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The Reaction between Mercury(II) and Organic Compounds. VII. The Formation Constant and Analytical Application of the *o*-(2-Thiazolylazo)-4-chlorophenol-Mercury(II) Complex

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The formation constants of the complex formed between *o*-(2-thiazolylazo)-4-chlorophenol, TACL, and mercury(II) in 2% v/v dioxane-water were $\log K_{\mathrm{HgR^+}}=6.2_1$ and $\log K_{\mathrm{HgR_2}}=6.1_0$ at $\mu=0.1$ and at room temperature. TACL was suggested as a suitable metallochromic indicator for the direct titrimetric determination of mercury(II) ions at pH 6.7—8.7 with an EDTA titrant. This optimum pH range was rather wide compared with that of the other metallochromic indicators, such as Cu-PAN, XO, and MTB. There were marked colour changes from deep blue to reddish-yellow or to violet at equivalence points. The mercury(II) ions up to 210 mg in 100 m*l* can be determined within an error of ±0.3% by this method.

o-(2-Thiazolylazo)-phenols have been found to be as excellent chromogenic reagents as pyridilazo phenols, and the properties of related chelates and analytical applications of them have hitherto been reported.

In preceding papers[1,2] the formation constants of the complexes formed between *o*-(2-thiazolylazo)-4-methoxy phenol (TAM) and *o*-(2-thiazolylazo)-cresol (TAC) and mercury(II) were shown. Moreover, these reagents were reported to be suitable metallochromic indicators for the direct titration of mercury(II) in a slightly alkaline medium. (In the case of the other indicators, such as Cu-PAN,[3] XO,[4] and MTB,[5] the optimum pHs of the direct titration for mercury(II) are pH 3—3.5(Cu-PAN) and pH 6 (XO and MTB).)

The present communication will describe the formation constant of the TACL-Hg(II) complex and its applicability to the metallochromic indicator for the determination of mercury(II) by titrimetry.

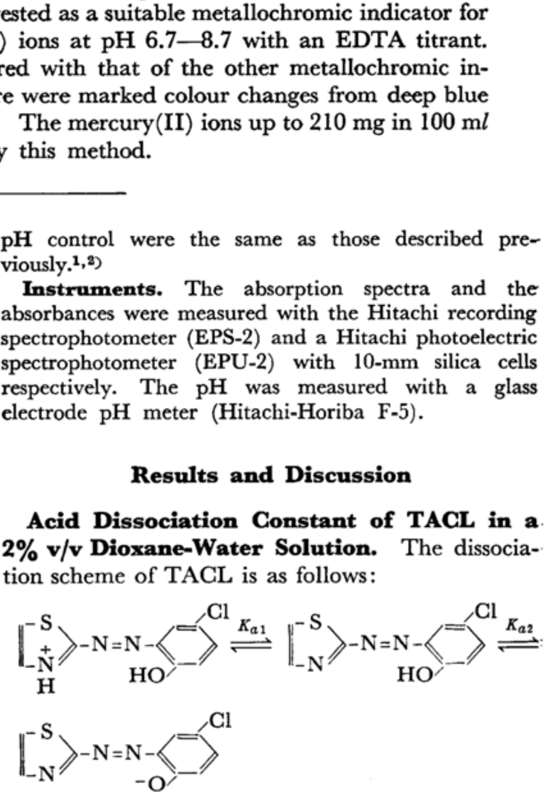
Experimental

Reagents. TACL was prepared according to the method reported in the literature[6] and was doubly recrystallized from hot ethanol. The purification of dioxane, the preparation of solutions of an EDTA titrant and of a stock solution of mercury(II), and the method of pH control were the same as those described previously.[1,2]

Instruments. The absorption spectra and the absorbances were measured with the Hitachi recording spectrophotometer (EPS-2) and a Hitachi photoelectric spectrophotometer (EPU-2) with 10-mm silica cells respectively. The pH was measured with a glass electrode pH meter (Hitachi-Horiba F-5).

Results and Discussion

Acid Dissociation Constant of TACL in a 2% v/v Dioxane-Water Solution. The dissociation scheme of TACL is as follows:



Each constant is given by Eq. (1):

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

The acid dissociation constants were obtained spectrophotometrically. For the second step only, Eq. (2) is given:

$$\log\frac{A-\varepsilon_{\mathrm{HR}}C_{\mathrm{R^-}}}{\varepsilon_{\mathrm{R^-}}C_{\mathrm{R^-}}-A}=\mathrm{pH}+\log K_{a2} \qquad (2)$$

where A is the total absorbance, $C_{\mathrm{R^-}}$, the analytical concentration of TACL, and $\varepsilon_{\mathrm{HR}}$ and $\varepsilon_{\mathrm{R^-}}$, the molar absorptivities of the HR and $\mathrm{R^-}$ species respectively.

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

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

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

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

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

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

[6] A. Kawase, *Bunseki Kagaku* (*Japan Analyst*), **11**, 621 (1962).

Table 1. Acid dissociation constant of TACL and formation constant of Hg(II)-TACL chelate

Acid dissociation constant of TACL	Chelate			
	Composition	λ_{max}, mμ	ε_{max}	Formation constant
$pK_{a1} < 0.5$	1 : 1	650	8.71×10^3	$\log K_{HgR^+} = 6.2_1$
$pK_{a2} = 7.7_0$	1 : 2	665	1.51×10^4	$\log K_{HgR_2} = 6.1_0$

2% v/v dioxane-water solution; $\mu = 0.1$ with potassium nitrate; room temp.

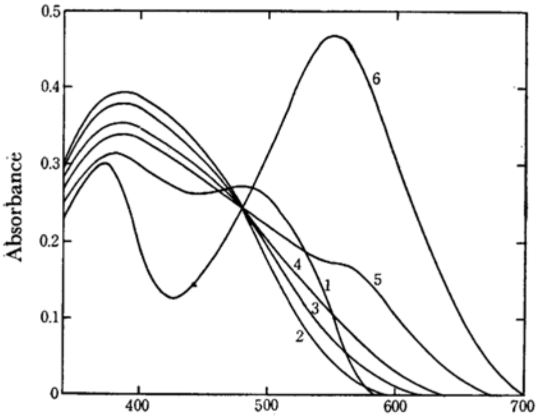

Fig. 1. Absorption spectra of TACL at different pH values. Concn. $= 4.00 \times 10^{-5}$ M, $\mu = 0.1$, Solvent = 2% v/v dioxane-water.
Curve 1 = pH 0.58 Curve 4 = pH 7.00
2 = 1.0—4.47 5 = 7.60
3 = 6.45 6 = 10.15

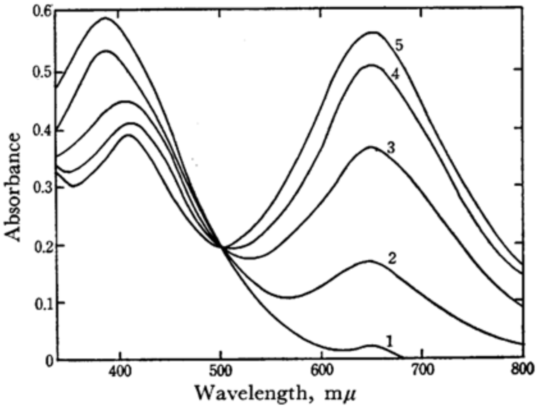

Fig. 2. Absorption spectra of Hg(II) and TACL mixture consisting of excess Hg(II) against TACL at different pH values. Concn.: TACL $= 6.66 \times 10^{-5}$ M, Hg(II) $= 6.66 \times 10^{-4}$ M, $\mu = 0.1$, Solvent $= 2\%$ v/v dioxane-water.
Curve 1 = pH 3.60 Curve 4 = pH 6.22
2 = 4.72 5 = 7.20—7.69
3 = 5.53

The absorption spectra of TACL in a 2% v/v dioxane-water solution at various pHs are shown in Fig. 1. They have the isosbestic point at 478 mμ and the absorption maxima at 550 mμ. At about pH > 7.6, TACL is red in colour due to the R^- species. By Eq. (2), the pK_{a2} value was obtained from the absorbances at 550 mμ. The precise pK_{a1} value was, however, not estimated because it may be considered to be in the pH < 0 region. The values, which almost entirely conformed to those obtained in 20% v/v dioxane-water,⁶⁾ are listed in Table 1.

Absorption Spectra of Hg(II)-TACL Chelate in the Dioxane-Water Solution. The spectra of the mercury chelates were scanned for a 2% v/v dioxane-water solution containing various concentrations of the components at different pHs. Figure 2 shows the spectra of the mixture composed of excess mercury(II) and TACL (ten times as much mercury as TACL). From a pH of about 4.5 spectra were obtained with the isosbestic point at 502 mμ and the absorption maxima at 650 mμ, which was attributed to deep blue colour. Besides the mercury(II)-TACL chelate, an analogous blue colour was shown in the case of only the Ni(II)-TACL chelate,⁶⁾ TACL has, therefore, been suggested as a suitable metallochromic indicator for the titrimetric determination of mercury(II) ions with a proper titrant.

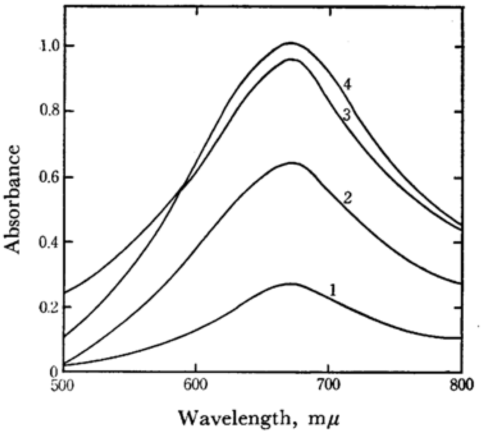

Fig. 3. Absorption spectra of Hg(II) and TACL mixture consisting of excess TACL against Hg(II) at different pH values. Concn.: TACL $= 6.66 \times 10^{-4}$ M, Hg(II) $= 6.66 \times 10^{-5}$ M, $\mu = 0.1$, Solvent = 2% v/v dioxane-water,
Curve 1 = pH 5.40 Curve 3 = pH 6.26
2 = 6.01 4 = 7.09

The spectra in the case of a reagent excess (ten times as much TACL as mercury) are illustrated in

Fig. 3. They were scanned using the TACL solution as the reference because the mixture showed a strong absorption caused by the predominant concentration of TACL itself.

Composition of the Chelate. By comparing the spectra shown in Figs. 2 and 3 it was found that almost all the figures of the curves, the wavelength, and the pH at the absorption maxima coincided; only their molar absorptivities differed. The molar absorptivities in Fig. 3 were nearly twice those in Fig. 2. Therefore the formation of the 1 : 1 chelate, HgR^+, was considered in the case of the mercury(II) excess (Fig. 2), and that of 1 : 2, HgR_2, in the case of the TACL excess (Fig. 3). The same situations have been described with respect to the analogous chelates formed between mercury(II) and thiazolylazo dyestuffs.[1,2]

Formation Constants of the Chelate. When the concentration of mercury(II) is in great excess in comparison with that of TACL, the successive formation constant can be calculated by Eq. (3):[1,2]

$$\log K_{\mathrm{HgR^+}} = \log \frac{[\mathrm{HgR^+}]}{[\mathrm{HR}]} + \mathrm{pHg} + \mathrm{p}K_{a2} - \mathrm{pH} \qquad (3)$$

Equation (3) indicates that the plot of $\log[\mathrm{HgR^+}]/[\mathrm{HR}]$ against pH should give a straight line with a slope of unity, and that the formation constant can be calculated from the pH at which $\log[\mathrm{HgR^+}]/[\mathrm{HR}]$ equals zero, the acid dissociation constant of TACL, and the initial concentration of mercury(II) ions. Figure 4a shows the plot of $\log[\mathrm{HgR^+}]/[\mathrm{HR}]$ *versus* pH. The pHg value was estimated here on the assumption that it should be decreased by 10% from the initial concentration belonging to the 1 : 1 chelate formation because of the initial ratio of the components, $[\mathrm{Hg^{2+}}]/[\mathrm{TACL}]=10$. As a result, the successive formation constant, $\log K_{\mathrm{HgR^+}}$, calculated was 6.2_1.

The second successive formation constant can be obtained indirectly from the over-all formation constant using Eq. (4):[1,2]

$$\log \frac{[\mathrm{HgR_2}]}{[\mathrm{Hg^{2+}}]} = \log K_{\mathrm{HgR^+}}\cdot K_{\mathrm{HgR_2}} + 2\log[\mathrm{HR}]_t - 2\mathrm{p}K_{a2} + 2\mathrm{pH} \qquad (4)$$

where $[\mathrm{HR}]_t$ is the total concentration of TACL. Equation (4) shows that the over-all formation constant can be calculated by the pH at which $\log[\mathrm{HgR_2}]/[\mathrm{Hg^{2+}}]$ equals zero, the acid dissociation constant of TACL, and an experimental concentration of $[\mathrm{HR}]_t$. Figure 4b shows the plot of $\log[\mathrm{HgR_2}]/[\mathrm{Hg^{2+}}]$ *versus* pH. In this case of a reagent excess, the $[\mathrm{HR}]_t$ value was calculated by assuming that the initial concentration of the ligand may be decreased by 20% due to the 1 : 2 chelate formation because the initial mixture was composed of $[\mathrm{TACL}]/[\mathrm{Hg^{2+}}]=10$. The over-all formation constant obtained was $\log K_{\mathrm{HgR^+}}\cdot K_{\mathrm{HgR_2}}=12.3_1$; therefore the second successive formation constant, $\log K_{\mathrm{HgR_2}}$, was 6.1_0. These values are listed in Table 1.

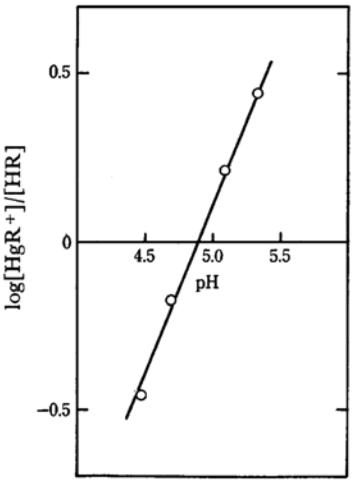

Fig. 4a. Plot of $\log[\mathrm{HgR^+}]/[\mathrm{HR}]$ *vs.* pH.

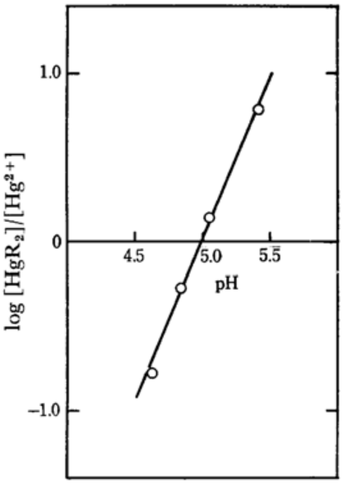

Fig. 4b. Plot of $\log[\mathrm{HgR_2}]/[\mathrm{Hg^{2+}}]$ *vs.* pH.

Applicability of TACL as a Metallochromic Indicator for Hg(II). In the case of the titrimetric determination of mercury(II) ions with a proper titrant (EDTA), and with TACL as the indicator, a sharp colour change may be expected because of the large difference in formation constant between the TACL-Hg(II) obtained as above and the HgY ($\log K_{\mathrm{HgY}}=21.8$).

pH. Photometric titrations were carried out at various pHs. The concentration of mercury(II) was 5×10^{-4} M and several drops of an alcoholic TACL solution (*ca.* 10^{-2} M) were added to the sample solution. A deep blue solution was thus obtained. The concentration of the aqueous EDTA titrant was 10^{-2} M. The pH was adjusted with a 0.1 M phosphate buffer. As can be seen in Fig. 5, in the pH range of 6.7—8.7 the sharp colour changes were observed at the equivalence point. This optimum pH range seems to be rather wider than that indicated by the other indicators (BT:

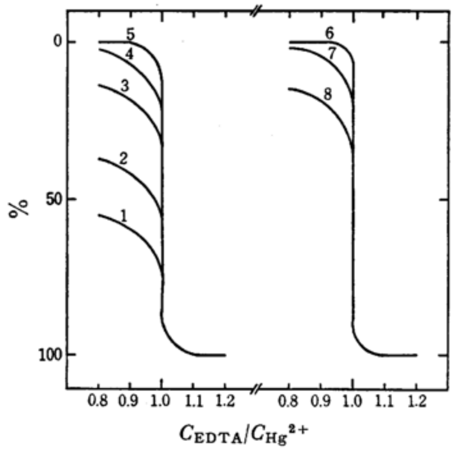

Fig. 5. Photometric titration curves.
$C_{Hg^{2+}}=5\times10^{-4}$ M, TACL $=4\times10^{-5}$ M,
EDTA $=0.1$ M, Buffer = phosphate system.
Curve 1 = pH 4.1 Curve 5 = pH 6.9
2 = 5.0 6 = 8.2
3 = 5.9 7 = 8.7
4 = 6.5 8 = 9.1

pH 3—3.5; XO and MTB: pH 6). At the other pHs tested, colour changes were observed before the equivalence point, whereas no colour change such as a tailing of the colour after the equivalence point was shown at any of the tested pHs.

Error. Recovery tests were carried out at various concentrations of mercury(II) ions at pH 8.0. Table 2 shows that only a small error, within ±0.3, was given at the concentrations of mercury(II) up to 211.04 mg/100 m*l* (corresponding to 1.05×10^{-2} M as Hg^{2+}). The negative error was increased at concentrations of mercury(II) higher than about 10^{-2} M. Accordingly, it is desirable to keep the concentration of mercury(II) below *ca.* 10^{-2} M.[*1]

Effect of Diverse Ions. An interference study was also carried out. The depression of the absorbances at 650 mμ was checked after the titration of aqueous sample solutions containing various amounts of diverse ions with the EDTA titrant (10^{-2} M). A 100 m*l* of the sample solution (5×10^{-4} M as Hg(II) ions) was kept at pH 8.0. The results are listed in Table 3. Negative errors were given by anions which can form complex ions with mercury(II), whereas positive errors were given by metal ions which can form complexes with the EDTA titrant. Cyanide, thiocyanate, ammonium, and halide except considerable amounts of chloride gave the negative errors. On metal ions, a large positive error was given by nickel(II); the Ni(II)-TACL chelate showed a blue colour analogous to that of the Hg(II)-TACL chelate. Cobalt(II), zinc(II), cadmium(II), and copper(II)

Table 2. Recovery of mercury(II) at various concentration at pH 8.0

Taken mg as Hg^{2+}/100 m*l*	Found mg as Hg^{2+}/100 m*l*	Recovery %	Error %
10.28	10.25	99.7	−0.3
20.50	20.50	100.0	0.0
25.76	25.73	99.9	−0.1
34.62	34.55	99.8	−0.2
40.18	40.22	100.1	+0.1
48.05	48.00	99.8	−0.2
103.55	103.99	100.3	+0.3
211.04	210.97	99.9	−0.1
274.52	258.31	94.1	−5.9
334.31	312.23	93.4	−6.6

Table 3. Effects of diverse ions (100 m*l* of 5×10^{-4} M mercury(II), pH = 8.0)

Ion	Added amounts as ion, mg	Recovery of mercury(II), %	Error %
Cl^-	5.0	100.0	0.0
	10.0	100.2	+0.2
	20.0	99.7	−0.3
Br^-	0.5	98.2	−1.8
	1.0	90.4	−9.6
I^-	0.5	92.7	−7.3
	1·0	90.4	−9.6
CN^-	0.1	98.5	−1.5
	0.5	95.6	−4.4
SCN^-	0.1	99.6	−0.4
	0.5	93.2	−6.8
NH_4^+	5.0	99.7	−0.3
	7.0	98.4	−1.6
Ag^+	10.0	100.0	0.0
Ca^{2+}	10.0	100.1	+0.1
Sr^{2+}	10.0	100.0	0.0
Ba^{2+}	10.0	99.8	−0.2
Co^{2+}	1.0	99.5	−0.5
	2.0	102.9	+2.9
Ni^{2+}	0.5	101.3	+1.3
	1.0	109.5	+9.5
Cu^{2+}	1.0	100.1	+0.1
	2.0	101.7	+1.7
	3.0	109.8	+9.8
Zn^{2+}	0.5	100.0	0.0
	1.0	101.1	+1.1
Cd^{2+}	0.5	99.9	−0.1
	1.0	100.9	+0.9
Al^{3+}	10.0	100.0	0.0
Cr^{3+}	10.0	99.9	−0.1
Fe^{3+}	10.0	99.9	−0.1

Metal ions were added as nitrate.

[*1] At concentrations higher than 10^{-2} M, mercury(II) oxide was apt to form. The excess ammoniacal buffer system may be suitable in this case: *cf.* N. Iritani, T. Tanaka and H. Sakai, *Nippon Yakugaku Zassi (J. Pharm. Soc. Japan)*, **76**, 1068 (1956); *ibid.*, **77**, 106 (1957).

ions gave errors. However, no interference was caused by the presence of silver(I), calcium(II), strontium(II), barium(II), chromium(III), iron(III), and aluminium(III) ions up to 10 mg.

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

In view of the above data, it may be suggested that TACL can also be utilized as a metallochromic indicator of mercury(II), for its sensitivity and accuracy are as good as those of TAC1) and TAM.2)

On the basis of the above results, the recommended procedure for the direct titrimetric determination of mercury(II) ions using TACL as the indicator is as follows: Take about 100 m*l* of a sample solution containing not more than 10^{-2} M as mercury(II) ions at pH 6.7—8.7, adjusted with a 0.1 M phosphate buffer system. Add several drops of an alcoholic solution of TACL (*ca.* 10^{-2} M) to the sample solution, and then titrate with the EDTA titrant (10^{-2} M aq. soln.). Near the end-point, carry out the titration slowly and with constant shaking. The colour change is sharp and reversible.

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