of the results of determination of the alkaloids by the dye (Solochrome Green V 150) has been given in Table 2.

References

EXTRACTION OF HG(II) WITH CAPROIC ACID

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Received 13 February 1978; accepted 10 May 1978

The extraction of Hg(II) into chloroform containing hexanoic acid has been studied. The effect of various variables like metal and acid concentrations and pH of the aqueous phase on extraction has been investigated. These studies indicate that the extracting species is monomeric and involves four hexanoic acid molecules per Hg2+ ion; two of the acid molecules being utilized for solvation. The corresponding extraction equilibrium can be written as

\[ \text{Hg}^{2+} + 2(\text{HR})_2 \rightarrow (\text{HgR}_2)_2(2\text{HR})_2 + 2\text{H}^+ \]

In recent years considerable interest has grown in the extraction of metals by aliphatic monocarboxylic acids. Schweitzer et al. have studied the extraction of some metals in caproic acid systems and observed that the metals are extracted as solvated metal carboxylates either in monomeric or polymeric form. A survey of literature revealed that practically no work has been done on the identification of extracting Hg(II) carboxylate species. Only the extraction behaviour with some carboxylic acids is studied. Fletcher and Wilson and Plaksir and Anisimova have reported the extraction of Hg(II) with naphthenic acid and assigned it a position in a selectivity series of metals. Using these data the extracting mercury(II) species is identified and the equilibria involved are discussed.

Mercuric nitrate (GR) was dissolved in doubly distilled water, and to this a few drops of conc. HNO3 were added to prevent hydrolysis. The solution was standardized with sodium chloride using diphenylcarbazone indicator. Caproic acid was standardized by usual acid-alkalimetric titration. All other reagents were also of AR grade and used as such 200Hg radioisotope supplied by Bhabha Atomic Research Centre, Bombay (India), was used as a tracer.

In each set equal volumes (10 ml) of the aqueous [1×10^{-4} M Hg(II)] or any other concentration] and organic phases (0-25M or any other concentration of caproic acid) were shaken at room temperature, (20° ± 2°). The ionic strength of the aqueous phase was maintained at 0-1M by adding NaN03 solution. After equilibration the two phases were separated and the pH of the aqueous phase determined by a Cambridge bench pH-meter. Suitable aliquots of the two phases were counted using a NaI(Tl) well-type scintillation counter and the distribution ratio calculated by the usual method.

The data on the extraction of Hg(II) by caproic acid dissolved in chloroform have been analysed following the method of Tanaka et al.

The total concentration of mercury in the organic phase is given by Eq. (1)

\[ \log C_{\text{Hg}, \text{org}} = j \left( \log C_{\text{Hg}, \text{aq}} - \log \alpha(\text{Hg}) - 2 \log [\text{H}^+] \right) \]

\[ + \log \sum_{i=0}^{n} K_{f} \left[ (\text{HR})_2 \right]_i \left[ (\text{HR})_2 \right]_0 + j \log j \ldots (1) \]

where \( C_{\text{Hg}, \text{org}} \) and \( C_{\text{Hg}, \text{aq}} \) denote total mercury concentrations in organic and aqueous phase respectively, \( \alpha(\text{Hg}) \), the side reaction coefficient taking into account the hydrolysis as well as complexation of Hg2+ in the aqueous phase. In the above equation, the concentration of caproic acid \((\text{HR})_2\) being kept constant, a plot of \( \log C_{\text{Hg}, \text{org}} \) vs \( \log C_{\text{HR}, \text{aq}} - \log \alpha(\text{Hg}) - 2 \log [\text{H}^+] \) should be linear with a slope of \( j \) from which the degree of polymerization is determined.

When only one species \((\text{HgR}_2)_2(\text{HR})_2\) is predominant in the organic phase, Eq. (1) is simplified to

\[ \log C_{\text{Hg}, \text{org}} = j \left( \log C_{\text{HR}, \text{aq}} - \log \alpha(\text{Hg}) - 2 \log [\text{H}^+] \right) \]

\[ = j \log K_{f} + j(1 + x/2) \log \left[ (\text{HR})_2 \right] \ldots (2) \]

According to this expression the plot of experimentally determinable values log \( C_{\text{Hg}, \text{org}} - j \log C_{\text{HR}, \text{aq}} - \log \alpha(\text{Hg}) - 2 \log [\text{H}^+] \) against log \left[ (\text{HR})_2 \right] provides
us with a means to determine the number of caproic acid molecules incorporated in the extracted species.

Plots were drawn between log D and equilibration pH of the aqueous phase at different metal ion concentrations keeping caproic acid concentration constant. The curves at the different metal ion concentrations are coincident indicating the absence of any polymeric species in the system. Most of the points lie on a linear plot with a slope around 2, indicating the release of two protons per metal ion in the reaction of Hg(II)-caproic acid.

The degree of polymerization of the extracted species is also checked by plotting log CHg,o against log C[Hg] at different total caproic acid concentrations and pH = 2 (Fig. 1). At these pH values the hydrolysis of Hg(II) in the aqueous phase is assumed to be negligible [x(Hg) = 1] or Hg^{2+} = C[Hg]. The linear plots approximately corresponding to the slope of unity are obtained, thereby suggesting the value of j = 1 and absence of any predominant polymeric extracted species in the system.

The number of caproic acid molecules (R and/or HR) incorporated in the extracted species is confirmed by the slope of the linear plot obtained by plotting (log D + 2 log [H^+] vs log [(HR)]_0) at constant C[Hg] (Fig. 2). The slope of the linear plot is approximately 2, i.e. (1+x)/2 = 2 or x = 2.

Thus the number of free acid molecules in the species is two.

Based on the above observations the composition of the extracted species can be written as \( \text{HgR}_2\text{2HR} \) and the corresponding extraction equilibrium is

\[
\text{Hg}^{2+} + 2(\text{HR})_2 \rightarrow [\text{HgR}_2\text{2HR}] + 2\text{H}^+ 
\]

Very high extraction (>90%) of the hexanoate under the experimental conditions suggests the possible absence of water molecules in the extracted species.

One of the interesting feature of the extraction of Hg(II) with caproic acid is the lack of polymerization of the extracted species. A large number of extracting metal carboxylate species reported by Tanaka et al.\(^\text{10,11}\) contain polymeric species also. Regarding this system, another important point which needs to be mentioned is the predominance of a single extracting species. In the extraction of Pb(II), Cu(II) and In(III) more than one major extracting species has been identified.

The financial assistance by the UGC, New Delhi, is gratefully acknowledged.

References