Letters to the Editor

A Color Reaction of Cadmium(II) with Dithizone in Methyltrioctylammonium Thiocyanate Medium

Hideo AKAIWA, Hiroshi KAWAMOTO and Etsuo HIYAMUTA

Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376

Keywords Dithizone, methyltrioctylammonium chloride, thiocyanate, cadmium(II), spectrophotometry

The extraction of cadmium(II) with dithizone(H_2dz) from strongly alkaline solution has been employed for the purpose of separation of the element from zinc(II). In this case, cadmium(II) is extracted as dithizonatocadmium(II), while zinc(II) remains in the aqueous phase as zincate ion.[1] Although this method is rather popular, it is generally hard to obtain a successful result probably due to the difficulty in purifying sodium hydroxide. Recently, the authors reported that the above purpose could be achieved by employing the synergistic extraction of cadmium(II) with a mixture of dithizone and 1,10-phenanthroline.[2] On the other hand, Pribil and Veseley reported the mutual separation of cadmium(II) and zinc(II) using methyltrioctylammonium chloride(MTOA=$R_3R'N{\cdot}Cl$).[3] This system was reexamined into a new spectrophotometric method of determination of a trace amount of cadmium(II) by the authors.[4] The separation procedure in the above method, however, is somewhat complicated.

In the work described below, we found an interesting phenomenon *i. e.*, upon extraction of cadmium(II)and zinc(II) with a mixture of dithizone and MTOA from a thiocyanate medium, only cadmium(II) forms an orange colored species which may be useful for the spectrophotometric determination of cadmium(II) in the presence of a large amount of zinc(II).

Experimental

Reagents and apparatus

Standard solution of cadmium(II): A stock solution (Cd: 1000 mg dm^{-3}) was prepared by dissolving a weighed amount of cadmium (II) acetate, $Cd(CH_3COO)_2{\cdot}2H_2O$ in demineralized water.

Dithizone solution: Dithizone stock solution(0.01 w/v%) was prepared by dissolving the reagent in chloroform and stored in a refrigerator.

MTOA solution: Twenty five grams of MTOA(Capriquat) was dissolved in chloroform and the volume of the solution was adjusted to 250 cm^3 by adding chloroform.

All reagents obtained from Wako Pure Chemicals were of guaranteed grade.

The absorbance measurements were conducted with a Hitachi 200-10 type spectrophotometer and 1.00 cm glass cells. The pH of aqueous phase after the extraction was measured with a Hitachi-Horiba F-7ss type pH meter. Cadmium(II) and zinc(II) remaining in the aqueous phase were determined with a Hitachi 170-30 type atomic absorption spectrophotometer.

Procedure

The pH of the aqueous solution containing cadmium(II) or zinc(II) and potassium thiocyanate was preliminarily adjusted by adding sodium acetate and acetic acid. The chloroform phase was prepared by mixing 5 cm^3 of 0.002% dithizone solution with an equal volume of 10% MTOA. Each 10.0 cm^3 of the aqueous and the organic phase was placed together in a 100 cm^3 separatory funnel, and the mixture was shaken vigorously for 15 min at room temperature(*ca.* 293K). During the extraction process, MTOA was converted to thiocyanate type. After the phases were allowed to separate, the absorption spectrum of the organic phase and the pH of the aqueous phase were measured. Cadmium(II) and zinc(II) remaining in the aqueous phase were also determined.

Results and Discussion

Both cadmium(II) and zinc(II) could be extracted from thiocyanate medium with MTOA. The extracted species were estimated by the conventional slope analysis to be $[R_3R'N^+]_2[Cd(SCN)_4^{2-}]$ and $[R_3R'N^+]_2[Zn(SCN)_4^{2-}]$, respectively. The former was found to react with dithizone causing a change in color of the organic phase, whereas the latter did not react with dithizone. In order to estimate the composition of the colored complex of cadmium(II), the molar ratio method was applied and the result indicates that the species contains $Cd(Hdz)_2$ in its composition. However, the extracted species is, at least, different from the well-known red $Cd(Hdz)_2$ in color, suggesting that the species might be formed by further coordination of

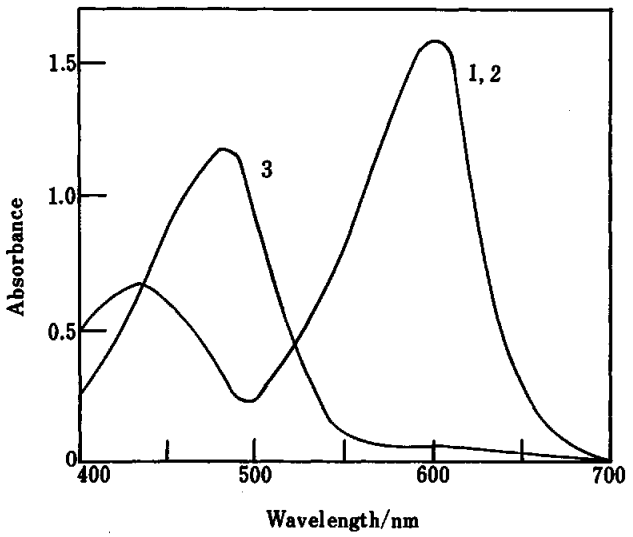

Fig. 1 Absorption spectra. The aqueous phase-KSCN, 5.0%; pH 5.5. The organic phase-H_2dz, 0.001%; MTOA, 5.0%. Curve 1, reagent blank; 2, Zn(II) 100 μg; 3, Cd(II) 100 μg.

thiocyanoto ligand to $Cd(Hdz)_2$ and the color change in the organic phase may occur according to the following reaction:

$$[R_3R'N^+]_2[Cd(SCN)_4^{2-}]_{org} + 2H_2dz_{,org} \rightleftharpoons [R_3R'N^+][Cd(Hdz)_2(SCN^-)_{org} + R_3R'N\cdot SCN_{org} + 2SCN^- + 2H^+$$

where the subscript org denotes the organic phase. From the slope analysis conducted by assuming the distribution ratio,

$$D = \{[[R_3R'N^+]_2[Cd(SCN)_4^{2-}]]_{org} + [[R_3R'N^+][Cd(Hdz)_2(SCN)^-]]_{org}\}/\sum_x [Cd(SCN)_x^{2-x}],$$

the colored species was concluded to be $[R_3R'N^+][Cd(Hdz)_2(SCN)^-]$. In general, cadmium(II) tends to form stable octahedral complexes, while tetrahedral structure is favorable to zinc(II) complexes. This structural difference probably enables the ligand exchange in thiocyanatocadmium(II) and the orange colored $[R_3R'N^+][Cd(Hdz)_2(SCN)(H_2O)^-]$ results. On the other hand, tetrahedral $Zn(SCN)_4^{2-}$ may be stable and inactive toward dithizone.

Table 1 Determination of cadmium(II) in the presence of zinc(II)

Zn(II) added/μg	Cd(II) found/μg
100	10.0
300	10.2
500	10.5
1000	10.7
3000	11.3
5000	11.1

Cd(II) taken: 10.0 μg

The above extraction mechanism is also supported by the spectra shown in Fig. 1. The spectrum obtained by the extraction of zinc(II) with a mixture of dithizone and MTOA agreed exactly with that of the reagent blank, indicating that zinc(II) does not react with dithizone in the present condition. On the contrary, cadmium(II) forms the orange colored species, *i.e.*, $[R_3R'N^+][Cd(Hdz)_2(SCN)(H_2O)^-]$ having an absorption maximum at 480 nm.

A brief study on the extraction system was done aiming at the spectrophotometric determination of cadmium(II). The calibration curve prepared at pH 5.5 was linear in the cadmium concentration range of zero to 1.5 μg cm^{-3}, the sensitivity being 0.0033 μgCd cm^{-2} at 480 nm. Effect of zinc(II) on the determination of cadmium(II) was examined and the results are summarized in Table 1. The coexistence of 500-fold amount of zinc(II) was tolerated within a relative error of 13%.

From the above results, the present extraction system is concluded to be applicable to the spectrophotometric determination of cadmium(II) without separating zinc(II) preliminarily.

References

1. E. B. Sandell: "*Colorimetric Determination of Traces of Metals*", p. 350, Interscience Publishers, New York (1959).
2. H. Akaiwa, H. Kawamoto and E. Yoshimatsu, *Bull. Chem. Soc. Jpn.*, **52**, 3718 (1979).
3. R. Pribil and V. Vesely, *Collection Czechoslov. Chem. Commun.*, **37**, 13 (1972).
4. H. Akaiwa, H. Kawamoto and T. Takenouchi, *Bunseki Kagaku*, **27**, 449 (1978).

(Received June 20, 1985)
(Accepted June 25, 1985)