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The Reaction between Mercury(II) and Organic Compounds. VIII. Titrimetric Determination of Mercury(II) with *o*-(2-Thiazolylazo)-2,4-dichlorophenol as a Metallochromic Indicator

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The reaction between mercury(II) and *o*-(2-thiazolylazo)-2,4-dichlorophenol (TADC) was investigated spectrophotometrically. A mixture containing TADC and a large excess of mercury(II) showed the absorption maxima in the range of pH 2.3—5.0 at 570 mμ. The composition of the chelate was considered to be as Hg(II) : TADC = 1 : 2. No homologous color was obtained by the reaction between TADC and the other metal ions in the above pH range. Therefore, TADC was suggested as a suitable metallochromic indicator for the direct titrimetric determination of mercury(II) ions with EDTA at pH 3.8—5 (citric acid plus disodium hydrogenphosphate buffer). Sharp color changes were observed from deep violet to orange or to reddish orange at an equivalence point. The titrimetry could be carried out satisfactorily within a range of error of $\pm 0.5\%$ at mercury(II) concentrations of more than 2×10^{-4}M by the present method.

The stability constants of the complexes formed between the *o*-(2-thiazolylazo)-phenols and mercury(II) and the availability of these reagents as chromogenic or spectrophotometric reagents for the determination of mercury(II) were reported previously.[1-3]

In the present paper, the reactivity of mercury(II) ions with *o*-(2-thiazolylazo)-2,4-dichlorophenol (TADC) was studied spectrophotometrically, and the applicability of TADC as a chromogenic reagent for the determination of mercury(II) ions was examined. In previous papers[1-3] it was reported that titrimetric determinations of mercury(II) ions using *o*-(2-thiazolylazo)-cresol (TAC),[1] *o*-(2-thiazolylazo)-4-methoxyphenol (TAM)[2] and *o*-(2-thiazolylazo)-4-chlorophenol (TACL)[3] as indicators were carried out in a weakly alkaline medium in all cases. As for the titrimetry using TADC as a metalloindicator, the optimum pH range was found to be 3.8—5. (This range was wider than those of Cu-PAN (pH 3—3.5),[4] XO (pH 6),[5] and MTB (pH 6).[6]) Therefore, there was no trouble in precipitating mercury(II) oxide in this acidic medium; thereby a considerably larger amount of mercury(II) ions than those reported in previous papers[1-3] could be determined accurately. Sharp color changes, *i. e.*, from deep violet to orange or to reddish orange, were observed at equivalence points. Except for a few anions and nickel(II), there were no interfering ions. Accordingly, TADC was also considered to be as a suitable metallochromic indicator as TAC, TAM and TACL for the direct titrimetric determination of mercury(II) ions with EDTA in an acidic medium.

Experimental

Preparation of TADC. TADC was prepared according to the method in the literature.[7] Several recrystallizations were repeated from hot ethanol. This crystals were obtained in a yield of 18%; mp 112—116°C (decomp.). Found: C, 40.04; H, 1.90; N, 14.65%. Calcd for $C_9H_5N_3OSCl_2$: C, 39.44; H, 1.84; N, 14.65%. IR: 3420 cm^{-1} (νO–H); 3100 cm^{-1} (νC–H of phenyl); 1248 cm^{-1} (δO–H); 1170 cm^{-1} (νC–O) and 730 cm^{-1} (νC–Cl).

Buffer Solutions. Buffer solutions with definite pHs were prepared by properly mixing 0.1M citric acid and 0.1M disodium hydrogenphosphate solutions.

The methods of purifying dioxane and of preparing a solution of the EDTA titrant and a stock solution of mercury(II) were the same as those described previously.[1-3]

Instruments. The absorption spectra were obtained with a Hitachi recording spectrophotometer (EPS-2) and a Hitachi electric spectrophotometer (EPU-2) with 10-mm silica cells. The infrared spectrum was obtained using an infrared spectrometer (DS-403G, Japan spectro-

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[1] F. Kai, *Anal. Chim. Acta*, **44**, 129 (1969).

[2] F. Kai, *ibid.*, **44**, 242 (1969).

[3] F. Kai, This Bulletin, **42**, 2250 (1969).

[4] H. Flaschka and H. Abdine, *Chemist-Analyst*, **45**, 58 (1956).

[5] H. Körbl, R. Pribil and A. Emf, *Chem. Listy*, **50**, 1440 (1956).

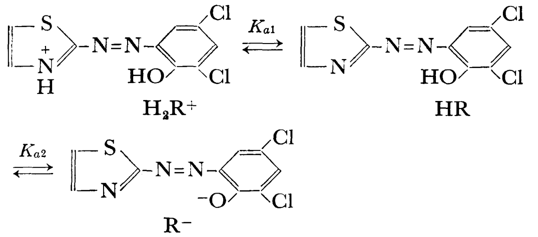
[6] H. Körbl, R. Pribil and A. Emf, *ibid.*, **51**, 1061 (1957).

[7] A. Kawase, *Bunseki Kagaku*, **11**, 621 (1962).

scopic Co., Ltd.). The pH was measured with a glass electrode pH meter (Hitachi-Horiba, F-5).

Results and Discussion

Acid Dissociation Constant of TADC in a 10% v/v Dioxane-Water Solution. The dissociation scheme of TADC is as follows:



The constants were obtained spectrophotometrically. If the acid dissociation constants are given by:

$$K_{a1} = \frac{[HR][H^+]}{[H_2R^+]} \text{ and } K_{a2} = \frac{[R^-][H^+]}{[HR]} \qquad (1)$$

then the second step of the dissociation could be given as:

$$pK_{a2} = pH - \log\frac{A-\varepsilon_{HR}C_R}{\varepsilon_R\text{-}C_R-A} \qquad (2)$$

where A is the total absorbance; C_R, the analytical concentration of TADC, and ε_x, the molar absorptivity of the species x.

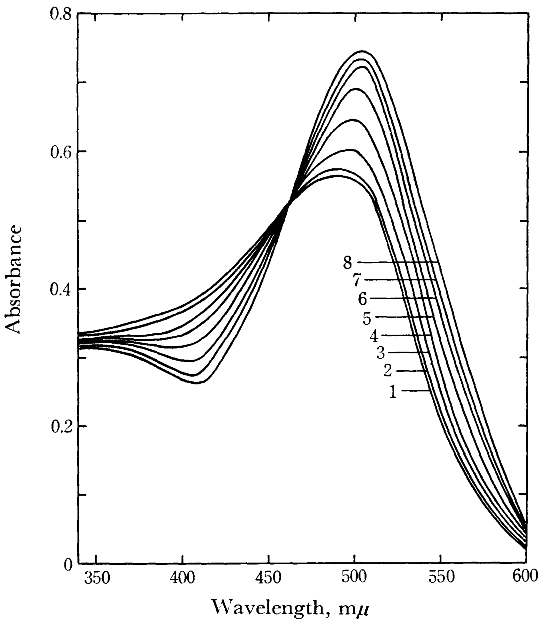


Fig. 1. Absorption spectra of TADC in 10% (v/v) dioxane-water at various pH values.
TADC=8×10⁻⁵M; μ=0.1 (KNO_3); room temp.; Ref.=water.
pH: 1=4.80; 2=5.04; 3=5.26; 4=5.50; 5=5.73; 6=6.01; 7=6.26; 8=above 6.45

The molar absorptivity was calculated from the horizontal lines of the pH-absorbance plots.

The absorption spectra of TADC scanned over pH 4.8—6.45 are illustrated in Fig. 1. There is an isosbestic point at 463 mμ, and the absorption maximum appears at 505 mμ. At higher pH values than 4.7 it is red or orange.

Though the figure is not given, the absorption curves in the range of pH 3.3—4.7 also showed the absorption maxima near 500 mμ, in accordance with the increasing pH values, but they have no isosbestic point at 463 mμ. The pK_{a2} value, therefore, was calculated from the absorbance at 505 mμ between pH 4.8 and 6.45 having the isosbestic point at 463 mμ, by means of Eq. (2). As a result, the second acid dissociation constant, pK_{a2}, was obtained as 5.3_8 in 10% v/v dioxane-water at $\mu=0.1$ (KNO_3) and at room temperature. This value was, of course, lower than that of the mono-chloro derivative,[3] but was almost the same as that obtained in 20% v/v dioxane-water.[7]

The first step acid dissociation constant, pK_{a1}, was not estimated precisely because it was considered to be at a pH<0 value.

Absorbances and Absorption Spectra of the Mercury(II)-TADC Chelate in a Dioxane-Water Solution. A mixture of a large excess of mercury(II) and TADC was a clear violet. The maximum absorbance was obtained when the solution was prepared by mixing mercury(II) of 50-fold against TADC at pH 4.15 (Fig. 2). Figure 3 shows the absorption spectra of this mixture at various pHs, using water as the reference. In the pH range 2.3—5.0, the spectra showed an isosbestic point at 450 mμ and the absorption maxima at 570 mμ. The maxi-

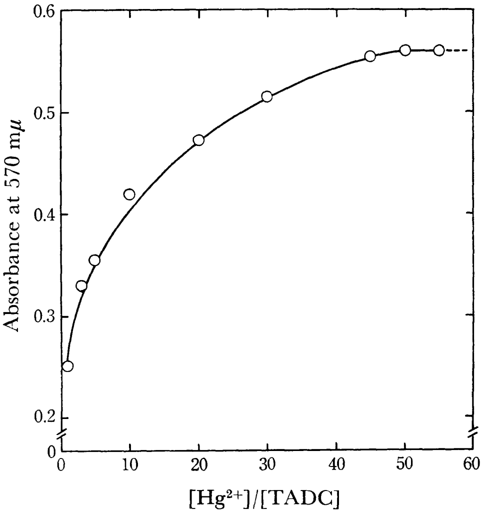


Fig. 2. Absorbances of TADC solutions with increasing mercury(II) concentration in 10% (v/v) dioxane-water at pH 4.15.
[TADC]=1×10⁻⁴M; μ=0.1 (KNO_3); room temp.; Ref.=water

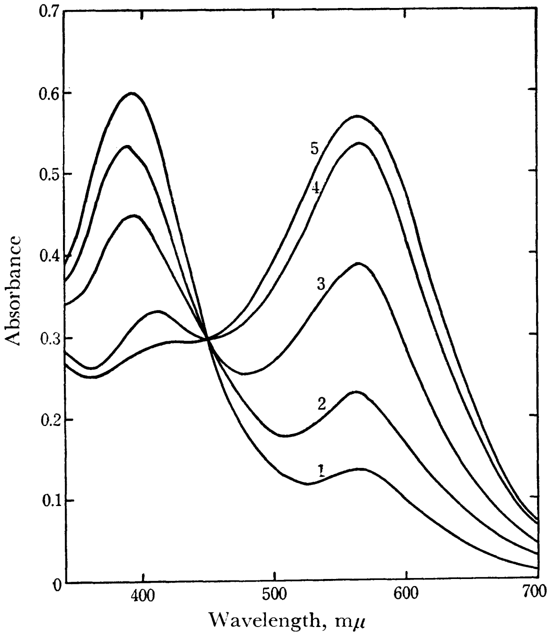


Fig. 3. Absorption spectra of TADC solutions in the presence of excess of mercury(II) at various pH.
10% dioxane; $\mu = 0.1$ (KNO_3); room temp.; Ref.=water; TADC$=10^{-4}$M; Hg(II)$=5\times10^{-3}$M.
pH: 1=2.29; 2=2.78; 3=3.35; 4=4.16; 5=5.03

mum molar absorptivity obtained from Fig. 3 was 11000; this was calculated by assuming the composition of the chelate to be mercury(II) : TADC=1 : 2. No discoloration was observed for 24 hr. Thus, it was suggested that TADC could by used as a suitable metallochromic indicator for the direct titration of mercury(II) ions in an acidic medium.

The absorption spectra of the mixtures containing equimolar solutions could not be scanned because precipitation tended to occur in a 10% v/v dioxane-water solution.

The pH adjustments in all the solutions described above were made with a citric acid and disodium hydrogenphosphate buffer system because the characteristic violet colour of the chelate was shown only when the pH adjustment was made with this buffer, whereas with other buffer systems, *e. g.*, a phosphate system and an acetic acid and sodium acetate system, the colour was not violet, but orange or reddish orange being considered to be a color due to a free reagent at those pHs. The reason of this phenomenon can not be explained.

Compositions of the Chelate. In order to examine the composition of the chelate, continuous variation plots at pH 4.50 and mole-ratio plots at pH 4.00 were made. In the case of continuous variation, the total concentration of mercury(II) plus TADC, and in the case of the mole ratio, the mercury(II) concentration, was kept constant at 10^{-4}M. The results are shown in Fig.4. As is shown in this figure, mercury(II) probably forms only a 1 : 2 chelate with TADC, regardless of the pH value. Moreover, the round refraction points of these plots suggest that the chelate is unstable.

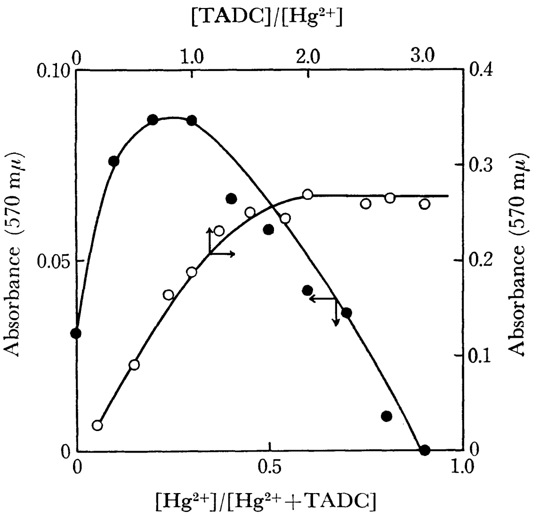


Fig. 4. Composition of the Hg(II)-TADC chelate.
—●— continuous variation. [Hg^{2+}+TADC]$=1\times10^{-4}$M; pH=4.50.
—○— mole ratio. [Hg^{2+}]$=1\times10^{-4}$M; pH=4.00.
10% (v/v) dioxane-water; $\mu=0.1$ (KNO_3); room temp.; Ref.=water

Photometric Titration Curve. Photometric titrations at various pHs were carried out. The concentration of mercury(II) was 10^{-2}M, and several drops of alcoholic TADC solution (*ca.* 10^{-2}M) was added to the sample solution. A deep violet solu-

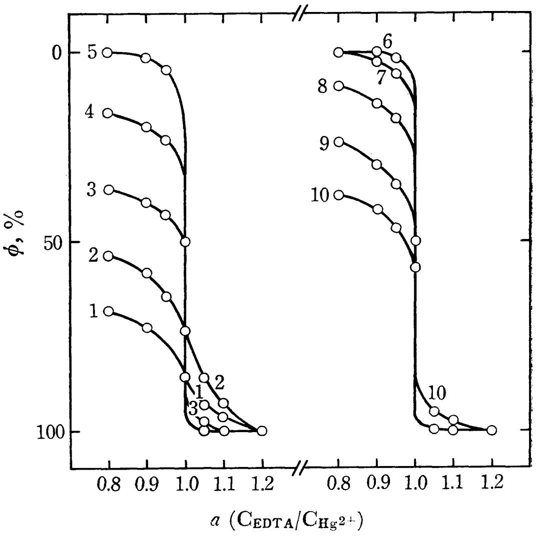


Fig. 5. Photometric titration curves.
$C_{Hg^{2+}}=10^{-2}$M; 10^{-1}M EDTA; Citric acid+Na_2HPO_4 buffer soln.
pH: 1=2.60; 2=2.90; 3=3.20; 4=3.59; 5=3.82; 6=4.49; 7=4.99; 8=5.51; 9=6.00; 10=6.50

tion was thus obtained. The concentration of the aqueous EDTA titrant was 10^{-1}M. The ϕ values were checked by means of the absorbances at 570 mμ. As can be seen in Fig. 5, in the pH range 3.8—5, sharp color changes, *i. e.*, from deep violet to orange or to reddish orange, were observed at the equivalence point. At the other pH values tested, color changes were observed before the equivalence point. In the pH 2.6—3.2 range and at 6.5, a tailing of the color change after the equivalence point was observed. The optimum pH range for the titration, therefore, was pH 3.8—5. This pH range was wider than that of such other indicators as Cu-PAN,[4] XO,[5] and MTB[6] used in acidic media.

Detectable Limit of Mercury(II). The detectable limit of the mercury(II) concentration by the titrimetry using TADC as the indicator was determined by checking the recoveries of mercury(II) ions at pH 4.50. Table 1 shows that there were large errors at concentrations of mercury(II) up to 2.74 mg/100 m*l* (corresponding to *ca.* 10^{-4}M as Hg(II)). These large errors can, for the reason mentioned in Fig. 2, be attributed to the weak color intensity of the chelate, which results in an uncertainty of color changes at the equivalence point. On the other hand, small errors within an accuracy range of ±0.5% were given at concentrations of more than 5.61 mg/100 m*l* (corresponding to *ca.* 2×10^{-4}M). Because of the lesser hydrolytic property of mercury(II) owing to an acidic media, the concentration of mercury(II) ions being determined was considerably higher than those[*1] reported previously for TAC, TAM, and TACL.

Table 1. Recovery of mercury(II) at various concentration at pH 4.50

Taken mg as Hg^{2+}/100 m*l*	Found mg as Hg^{2+}/100 m*l*	Error %
1.35	1.11	−10.4
2.26	2.36	+ 4.6
2.74	2.71	− 1.0
5.61	5.58	− 0.5
88.17	88.43	+ 0.3
104.90	104.79	− 0.1
250.30	251.30	+ 0.4
366.42	367.89	+ 0.4
487.19	485.73	− 0.3

Effect of Diverse Ions. An interference study was carried out. The depressions of the absorbances at 570 mμ were checked after the titration of aqueous sample solutions containing various amounts of diverse ions with an EDTA titrant (10^{-2}M). A 100 m*l* portion of the sample solution (10^{-3}M as Hg(II) ions) was kept at pH 4.5. The results are listed in Table 2. Negative errors were given by anions which form complex ions with mercury(II), whereas positive errors were given by metal ions forming complexes with the EDTA titrant. Cyanide, thiocyanate, ammonium, and halide, except when there is an excess of chloride, gave negative errors. As to metal ions, a large positive error was given by nickel(II) because the Ni(II)-TADC chelate showed an analogous violet color to that of the Hg(II)-TADC chelate at this pH. A 3 mg of cobalt(II), a 5 mg of iron(II) and a 10 mg of cadmium(II) gave small positive

Table 2. Effects of diverse ions (100 m*l* of 10^{-3}M mercury(II)), pH=4.50

Ion	Added amounts as ion, mg	Recovery of mercury(II), %	Error %
Cl^-	5.0	100.0	0.0
	10.0	100.1	+ 0.1
	20.0	100.0	0.0
Br^-	0.5	98.6	− 1.4
	1.0	91.1	− 8.9
I^-	0.5	93.5	− 6.5
	1.0	90.7	− 9.3
CN^-	0.5	96.9	− 5.1
	1.0	89.9	−10.1
SCN^-	0.1	99.1	− 0.9
	0.5	91.5	− 8.5
NH_4^+	5.0	99.8	− 0.2
	10.0	98.9	− 1.1
Ag^+	15.0	100.0	0.0
Cu^+	10.0	100.2	+ 0.2
Ca^{2+}	10.0	100.0	0.0
Sr^{2+}	10.0	99.9	− 0.1
Ba^{2+}	10.0	100.1	+ 0.1
Mn^{2+}	10.0	99.9	− 0.1
Fe^{2+}	5.0	100.3	+ 0.3
	10.0	105.5	+ 5.5
Co^{2+}	3.0	103.4	+ 3.4
	8.0	103.9	+ 3.9
Ni^{2+}	1.0	102.8	+ 2.8
	5.0	109.2	+ 9.2
Cu^{2+}	10.0	99.9	− 0.1
Zn^{2+}	10.0	100.1	+ 0.1
Cd^{2+}	5.0	100.2	+ 0.2
	10.0	101.0	+ 1.0
	15.0	104.4	+ 4.4
Pb^{2+}	10.0	100.0	0.0
Al^{3+}	10.0	100.0	0.0
Cr^{3+}	10.0	99.9	− 0.1
Fe^{3+}	10.0	100.0	0.0

Metal ions were added as nitrate.

[*1] In previous papers[1—3] it was reported that the detectable limit was restricted to concentrations below 10^{-2}M, because hydrolysis of mercury(II) is likely to occur at concentrations higher than 10^{-2}M, as a result of the weakly alkaline media.

errors. However, no interference was caused by the presence of silver(I), copper(I), calcium(II), strontium(II), barium(II), manganese(II), lead(II), aluminum(III), chromium(III), and iron(III) ions up to 10 mg. Iron(III) ions seem generally to give a positive error, for the formation constant of FeY ($\log K_{\mathrm{FeY}}=25.1$) is larger than that of HgY ($\log K_{\mathrm{HgY}}=21.8$). However, there was no error by iron(III) ions in this experiment. It seems reasonable to assume that iron(III) forms, with the citric acid used as the buffer solution, a stable chelate whose formation constant ($\log K_{\mathrm{Fe-citr.}}=25.0$[8]) is larger than that of the iron(III)-EDTA chelate.

The titration could be carried out accurately without heating the sample solution.

The above observations demonstrate that TADC can be utilized as a metallochromic indicator of mercury(II) with as high a sensitivity and accuracy as TAC, TAM, and TACL.

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8) R. C. Warner and I. Weber, *J. Amer. Chem. Soc.*, **75**, 5086 (1953); R. E. Hamm, C. M. Shull and D. M. Grant, *ibid.*, **76**, 2111 (1954).