability in the absence of TBA as compared to $Pb(TTA)_2$ in the presence of TBA under similar conditions.

Synergic coefficnet (S.C.) was calculated using the relationship:

$$S.C. = \log [D_{syn} (D_{TTA} + D_{TBA})^{-1}] \quad (14)$$

at pH 3 was found to be 2.85, indicating a strong synergic effect of TBA on the extraction of lead with HTTA. The equilibrium constant (log $K_{2,0}$ and log $K_{2,1}$) from equation (2) and (4), as well as stability constant (log $\beta_{2,1}$) from equation 6 at pH 3 were calculated and found to be -7.27, - 4.12, and 3.15 respectively with a standard deviation upto $\pm$ 0.2. Similarly at pH 5.5, the equilibrium constants (log K_2 and log K_1) from equation (10) and (12) were computed and found to be -9.12 $\pm$ 0.3 and - 10.08 $\pm$ 0.2 respectively. The data indicate that at pH 3, the stability of synergic adduct is greater as compared to that formed at pH 5.5 and different mechanisms are operative at these pH values

Experimental

Reagents

All the reagents were of Analar grade and used as such. Buffer solutions of pH 1 to 6 were prepared by mixing appropriate volumes of 0.1M $NaClO_4$ and $HClO_4$ solutions.

Stock solution of lead (1 g/l) was prepared by dissolving appropriate amount of specpure lead oxide (Johnson Matthey Chemical, Limited) in

minimum amount of suprapure nitric acid then heated nearly to dryness with 2 ml of 70% perchloric acid. The resulting residue was dissolved in 0.1M $HClO_4$. Fresh standard solutions of lead (5×10^{-5}M) were prepared by appropriate dilutions of this stock solution just before use.

Procedure

5×10^{-5}M lead solution was prepared by the appropriate dilution of the stock solution and were used throughout. Five ml of dilute lead solution was equilibrated for ten minutes with an equal volume of chloroform containing HTTA/TBA of desired concentration. After centrifugation, 4 ml of aqueous phase was separated and shaken with an equal volume of chloroform for the five minutes in another vial. The centrifugally separated aqueous phase was neubilized in an air-acetylene flame of atomic absorption spectrophotometer, Hitachi Model Z-8000 using hollow cathode lamp of lead under the conditions given in Table 1. A blank was prepared and treated under identical experimental conditions using chloroform without HTTA and TBA. The signal evaluation was made by subtracting the absorbance of blank from the absorbance of sample. All experiments were conducted at least in triplicate at 23 $\pm$ 2°C. The distribution ratio (D) was calculated by using the equation:

$$D = [C_T - C_{EX}]/C_{EX}$$

where C_T and C_{EX} deonotes the total concentration of lead in equeous phase before and after extraction, respectively.

Table 1: Optimized instrumental conditions used for the measurement of lead.

Parameter	
Lamp current	7.5 mA
Resonance abs. line	283.3 nm
Width of slit	1.3 nm
Type of burner	Standard
Burner height	7.5 mm
Fuel (C_2H_2) pressure	0.3 Kg cm^{-2}
Oxidant (air) pressure	1.6 Kg cm^{-2}

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