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EXTRACTION OF LEAD (II) BY TRILAURYLAMMONIUM BROMIDE

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Two-phase emf titrations were performed to study the mode of extraction of lead (II) by trilaurylammonium bromide, BHBr, dissolved *o*-xylene from 5.0 M Br,) 0.10 M (H) aqueous medium at 25± 0.2^{o} Assuming ideal behaviour of the organic phase experimental data were analysed by equilibrium law. Best fit to the data was obtained by assuming the presence of complexes $BH(PbBr_3)$, $K_{1,1} = (1.93 \pm 0.15)$ M^{-3}; $(BH)_2\ (PbBr_4)$, $K_{1,2} = (1.14 \pm 0.04) \times 10^2\ M^{-4}$ and $(PbBHBr)_3$, $K_{3,3} = (3.58 \pm 0.28) \times 1o^4$ M^{-11}. Aggregates of the salt BHBr, which are normally present in the organic phase do not play any significant role in the extraction of Pb(II) from the aqueous phase.

INTRODUCTION

During the last decade, long-chain amines and quaternary ammonium salts have been extensively used as ion-exchangers in the hydro-metallurgy and production of metals related to nuclear technology. [1 – 4] By potentiometric, osmometric and other methods [5 – 9]., it is known that alkylammonium salts form aggregates particularly in nonpolar solvents. The equilibrium system trilaurylamine-hydrobromic acid (TLA – HBr) with o-xylene as the diluent, has already been investigated [10]. In addition to the mono-meric species trilaurylammonium bromide (BHBr), the system is reported to contain $(BHBr)_2$, $(BHBr)_3$, and a larger aggregate of the order of $(BHBr)_{30}$. There exists some controversy in regard to the mode of extraction of metals by these alkylammonium salts. The present work was undertaken with the aim to investigate, if the metal ions from the aqueous phase are extracted through polyionization of the aggregates of BHBr or through monoionisation, irrespective of the degree of polymerization of BHBr. For this purpose, the distribution of macroamounts of Pb (II) covering a broad range in Pb(II) and BHBr concentrations have been studied.

EXPERIMENTAL

Reagents and Solutions: All chemicals used were analytical grade reagents. Trilaurylamine, (TLA) of 99 percent purity was obtained from Fluka. Freshly distilled mercury was used to prepare lead amalgams. Pb (II) solution was prepared by dissolving recrystallized lead bromide in LiBr solution. The total ionic concentration of the aqeous phase was kept at 5.0 M bromide (Br), containing 0.10 M($\bar{H}$) added as hydrobromic acid. Pb(II) in this solution was standardized gravimetrically by weighing as lead sulphate. Five different concentrations of TLA, with *o*-xylene as the diluent, were converted into the corresponding ammonium bromide salt, BHBr, by equilibrating them with 0.10 M hydrobromic acid whose total bromide concentration was also adjusted at 5.0 M (Br) by the addition of LiBr.

Experimental Technique. The essential features of the two-phase emf titration technique have been described elsewhere [11]. Slight modification in the titration flask was made to cater for the Pb-Hg, amalgam electrode instead of the glass electrode used originally. The Pb – Hg, electrode, used to measure the concentration of Pb (II) in the aqueous phase was connected to the reference Ag-AgBr (s) electrode through a Wihelm-bridge [12].

The measuring cell can be described as,

$$\text{Pb-Hg} \left| \begin{array}{c} Li^+ + 0.10\ MH^+ + Pb\ (II) \\ 5.0M(Br)\ (\text{Test solution}) \end{array} \right\| \begin{array}{c} LiBr \\ 5.0M(Br) \end{array} \left| \ \text{AgBr (s)-Ag} \right.$$

From a burette a known volume of the BHBr (organic phase) is periodically added and equilibrated with the test solution. The emf of the system was measured by a Cambridge vernier potentiometer. Argon gas free from oxygen, was continuously bubbled through the test solution in the titrating flask to insure proper functioning of the Pb – Hg electrode [13]. The titrating flask was thermostated in an oil bath kept at 25 ± 0.2^{o}. Titration for each BHBr concentration was completed in at least two separate experiments, such that the readings from one titration partly overlapped the other. Any titration in which the overlapping portions differed by more than 0.02 mv in emf was repeated. At the end of some titrations, the reversibility of the system and the response of the Pb – Hg electrode were checked by introducing known amounts of Pb (II) in the aqueous phase.

RESULTS AND DISCUSSION

The results of titrations for five different concentrations of BHBr are given in Fig. 1. The volume per cent and the corresponding molarities of BHBr are given in Table 1.

Table 1. concentrations of BHBr.

Volume per cent	Molarity M	Symbol in the graph
2.5	0.0394	X
5.0	0.0777	□
10.0	0.1576	●
15.0	0.2327	Δ
20.0	0.3118	O

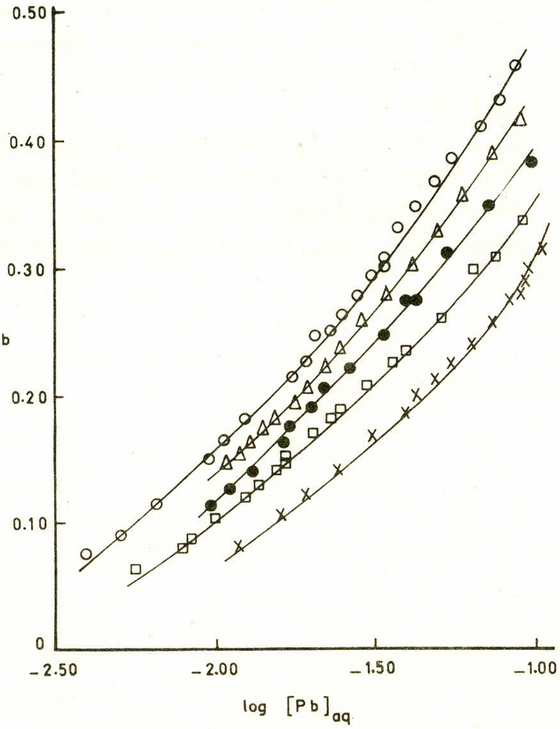

Fig. 1. Z_{pb} plotted against-log Pb_{aq} for five BHBr concentrations. The symbols are given in Table 1. The curve have been calculated from the proposed mechanism.

The data in Fig. 1 have been plotted as Z_{pb} as a function of the equilibrium – 10 g $[Pb]_{aq}$, where

$$ZP_b = \frac{[Pb]\ org}{[BHBr]_{Tot}} \tag{1}$$

ZP_b, therefore, represents the average number of metal atoms attached per molecule of BHBr. From Fig. 1 it can be seen that the curves for different BHBr concentrations do not coincide, indicating the formation of polynuclear complexes. At higher values of log $[Pb]_{aq}$ titration curves for the various concentrations of BHBr, appear to be converging to a single curve showing the presence of a mononuclear species in that region. The general equilibrium reaction can be described as:

$$Pb^{2+}(aq) + 2p\ \bar{Br}(aq) + q(BHBr)(org) = (PbBr_2)p\,(BHBr)_q\,(org) - \tag{2}$$

The equilbrium system has been studied at constant ionic medium of 5.0 M Br^-. It is, therefore, assumed that the activity coefficients of the reactants and products remain practically constant. Applying equilibrium law to equation (2).

$$k_{pq} = [(PbBr_2)_p (BH\bar{Br})_q]_{org} \times [(Pb^{2+})]_q^{-p} [Br]_{aq}^{-q}\ [BHBr]_{org}^{-q} \tag{3}$$

Where the square brackets represent the concentration of the species in equilibrium. k_{pq} is the equilibrium constant, p and q are the integers depending upon the compositon of the complex. It is to be noted that the case when p = o in equation (2) refers to the aggregation of the BHBr only. The equilibrium data were anlysed by the improved version of the computer programme LETAGROPVRID [14]. In this programme many different values of (p,q,k_{pq}) were tried and the minimum in error square sum, $U = \sum^{N} (Z_{cal} - Z_{expt})^2$, between the calculated and computed values of Z was sought. N is the total number of the experimental points, which were 89 in this investigation. For obtaining the best fit, the computer programme is also capable of chosing or rejecting the possible presence of other complexes. In preliminary calculations, more than twenty combinations of p, q and k_{pq} were tried. The following set of values for log $\{k_{pq} \pm 3\,\sigma(k_{pq})\}$ gave the best fit.

log $k_{1,1} = 1.93 \pm 0.15\ M^{-3}$, log $k_{1,2} = (1.14 \pm 0.04) \times 10^2\ M^{-4}$ log $k_{3.3} = (3.58 \pm 0.28) \times 10^4\ M^{-11}$, U = 1.39 X

10^{-2}, and $^{\sigma}z = 0.013$, where σ is the standard deviation in ZP_b or k_{pq} as the case may be, M being the units of k_{pq}. The fit between the experimental data and that calculated on the basis of the proposed mechanism has been shown in Fig. 1, which is satisfactory.

DISCUSSION

The two-phase emf titration technique is very useful in the study of complex equilibria. Besides precision, the experimental data obtained cover a broad range in the concentration of the reactants. Although no prior assumptions regarding the nature of the extracted species were made, anionic species $(PbBr_3)^{1-}$ and $(PbBr_4^{2-})$ have been found to be extracted in the equilibrium system. Similar speices of the type $(PbBr_n^{2-n})$ with values of n = 3 and 4 have independently reported [15 – 16] to predominate in the $(PbBr_2 - LiBr)$ system, which agree to our interpretation. The results clearly indicate that BHBr in the organic phase behaves monomerically for the extraction of Pb(II). Computer calculations excluded the presence of a large aggregate like 30, 30, although this was indicated in the (TLA – HBr) system. The presence of atrimeric species is however, common to both the (TLA – HBr) and (Pb – BHBr) systems, but the concomitant presence of the species 0,3 and 3,3 in the system Pb – BHBr was ruled out in favour of a 3,3 complex alone. This indicates that the trimeric species in the extraction of Pb(II) is not formed through the polyionization of $(BHBr)_3$.

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