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The Formation of Ternary Complexes Involving Mercury(II) and Phenolphthalein Complexone

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Organic reagents (R) with two iminodiacetate group in a molecule react with mercury(II) to give the corresponding mercury(II) complexes. These complexes then react with anions (X), such as cyanide, thiocyanate, iodide, bromide, and thiosulfate, to form the corresponding mixed-ligand complexes. The molar ratio of Hg(II) : R : X in these mixed-ligand complexes is found to be 1 : 1 : 1.[1,2] In the mixed-ligand complex of thymolphthalein complexone (TPC), the ratio is also 2 : 1 : 1.[2] In this paper phenolphthalein complexone (PPC), which has a structure analogous to TPC, will be discussed with regard to reactions with mercury(II) and anions.

Experimental

Reagents and Apparatus. All the reagents were of an analytical grade and were used without further purification. A PPC solution of 1×10^{-2} M was prepared by disolving Dotite PPC (121.7 mg) with small amounts of water, adding 100 m*l* of methanol, and diluting to 200 m*l* with water. This solution was diluted to a suitable concentration with water when used. Standard mercury(II) (F=1.041) and cyanide solutions of 1×10^{-2} M and a buffer solution were prepared as in a preceding experiment.[1]

The absorbances of the solutions were measured by means of a Hitachi Perkin Elmer 139-type spectrophotometer, while the absorption spectra were recorded by means of a Shimadzu Multipurpose Recording Spectrophotometer, MPS-50L type, with quartz cells of an optical length of 10.0 mm. The pH values were measured by means of a Hitachi-Horiba M-5-type pH meter.

Results and Discussion

Reaction of Mercury(II) with PPC. Absorption Spectra: At pH 10.8, a PPC solution showed a weak absorption spectrum with a peak at 565 mμ in the visible region (Fig. 1). When mercury(II) was added to the solution, it gave a strong absorption spectrum in which the peak was shifted to 574 from 565 mμ and in which a new absorption peak appeared at 384 mμ in the visible region. In view of these facts, it can be said that PPC reacted with mercury(II) to form a mercury (II) complex with a strong absorption in the visible region.

Effect of pH: The absorbances of the mercury(II) complex appeared adruptly from a neutral solution, and gave constant values between about pH 10.5 and 11.5.

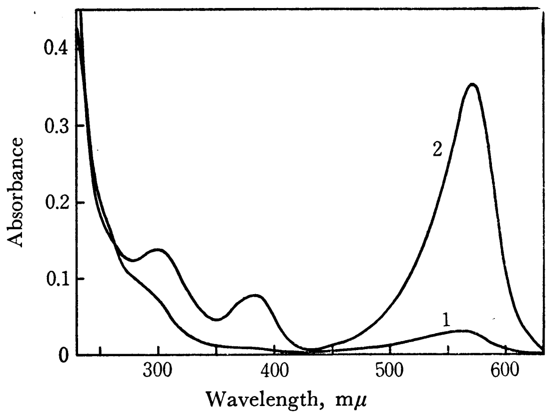

Fig. 1. Absorption spectra of mercury(II) complex and PPC at pH 10.8.
Reference: Water.
1) PPC: 2×10^{-5} M.
2) Hg(II): 1×10^{-5} M, PPC: 2×10^{-5} M.

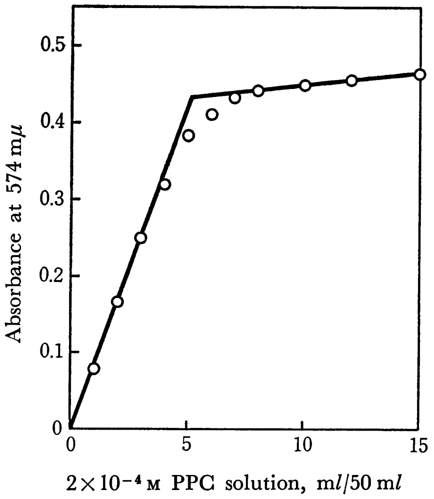

Fig. 2. Composition of mercury(II) complex (Molar ratio method).
Hg(II): 1×10^{-5} M, pH: 10.8, reference: water.

Composition of the Mercury(II) Complex: The molar ratio of mercury(II) to PPC in the mercury(II) complex was found to be 1 : 2 by the use of the molar-ratio (Fig. 2) and continuous-variation methods. The apparent stability constant (K) of the complex ($Hg(PPC)_2$) was found to be 1.0×10^{11} at an ionic strength of μ=0.10 and at pH 10.8 by the molar-ratio method.

Stability of the $Hg(PPC)_2$ and the PPC Solutions: The absorbance of the PPC solution (reagent blank) at pH 10.8 did not change for 2 hr. The absorbance of the mercury(II)-complex ($Hg(PPC)_2$) solution was constant for about 20 min, but it decreased at a rate of 1.0% an hour beyond this time.

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[1] T. Nomura, This Bulletin, **43**, 104 (1970).

[2] T. Nomura, R. Ikeda, and S. Komatsu, *Nippon Kagaku Zasshi*, **91**, 497 (1970).

Application for the Spectrophotometric Determination of Mercury(II): The above discussion shows that the spectrophotometric determination of mercury(II) with PPC was possible. Mercury(II) up to 60 μg could be determined with a good reproducibility by the following procedure, and the molar extinction coefficient was found to be 3.5×10^4.

Procedure: A mercury(II) sample solution containing up to 60 μg was treated with a buffer solution to adjust the pH to 10.5—11.5, 5 m*l* of a 2×10^{-4} M PPC solution were added, and then the mixture was diluted to 50 m*l* with water. The absorbance of the solution was measured after about 15 min at 574 mμ against the reagent-blank solution.

Reactions of $Hg(PPC)_2$ with Anions. Cyanide, iodide, and thiosulfate reacted with the mercury(II) complex to give the corresponding compounds, colored slightly. The molar ratio of the mercury(II) complex to these anions were determined by means of the molar-ratio (Fig. 3) and continuous-variation methods and by recording the absorption spectra of mercury(II)-complex solutions containing different amounts of the anions.

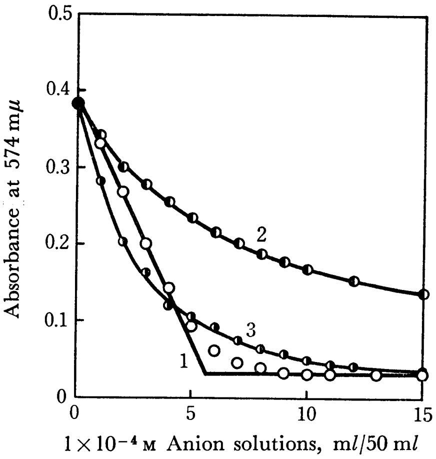

Fig. 3. Reactions of mercury(II) complex with anions. Hg(II): 1×10^{-5} M, PPC: 2×10^{-5} M, pH: 10.8, reference: water.
1) Cyanide (F=0.928). 2) Iodide (F=1.001).
3) Thiosulfate (F=1.000).

The absorption peak, at 574 mμ, of the mercury(II)-complex solution shifted linearly to 570 mμ with cyanide up to $CN^-/Hg(PPC)_2=1$. When an excess of cyanide was added, the absorption spectrum agreed with that of the PPC solution; the maximum absorption at 570 mμ shifted to 565 mμ, and the absorption peak at 384 mμ decreased. When an excess of iodide was added to the mercury(II)-complex solutions, the absorption peak at 574 mμ did not shift to 565 mμ, but to 569 mμ. From the results described above, it was found that cyanide and iodide (X_1) reacted with the mercury(II) complex as follows. When X_1 was added to the mercury(II) complex solution up to $Hg(PPC)_2/X_1=1$, a mixed-ligand complex ($Hg\text{-}PPC\text{-}X_1$) was formed and then the PPC was dissociated. When an excess of cyanide was added to the cyano mixed-ligand complex solution, the complex turned into mercury(II) cyanide and PPC. The iodo mixed-ligand complex, however, did not react with an excess of iodide to give mercury(II) iodide and PPC. From Fig. 3(1), it can be seen that the spectrophotometric determination of cyanide could be performed with the mercury(II) complex. This method was especially selective for cyanide because the only interfering anions were sulfide, thiosulfate, and iodide.

The mercury(II) complex reacted with thiosulfate in the molar ratio of 2 : 1. The absorption spectrum of this solution agreed with that of the PPC solution if an amount of thiosulfate about 3 times that in the molar ratio was added.

The absorption spectrum of the mercury(II)-complex solution did not change upon the addition of any other anions, such as fluoride, chloride, bromide, or thiocyanate. Therefore, it can be said that these anions did not react with the mercury(II) complex. The ammonium ion also did not react with this complex.