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Reaction of Mercury(II)–Ethylenediaminetetraacetate–Capriquat Complex with Potassium Iodide in 1,2-Dichloroethane and Its Application to the Spectrophotometric Determination of Mercury(II)

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Synopsis. A mercury(II)-ethylenediaminetetraacetate-methyltrioctylammonium chloride (Capriquat) complex in 1,2-dichloroethane reacts quantitatively with potassium iodide and forms an ion-pair of tetraiodomercurate(II) with a capriquat cation. The composition of the extracted species was determined to be $[Hg(edta)(Cq)_2]$. The reaction was applied to the spectrophotometric determination of mercury(II).

Irving and Al-Jarrah[1] have developed a useful method for separating mercury(II) from many metal ions, based on the extraction of several edta complexes with a methyltrioctylammonium chloride (Aliquat 336) solution in 1,2-dichloroethane.

The spectrophotometric determination of mercury(II) as a tetraiodo complex has been carried out by several authors.[2–4]

In the present work, it is reported that the mercury(II)–edta–methyltrioctylammonium chloride (Capriquat, abbreviated Cq^+Cl^-) complex in the dichloroethane extract reacts quantitatively with potassium iodide forming an ion-pair consisting of a tetraiodomer-curate(II) and a capriquat cation. The present methodhas the advantage that the determination is possible with a part of the extract needed.

Experimental

Reagents. A capriquat solution (0.1 mol dm^{-3}) was prepared by dissolving 12.5 g of capriquat (Dojindo Pharmaceutical Co.) in 250 cm^3 of 1,2-dichloroethane. All other chemicals used were of analytical reagent grade. A stock solution of mercury(II) was prepared from mercury(II) nitrate (Wako Chemicals Co.) and standardized volumetrically.[5] A stock solution of ethylenediaminetetraacetic acid (H_4edta) was prepared from its disodium salts.

A stock solution of potassium iodide (Wako Chemicals Co.) was prepared and stored in a subdued light environment. Deionized water was used.

Apparatus. A Hitachi 356 two-wavelength and double-beam spectrophotometer and a Shimadzu QV-50 spectrophotometer with 10-mm quartz cells were used for the absorptiometric measurements. An Iwaki Shaker, model KM, was used for the extraction.

Established Procedure. Into a 100-cm^3 separatory funnel were placed an aliquot of a mercury(II) solution containing less than 80 μg, 0.4 cm^3 of a 0.01 mol dm^{-3} Na_2H_2edta solution and 10 cm^3 of a phosphate buffer solution (pH 7.0) in the sequence. The mixture was diluted to 30 cm^3 with water. After the addition of 20 cm^3 of a 0.01 mol dm^{-3} capriquat solution, two layers were shaken for 10 min and allowed to stand for 10 min. The organic layer was drained into a beaker containing anhydrous sodium sulfate and dehydrated. A 10-cm^3 portion of the extract was placed into another separatory funnel and shaken with 10 cm^3 of a 0.03 mol dm^{-3} potassium iodide solution. The organic layer was transferred into a beaker, dehydrated as above and then subjected to optical measurements.

Results and Discussion

Extraction of the Mercury(II)–edta Complex with a Capriquat Solution. As shown by Irving and Al-Jarrah,[1] the mercury(II)–edta complex in the presence of a 10% excess of Na_2H_2edta is quantitatively extractable in the pH range from 3.5 to 11 by an equal volume of a 0.2 mol dm^{-3} Aliquat 336 solution in dichloroethane.

The results of present investigation, in which the extractability of mercury(II) was determined from the absorbance measurements according to the above procedure, were almost in accordance with those of Irving and Al-Jarrah. However, it is important to note that when the Na_2H_2edta concentration was increased above 0.01 mol dm^{-3}, a decrease in extractability of mercury(II) was observed, probably because of a competitive reaction between the $Hg(edta)^{2-}$ complex and the H_2edta^{2-} ions with the capriquat cations.

The extractability of mercury(II), as determined by repeatedly shaking the separated aqueous layer with a fresh capriquat solution in dichloroethane was found to be 93.3% for a single extraction at as aqueous-to-organic volume ratio of 3 : 2. At volume ratios higher than twice the aqueous layer up to the ratio of the organic layer, the extractability decreased.

Composition of Extracted Species. The distribution ratio D is evaluated to be

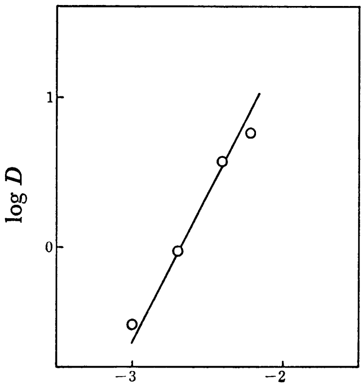

Fig. 1. A plot of log D *vs.* log [Capriquat] at pH 7.01 in the presence of 15 μmol dm^{-3} mercury(II) and 0.13 mmol dm^{-3} Na_2H_2edta.

The straight line was drawn based on the results of the method of least squares.

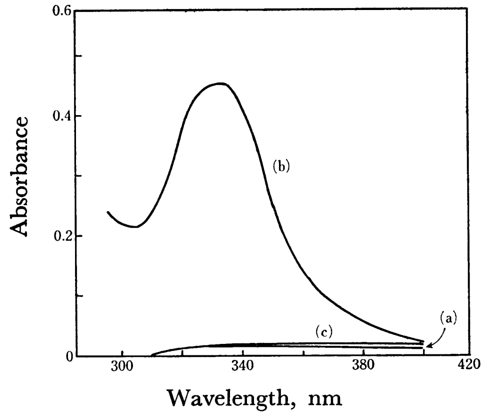

Fig. 2. Absorption spectra of dichloroethane extracts obtained from aqueous media buffered at pH 7.0 and containing 15 μmol dm^{-3} mercury(II) and 0.13 mmol dm^{-3} Na_2H_2edta.

Capriquat concentration in dichloroethane: 0.01 mol dm^{-3}.

a) $(Cq^+)_2[Hg(edta)^{2-}]$ ion-pair *vs.* dichloroethane, b) $(Cq^+)_2(HgI_4^{2-})$ ion-pair obtained by shaking with 0.03 mol dm^{-3} potassium iodide solution *vs.* dichloroethane, c) the reagent blank corresponding to curve (b).

$$D = \frac{(A/\varepsilon)}{C_i-(A/\varepsilon)} \tag{1}$$

where C_i is the initial concentration of $Hg(edta)^{2-}$ in the aqueous phase and ε is the molar absorption coefficient of the capriquat tetraiodomercurate(II) ion-pair. In an aqueous medium of pH 7.0 containing a large excess of Na_2H_2edta, mercury(II) exists in the form of $Hg(edta)^{2-}$. Hence, the slope of the plot of log D *vs.* log [Capriquat] should correspond to the molar ratio of the capriquat cation to the $Hg(edta)^{2-}$ anion. As is shown in Fig. 1, the plot has a slope of 1.99, clearly indicating that the composition of the extracted species *is estimated to be* $[Hg(edta)^{2-}(Cq^+)_2]$.

Absorption Spectra of Mercury(II) Complexes. The absorption spectra of the extract obtained according to the above procedure are given in Fig. 2. The ternary complex has an absorption maximum at 333 nm.

Effect of Potassium Iodide Concentration. A 10-cm^3 portion of the separated extract was shaken with an equal volume of an aqueous potassium iodide solution. It was found that a constant and maximum absorbance was obtained for potassium iodide concentration above 0.01 mol dm^{-3}. With various volumes of the potassium iodide solution, it was found that the maximum absorbance was obtained with 5—20 cm^3 of the 0.03 mol dm^{-3} potassium iodide solution.

Table 1. Effect of diverse ions

Mercury(II) taken: 88.8 μg

Interfering ion added	Tolerance limit, mg
Mg(II), Zn(II), NO_3^-, SO_4^{2-}	10
Al(III),[a] Cd(II), Co(II), Fe(II),[a] Mn(II), Pb(II), F^-,[c]	2
Sr(II)	1
Bi(III), Ca(II), Cr(III), Cu(II), Ni(II), Cl^-,[d]	0.5
Ag(I), Sn(II),[b]	0.1

a) Added as alum. b) Added as chloride. c) Added as ammonium salt. d) Added as potassium salt. Other metal ions were added as nitrates and anions as sodium salts.

Calibration Curve. Beer's law was obeyed in the concentration range from 1.1 to 8.8 μg cm^{-3} of Hg(II) in the extract. The molar absorption coefficient is 2.12×10^4 cm^{-1} mol^{-1} dm^3 and the Sandell sensitivity is 9.28×10^{-3} μg Hg(II) per cm^2.

Effect of Diverse Ions. The interference of diverse ions was investigated. Setting the tolerance limit for interfering ions causing an error at ±2.5% for mercury(II) recovery, the results summarized in Table 1 were found.

References

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