Solvent Extraction Study of Mercury(II) with Zolon Red (HZR)

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Zolon Red, Mercury(II)

The extraction of mercury(II) from the aqueous solutions of mercury(II) nitrate and mercury(II) chloride with zolon red (HZR) dissolved in n-butanol has been studied. The extraction of mercury(II) from the aqueous nitrate system has been found to be much better compared to that from the aqueous chloride system in the pH range of 1 to 6. The extraction of mercury with zolon red is simple, fast and selective. The composition of the extracted mercury zolon red compound has also been studied. Regeneration of the extracting solution of zolon red is readily achieved by stripping the mercury(II) with an aqueous cyanide solution.

Introduction

The awareness of the high toxicity of mercury(II) and its role in the environment has generated considerable interest in discovering better methods for the removal of mercury(II) at micro and macro levels from the industrial waste solutions. Solvent extraction techniques which have been applied very successfully in the nuclear technology and copper extraction are receiving increasing attention in the search for efficient method for the removal and recovery of mercury(II) from the industrial waste solutions such as the effluents from chloroalkali plants. The number of extractants for mercury(II) reported in the literature are dithizone [1], tribenzylamine [2], high molecular weight amines [3], macrocyclic polyethers [4] and polyurethane foams [5, 6]. Of these extractants, the successful applications of the high molecular weight amines [7] in the nuclear technology attest for their industrial potential for removal of mercury from aqueous solutions. This paper describes the solvent extraction study of mercury(II) with zolon red (HZR) from the aqueous nitrate and chloride systems in the pH range between 1 and 6. Zolon red has already been reported to form coloured compounds with several metal ions including mercury(II) in our earlier papers [8, 9].

Experimental

All chemicals used in this investigation were of standard reagent quality. Zolon red was synthesised by the method reported in our previous papers [8, 9]. Its saturated solution of 0.025 M concentration in n-butanol served as organic phase. The stock solutions for mercury(II) nitrate and mercury(II) chloride were prepared by dissolving the respective salts in distilled water. The buffer solutions for the pH range between 1–6 were prepared by the standard method described in text books of practical inorganic chemistry [10].

The extraction of mercury(II) was carried out by placing 5 ml of mercury(II) salts solutions in a small flask and adjusting pH by a buffer solution and finally adding 25 ml of zolon red solution. The mixture was shaken for about twenty minutes at about 25 °C and was allowed to separate into two layers in a separatory funnel. The aqueous and organic phases were separated and analysed for mercury(II). The concentration of mercury(II) in the aqueous phases was determined by the gravimetric method [10] of precipitating mercury(II) as sulphide. The mercury(II) concentration in the organic phases were calculated by difference between the initial and final values of the aqueous phases. The mercury(II) concentration in the organic phases were also checked by a method where a known volume of organic phase was evaporated to dryness followed by an addition of concentrated nitric acid and evaporation to dryness again. The residue was dissolved in dilute nitric acid and made up to exactly 25 ml and then determining the concentration of mercury(II) as in the case of the aqueous phases.

A saturated alcoholic solution of zolon red was added to the aqueous solution of mercury(II) nitrate of 0.1 M concentration buffered with 10⁻⁵ M solution of sodium acetate. Mercury(II) gave red precipitates with zolon red which were soluble in excess alcoholic solution of zolon red. The red precipitates of mercury zolon red when first formed, appeared as colloids but on standing separated as red precipitates which then were filtered off, dried and analysed for a stoichiometric ratio of mercury(II) to zolon red (Hg:ZR) which was found to be 1:2.

Infra-red spectra of zolon red, mercury zolon red in Nujol mull were obtained with Perkin Elmer 257
Results and Discussion

The extraction reaction of mercury(II) with zolon red from the aqueous nitrate and chloride solution is of the type:

\[
HZR \rightleftharpoons H^+ + ZR \tag{1}
\]

\[
2 HZR + Hg^{2+} \rightleftharpoons Hg(ZR)_2 + 2 H^+ \tag{2}
\]

Zolon red, a weak acid dissociates and forms red coloured compound with mercury(II). The red coloured compound to be referred as mercury zolon red, Hg(ZR)_2, is insoluble in aqueous solutions but soluble in acids and organic solvents. The solubility of mercury zolon red in acids and incomplete precipitation of mercury(II) in the absence of sodium acetate buffer suggest that the reaction between mercury(II) ions and zolon red is reversible. The removal of dissociated hydrogen ion by a buffer solution shifts the equilibrium of the reaction towards the right and results in a complete precipitation of mercury(II). A quantitative precipitation of mercury(II) from an aqueous solution of mercury(II) nitrate of \(10^{-2}\) M concentration occurred at pH 4 with the saturated alcoholic solution of zolon red. The analysis of the mercury zolon red compound indicated the stoichiometric ratio of 1:2 between mercury(II) and zolon red. Furthermore, the infrared and electronic absorption spectra in the visible region of zolon red and mercury-zolon red favoured the formation of mercury zolon red by ion-association. The infrared spectrum of zolon red had a broad band at 3410 cm\(^{-1}\) and a strong band at 1435 cm\(^{-1}\) assigned to -OH stretching and -OH bending vibrations. However, these bands were absent in the infrared spectrum of the mercury zolon red, thereby confirming the replacement of the hydrogen of the hydroxyl group by mercury(II).

Both zolon red and mercury zolon red showed maximum absorption at 520 nm in the electronic absorption spectra.

The extraction of mercury(II) from the aqueous solutions of mercury(II) nitrate and mercury(II) chloride with zolon red dissolved in n-butanol as a function of pH is shown in Fig. 1. The percentage extraction of mercury(II) in the case of the aqueous nitrate system is much higher than that of the chloride system. This can be attributed to a high concentration of mercury(II) ions in the aqueous phase, as mercury(II) nitrate has a higher dissociation constant than mercury(II) chloride. The dependence of the extraction of mercury(II) on its concentration in the aqueous phase has also been confirmed by an increase in the distribution coefficient of mercury(II) with increase in concentration of mercury(II) chloride in the aqueous phase as shown in Fig. 2. However, the distribution coefficient of mercury(II) decreases when the concentration of mercury(II) chloride in the aqueous is above 0.12 M. This decrease in the distribution coefficient of mercury(II) may be explained by the formation of a chlorocomplex, \((HgCl_2)^{2-}\) as well as insufficient amount of zolon red. As shown in Fig. 1, the decrease in the extraction of mercury(II) above pH 4 may be a reflection of increasing tendency to form hydroxy species of mercury(II). The distribu-
The extraction coefficient of mercury(II) as a function of the pH and the concentration of zolon red is shown in Figs. 3 and 4, respectively. The distribution coefficient of mercury(II) is highest at pH 4, and is also increased with increase in the concentration of Hg$^{2+}$ and $\text{ZR}^-$ ions, the concentration of $\text{ZR}^-$ ions being influenced by pH. The extraction efficiency was improved considerably when a required volume of zolon red solution was used in two or three fractions instead of utilising the same volume in a single extraction as expected.

Mercury zolon red compound was found to be soluble in acids and cyanide solutions, however the zolon red regenerated was destroyed by acids whereas it was found to be stable in the aqueous cyanide solution, while mercury(II) forms a cyano complex according to the reaction (3):

$$\text{Hg(ZR)}_{\text{org.}} + 4 \text{CN}^-_{\text{aq.}} = \text{Hg(CN)}_{\text{aq.}}^2 + 2 \text{ZR}^-_{\text{org.}} \quad (3)$$

The mercury(II) was stripped quantitatively as cyano complex from the organic phase with the aqueous cyanide solution (0.5 M KCN). The regenerated zolon red remained in the organic phase and was subsequently reused. Zolon red, thus for process application can be regenerated for recycle operations. Zolon red is a promising extracting reagent for mercury(II) and may find application in the treatment of mercury pollution and the recovery of mercury from the aqueous chloride solutions of industrial waste.