A Spectrophotometric Determination of Mercury(II) or Cadmium(II) by Solvent Extraction with 2, 2′-Dipyridyl Iron(II) Chelate

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The present paper will report on a continuation of our study concerning the solvent extraction of an anion with a metal chelate cation and its application to a spectrophotometric determination of the anion. Diamond et al.1) and Kuznetsov2) have described in their reviews that a large anion can be extracted into a polar solvent such as nitrobenzene with a large cation of onium or metal chelate. However, there seems to have been no mention of the solvent extraction of the anionic complex of a metal with a metal chelate cation. In our study, it is found that mercury (or cadmium) can be extracted into 1, 2-dichloroethane with 2, 2′-dipyridyl iron(II) chelate if the aqueous solution contains a large excess of iodide ions. Figure 1 shows the absorption spectra in the organic phase. Curve 1 (or 2) is a spectrum of the extract when mercury(II) (or cadminm) is absent in the aqueous solution. Curve 3 (or 4) is that of the extract when a small amount of mercury (or cadmium) is present. It may be observed that the presence of mercury(II) or cadmium ions leads to a considerable increase in the extraction. The absorbance maximum of the chelate cation in the organic phase is at 526 mμ. The maximum of the chelate cation in the aqueous solution was at

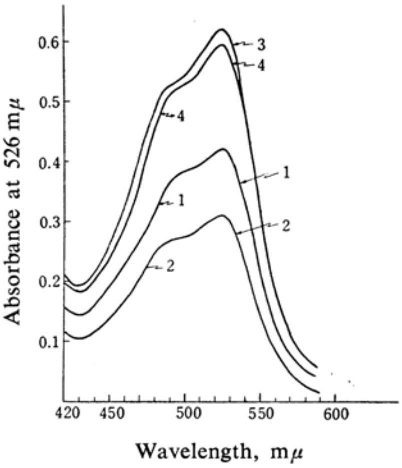

Fig. 1. Absorption spectra.

Reference : dichloroethane, pH : 6.5

Curve 1 : Spectrum of organic phase extracted from the aqueous solution (25 ml.) contained dip. (9.6×10^{-4} M), Fe(II) (2.4×10^{-4} M), NaAc (0.24 M) and KI (8.4×10^{-2} M) but Hg is absent.

Curve 3 : Spectrum of organic phase extracted from the aqueous solution (25 ml.) contained the same component as that of curve 1 and Hg (2 p.p.m.).

Curve 2 : Spectrum of organic phase extracted from the aqueous solution (25 ml.) contains dip. (6.4×10^{-4} M), Fe(II) (1.6×10^{-4} M), NaAc (0.24 M), KI (8.4×10^{-2} M) but Cd is absent.

Curve 4: Spectrum of organic phase extracted from the aqueous solution (25 ml.) contained the same component as that of curve 2 and Cd (1.6 p.p.m.).

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1) D. M. Diamond and D. G. Tuck, "Progress in Inorganic Chemistry," Vol. 2, Interscience publishers, Inc., New York (1960), pp. 139—150.

2) B. I. Kuznetsov, "The Chemical Basis for the Photometric Method by Solvent Extraction in Analytical Chemistry," State Printing Office of USSR, Moscow (1963), p. 11.

522 mμ, which coincides with the reported value.[3] This red shift of the spectrum may be attributed to the effect of the association of the cation and the anion in the organic layer. Feigl[4] has shown that 2, 2′-dipyridyl iron(II) chelate can be precipitated as a red crystal with a divalent complex anion, such as tetra-iodo-mercury(II) or cadmium. From these facts, it is quite likely that a chemical form of the extracted species is $\mathrm{Fe(dip)_3 \cdot HgI_4}$ or $\mathrm{Fe(dip)_3 \cdot CdI_4}$. To obtain optimum conditions for the determination of mercury(II) or cadmium, various factors were studied: the effect of the concentration of iron(II) ions and dipyridyl, the pH of the solution, the stability of the color, the shaking time, and the presence of diverse ions. The recommended procedure for the calibration curve is as follows:

1) For Cd: 2.0 ml. of the 2, 2′-dipyridyl solution (8×10^{-3} M), 2.0 ml. of the ferrous ammonium sulfate solution (2×10^{-3} M), 2.0 ml. of the sodium acetate solution (3 M), 7.0 ml. of the potassium iodide solution (0.3 M), and varying amounts (1∼7 ml.) of the standard cadmium solution (10 p. p. m.), were mixed, and the pH of the solution was adjusted to 6.5. After it had been diluted to 25 ml. with distilled water, the solution was shaken for 4 min. with 10.0 ml. of dichloroethane. The organic layer was then transferred to a flask containing 1 g. of anhydrous sodium sulfate, and the absorbance of the solution was measured at 526 mμ using the reagent blank as a reference. Beer's law is followed in the range of 0.4∼2.8 p. p. m. (Fig, 2).

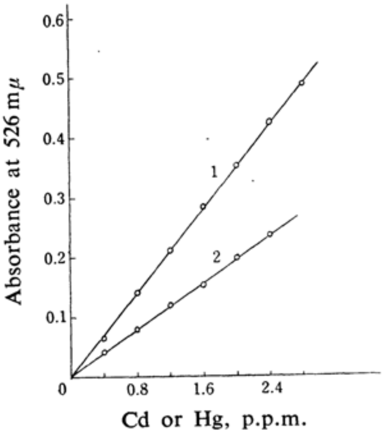

Fig. 2. Calibration curve.
Reference: Reagent blank, pH: 6.5
Curve 1: Dip. 6.4×10^{-4} M, Fe(II) 1.6×10^{-4} M, NaAc 0.24 M, KI 8.4×10^{-2} M, Cd<2.8 p.p.m.
Curve 2: Dip. 9.6×10^{-4} M, Fe(II) 2.4×10^{-4} M, NaAc 0.24 M, KI 8.4×10^{-2} M, Hg<2.4 p.p.m.

2) For Hg: 3.0 ml. of the 2, 2′-dipyridyl solution (8×10^{-3} M), 3.0 ml. of the ferrous ammonium sulfate solution (2×10^{-3} M), 2.0 ml. of the sodium acetate solution (3 M), 7.0 ml. of the potassium iodide solution (0.3 M) and varying amounts of the standard mercury(II) solution (10 p. p. m.) were mixed, and the pH of the solution was adjusted to 6.5. After it had been diluted to 25 ml. with distilled water, the solution was shaken for 6 min. with 10.0 ml. of the organic solvent. Then it was treated as in the procedure for cadmium. Beer's law is followed in the range from 0.4 to 2.4 p. p. m. Although several methods for the determination of mercury or cadmium are presented in the literature,[5] the proposed method is based on a new principle.

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[3] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 826 (1942).

[4] F. Feigl, "Spot Test, Part I, Inorganic Application," Elsevier Publishing Company (1954), p. 90.

[5] For instance, E. B. Sandell, "Colorimetric Determination of Traces of [Metals," Interscience publishers, Inc., New York (1959).