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Solution Equilibria and Stability of the Complexes of Pyridinecarboxylic Acids: Complexation Reaction of Mercury(II) with 2-Hydroxynicotinic Acid

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Summary. The solution equilibria of 2-hydroxynicotinic acid (*hyna*) complexes with mercury(II) have been studied spectrophotometrically in 50% (*v*/*v*) ethanol at 20°C and an ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). Three mercuric complexes are formed in solution in dependence on the acidity of the medium. The basic characteristics of the different complexes are determined and the analytical aspects of the complexation reaction are demonstrated. A critical investigation has also been presented of the solution equilibria and stability of the mixed complex of mercury(II) with *hyna* and thiosalicylic acid (*tsa*). The various complex transitions leading to the formation of the 1 : 1 : 1 Hg(*tsa*)(*hyna*) ternary complex in solution are investigated. The non-charged mono-ligand complex Hg(*hyna*) is used for UV-spectrophotometric determination of mercury at *pH* 4.5–5 ($\lambda_{max} = 325$ nm, $\varepsilon = 0.8 \cdot 10^4$ l mol^{-1} cm^{-1}). The system obeyed Beer's law up to 36.1 µg ml^{-1} of Hg(II). The optimum concentration range (Ringbom) is between 6 and 28.5 µg ml^{-1}. Interference caused by a number of ions was masked by the addition of fluoride ions.

Keywords. Mercury(II) determination; 2-Hydroxynicotinic acid; Spectrophotometry; Complexation equilibria.

Lösungsgleichgewichte und Stabilitätskonstanten von Komplexen der Pyridincarbonsäuren: Die Komplexierungsreaktion von Quecksilber(II) mit 2-Hydroxynikotinsäure

Zusammenfassung. Die Lösungsgleichgewichte von 2-Hydroxynikotinsäure (*hyna*) mit Hg(II) wurde spektrophotometrisch in 50% (*v*/*v*) Ethanol bei 20 °C und einer Ionenstärke von 0.1 mol dm^{-3} ($NaClO_4$) untersucht. In Abhängigkeit von der Acidität des Mediums werden drei Quecksilberkomplexe gebildet. Die grundlegenden Charakteristika der Komplexe wurden bestimmt und die analytischen Aspekte aufgezeigt. Die gemischten Komplexe von Hg(II) mit *hyna* und Thiosalicylsäure (*tsa*), insbesondere die verschiedenen Komplexübergänge zum ternären 1 : 1 : 1 Hg(*tsa*)(*hyna*)-Komplex, wurden ebenfalls untersucht. Der ungeladene Monoligandenkomplex Hg(*hyna*) kann bei *pH* 4.5–5 zur UV-spektroskopischen Quecksilberbestimmung eingesetzt werden ($\lambda_{max} = 325$ nm, $\varepsilon = 0.8 \cdot 10^4$ l mol^{-1} cm^{-1}). Das System gehorcht bis zu einer Hg(II)-Konzentration von 36.1 µg ml^{-1} dem Beerschen Gesetz. Der optimale Konzentrationsbereich (Ringbom) liegt zwischen 6 und 28.5 µg ml^{-1}. Interferenzen mit einer Reihe anderer Ionen konnten durch Maskierung mit Fluoridionen umgangen werden.

Introduction

Over the years there has been a steadily increasing interest in the complexes of pyridine derivatives due in part to their physiological properties. The metal complexes of pyridinecarboxylic acids are especially interesting model systems [1–12]. Their study is expected to aid in understanding the more complex natural systems. The pyridinecarboxylic acids and their derivatives are present in many natural products. They are also of special interest to the medicinal chemist because of the wide variety of physiological properties displayed by the natural as well as many synthetic acids. Based on preliminary results of a study of the complex equilibria of mercury(II) with pyridinecarboxylic acids, 2-hydroxynicotinic acid (*hyna*) was chosen for the detailed spectrophotometric study in water-ethanol medium. The work was aimed at establishing the complexation equilibria that exist in solution and at determining the basic characteristics of the complexes formed in solution. The solution equilibria and stability of Hg(II) ternary complex with *hyna* and thiosalicylic acid (*tsa*) were investigated. Various complex transitions leading to the formation of the Hg(*tsa*)(*hyna*) mixed complex were demonstrated and characterized. The analytical aspect of the complexation reaction of mercury(II) with *hyna* was studied and the optimum conditions favouring the UV-spectrophotometric determination of mercury using *hyna* as a complexing agent were determined.

Experimental

Analytical grade reagents and deionized water (or pure ethanol) were used for the preparation of solutions. A stock solution of $5 \cdot 10^{-3}$ mol dm^{-3} of mercury(II) perchlorate was prepared in 0.02 mol dm^{-3} of perchloric acid. The concentration of Hg(II) was determined by *EDTA* titration. 2-Hydroxynicotinic acid (*hyna*) and thiosalicylic acid (*tsa*) stock solutions ($5 \cdot 10^{-3}$ mol dm^{-3} each) were prepared by dissolving the accurately weighed amount of the pure reagent (Aldrich) in spectrograde ethanol. Standard solutions of NaOH (0.1 mol dm^{-3}) and $HClO_4$ (0.1 mol dm^{-3}) were also prepared. More dilute solutions of the reagents were obtained as required by accurate dilution. Solutions of diverse ions used for interference studies were prepared using AnalaR products of the nitrates, acetates, or chlorides of the metal ions and potassium or sodium salts of the anions to be tested. The acidity of the working solutions was adjusted by the addition of either dilute perchloric acid or sodium hydroxide. The ionic strength of solutions was kept constant at 100 mmol dm^{-3} ($NaClO_4$) except for some measurements that were performed in stronger perchloric acid.

The absorption spectra of solutions were recorded on a Perkin-Elmer (Lambda 3 B) spectrophotometer in the range 200–450 nm using 1 cm matched quartz cells. Values of the *pH* were obtained using a Radiometer *pH* meter model M 63 with a combined glass electrode of the type Radiometer (GK 2301 C). All measurements were carried out in 50% (*v*/*v*) ethanol and at 20°C. The *pH*-readings in ethanol-water medium were corrected as described elsewhere [13].

Standard Procedure for the Spectrophotometric Determination of Mercury(II) with hyna

Into an aliquot of mercury(II) solution containing less than 0.9 mg Hg (in a 25 ml calibrated flask) 2 ml of $2.5 \cdot 10^{-3}$ mol dm^{-3} solution of *hyna* and 2.5 ml of 1 mol dm^{-3} $NaClO_4$ were added. After mixing with the appropriate amount of pure ethanol the *pH* of the solution was adjusted to 4.5 with suitably selected dilute $HClO_4$. The resulting solution was made up to volume with deionized water and the absorbance was measured at 325 nm against a reagent blank similarly prepared and of the same *pH* as the test solution but containing no mercury. The absorbance of the solutions investigated remains constant for at least 24 hours.

Symbols Used

C_L = total concentration of the ligand *hyna*; C_X = total concentration of the ligand *tsa*; C_M = total concentration of the metal ion; ε_{1H}, ε_1 and ε_2, molar absorptivities of $[HgLH]^+$, HgL and $[HgL_2]^{2-}$ complexes; *q*, the number of protons liberated during the formation of a single complex species; K_{a1L} and K_{a2L}, $[LH^-][H^+]/[LH_2]$ and $[L^{2-}][H^+]/[LH^-]$; K_{a2X}, $[X^{2-}][H^+]/[XH^-]$; K_{1H}, K_{ka1},

K_2, equilibrium constants for the corresponding complexation reactions in binary systems; K_i, K_{ii}, K_{iii}, and K_{iv}, equilibrium constants for the corresponding complexation reactions in the ternary system under the conditions specified.

Results and Discussion

Acid-Base Equilibria of hyna in 50% (v/v) Ethanol

The solution spectra of *hyna* in 50% (*v*/*v*) ethanol were recorded at different *pH* values (cf. Fig. 1). The variation of absorbance with *pH* at $\lambda = 290$ nm or 320 nm reveals the existence of different acid-base equilibria in solution within the *pH* range 0.5–11.0. The proton dissociation constants corresponding to these equilibria were evaluated using the graphical logarithmic analysis of the absorbance versus *pH*

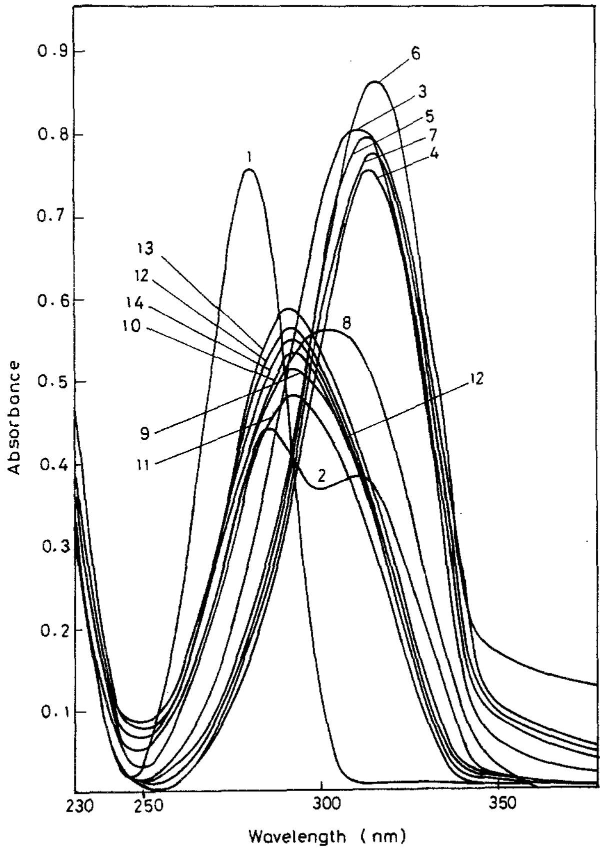
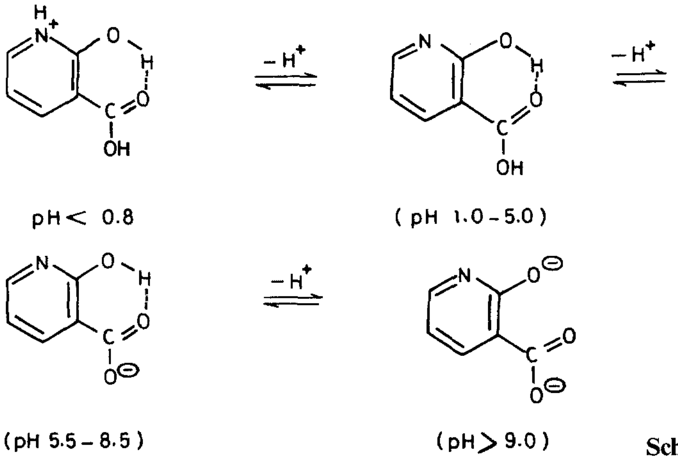


Fig. 1. Absorption spectra of 2.5 $\cdot 10^{-3}$ mol dm^{-3} *hyna* at different *pH* values in the presence of 50% (*v*/*v*) ethanol. *pH*: 1, 0.9; 2, 1.95; 3, 2.3; 4, 2.5; 5, 3.4; 6, 4.2; 7, 4.6; 8, 6.0; 9, 6.5; 10, 7.4; 11, 8.4; 12, 9.6; 13, 10.1; 14, 10.9

Table 1. Values of pK_a and λ_{max} for various forms of *hyna* in 50% (*v*/*v*) ethanol (species in parentheses)

pK_{a_i}	λ_{max} (nm)
	320 (LH_2)
6.20 ± 0.02 (LH_2/LH^-)	305 (LH^-)
9.65 ± 0.01 (LH^-/L^{2-})	290 (L^{2-})

graphs as described elsewhere [14]. The mean pK_{a_i} values are given in Table 1. According to our results, the protonation scheme of *hyna* can be represented by Scheme 1.



Scheme 1

Complexation Equilibria of Hg(II) *with hyna*

The complexation equilibria of Hg(II) with *hyna* were investigated at different *pH* values in equimolar solutions and in solutions containing an excess of reagent or metal ion. The spectra of solutions reflect unambiguously the formation of at least two complexed species in the *pH* range 2.5–5.2, depending on the acidity of the medium and the concentration of components (Fig. 2). It is worth mentioning that the solution spectra of the reagent (*hyna*) exhibit within this *pH* range an absorption band at 310 nm. The spectra of solutions containing an excess of metal ion and that of equimolar solutions are analogous and exhibit absorption bands with λ_{max} at 340 nm and 325 nm. In presence of excess *hyna* the solution spectra show different behaviour. The bands at 340 nm and 325 nm are overlapped within the *pH* range 2–4.2, while at *pH* 4.5–6.0 the spectra reveal a symmetrical band at 330 nm. At higher *pH* a double headed band at 300–320 nm is observed. The variation of absorbance with *pH* for the above solutions show the range of formation and existence of the basic complexation equilibria (within the *pH* range studied) which are sufficiently separated (cf. Fig. 3 curves a–c). For equimolar solutions or solutions containing excess metal ion, the absorbance versus *pH* graphs indicate the presence of a single chelate equilibrium at *pH* values <3.5, probably through interaction of Hg(II) with LH_2 of the reagent according to the general equation:

$$\mathrm{Hg}^{2+} + nLH_2 \overset{K_1\,(qH)}{\rightleftharpoons} \mathrm{Hg}L_n\mathrm{H}_{2n-q} + q\mathrm{H}^+ \; . \tag{1}$$

The graphs in both cases show a further increase of absorbance along the second ascending part of the curves up to *pH* ~ 5 presumably due to the complex transition to a species with less protons. Above *pH* 5.5 the absorbance shows an apparent decrease due to the hydrolysis of the complex. The absorbance-*pH* graphs for solutions containing excess ligand at $\lambda = 340$ nm reveal the existence of two basic equilibria within the *pH* range 2–6 that are sufficiently separated. In addition to Eq. (1) (*pH* 2–3.5) the second ascending part of these graphs is attained in the *pH*

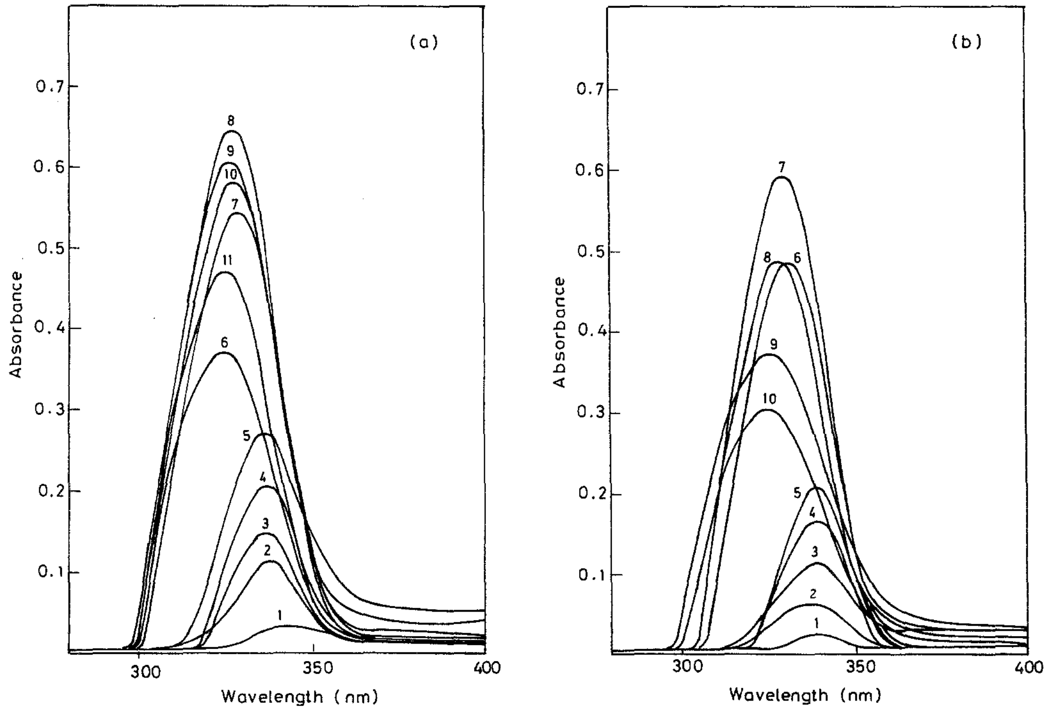


Fig. 2. Absorption spectra of Hg(II)-*hyna* complexes; 50% (*v*/*v*) ethanol, $\lambda = 325\,\mathrm{nm}$; (*a*) $C_L = C_M = 1.25\,\mathrm{mol\,dm^{-3}}$, *pH*: 1, 2.7; 2, 3.1; 3, 3.4; 4, 3.75; 5, 4.2; 6, 4.55; 7, 4.75; 8, 5.5; 9, 5.9; 10, 6.2; 11, 7.4; (*b*) $C_M = 3 \cdot 10^{-4}\,\mathrm{mol\,dm^{-3}}$, $C_L = 1 \cdot 10^{-4}\,\mathrm{mol\,dm^{-3}}$, *pH*: 1, 23; 2, 2.45; 3, 2.7; 4, 3.1; 5, 3.5; 6, 4.05; 7, 5.2; 8, 6.4; 9, 7.6; 10, 7.9

range 4.5–6.0, as a result of complex transition (2) with further ligand species coordinated,

$$\mathrm{Hg}L_n\mathrm{H}_y + pL\mathrm{H}_2 \overset{K_2\,(qH)}{\rightleftharpoons} \mathrm{Hg}L_{n+p}\mathrm{H}_c + q\mathrm{H}^+ \ , \qquad (2)$$

where

$$c = y + 2p - q \ .$$

The graphs have also a descending branch above *pH* 6 due to the hydrolysis effect.

The absorbance-*pH* graphs for all solutions investigated were interpreted using the previously-derived slope-intercept transformations [15, 16] of the equilibrium constants or conditional stability constants of the assumed chelates for conditions under which a single complex equilibrium predominates and for selected wavelengths. From the graphical logarithmic analysis of the absorbance-*pH* graphs, the following equilibria were proved to be set in solutions containing excess metal ion or in equimolar solutions:

$$\mathrm{Hg}^{2+} + L\mathrm{H}_2 \rightleftharpoons [\mathrm{Hg}L\mathrm{H}]^+ + \mathrm{H}^+ \ , \qquad (3)$$

$$\mathrm{Hg}L\mathrm{H}^+ \rightleftharpoons \mathrm{Hg}L + \mathrm{H}^+ \ , \qquad (4)$$

$$\mathrm{Hg}L + 2\mathrm{H_2O} \rightleftharpoons [\mathrm{Hg}L(\mathrm{OH})_2]^{2-} + 2\mathrm{H}^+ \ . \qquad (5)$$

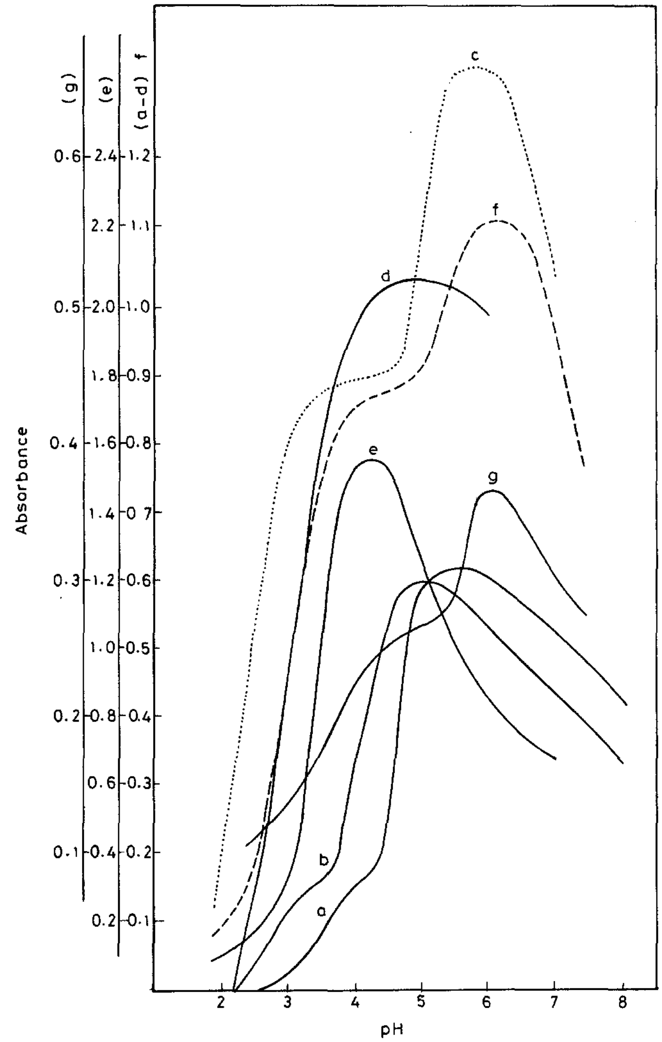


Fig. 3. Absorbance versus *pH* graphs for Hg(II)-*hyna* (curves *a*, *b*, and *c*) and Hg(II)-*tsa* (curves *d* and *e*) binary systems and Hg(II)-*tsa-hyna* (Hg*XL*) ternary system (curves *f* and *g*), 50% (*v*/*v*) ethanol. (*a*) $C_L = C_M = 1.25 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 325$ nm; (*b*) $C_L = 1 \cdot 10^{-4}$ mol dm^{-3}, $C_M = 3 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 325$ nm, (*c*) $C_L = 6.25 \cdot 10^{-4}$ mol dm^{-3}, $C_M = 1.25 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 340$ nm; (*d*) $C_X = C_M = 2.5 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 335$ nm; (*e*) $C_X = 7.5 \cdot 10^{-4}$ mol dm^{-3}, $C_M = 2.5 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 310$ nm; (*f*) $C_M = C_L = C_X = 2.5 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 340$ nm, (*g*) $C_M = 1.25 \cdot 10^{-4}$ mol dm^{-3}, $C_L = 6.25 \cdot 10^{-4}$ mol dm^{-3}, $C_X = 3.75 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 340$ nm

For solutions with excess reagent, the analysis of the absorbance-*pH* graphs confirm the presence of Eq. (6) at *pH* 4.5–6.0 in addition to Eq. (3) at *pH* 2–3.5,

$$[\mathrm{Hg}L\mathrm{H}]^{+} + L\mathrm{H}_2 \rightleftharpoons [\mathrm{Hg}L_2]^{2-} + 3\mathrm{H}^{+} \ , \tag{6}$$

$$[\mathrm{Hg}L_2]^{2-} + 2\mathrm{H}_2\mathrm{O} \rightleftharpoons [\mathrm{Hg}L(\mathrm{OH})_2]^{2-} + L\mathrm{H}^{-} + \mathrm{H}^{+} \ . \tag{7}$$

The analysis of the descending branch of the absorbance versus *pH* graphs for solutions with excess metal ion or equimolar solutions indicates unambiguously the hydrolysis of the Hg*L* complex to the hydroxocomplex $[\mathrm{Hg}L(\mathrm{OH})_2]^{2-}$ according to Eq. (5). On the other hand the analysis of this part of the absorbance-*pH* plots for solutions with excess ligand confirmed the existence of Eq. (7). The equations used for graphical and logarithmic transformations were given in our previous report [16].

The set of absorbance versus *pH* curves for varying metal ion excess was analysed under the conditions of the so-called "corresponding solutions" [16, 17] according to Eq. (A),

$$(pH)_{0i} = m/q\,(-\log C_M) + constant \ , \tag{A}$$

Table 2. Mean values of equilibrium constants ($\log K^*$), stability constants ($\log B$) and molar absorptivity of mercury complexes with *hyna*. Values are taken as averages for various component concentrations; charges are omitted; $I = 0.1\,\mathrm{mol\,dm^{-3}}$ ($NaClO_4$), 20°C, 50% (*v*/*v*) ethanol

Equilibrium	Constant	log constant	Molar absorptivity $\mathrm{l\,mol^{-1}\,cm^{-1}}$
$[MHL][H]/[M][H_2L]$	K^*_{1H}	(0.95 ± 0.01)[a]	$\varepsilon_{1H} = 0.25 \cdot 10^4$
		(0.8 ± 0.02)[b]	
		(0.7 ± 0.02)[c]	
$[ML][H]/[MHL]$	$K^*_{k_a}$	(-5.5 ± 0.01)[a]	$\varepsilon_1 = 0.8 \cdot 10^4$
		(-5.1 ± 0.02)[b]	
$[ML_2][H]^3/[MLH][H_2L]$	K^*_2	(-11.30 ± 0.02)[c]	$\varepsilon_2 = 1.2 \cdot 10^4$
$[ML(OH)_2][H]^2/[HgL]$	K^*_{OH}	(-10.3 ± 0.01)[a]	
		(-10.2 ± 0.01)[b]	
$[ML(OH)_2][LH][H]/[ML_2]$	K^-_{OH}	(-9.804 ± 0.02)[c]	
$[MLH]/[M][HL]$	B_{1H}	7.02[d]	
$[ML]/[M][L]$	B_1	10.81[e]	
$[ML_2]/[M][L]^2$	B_2	21.22[f]	
$[ML(OH)_2]/[M][L][OH]^2$	B_{OH}	29.16[g]	

[a] $A = f(pH),\ C_M/C_L = 5$

[b] $A = f(pH),\ C_M = C_L$

[c] $A = f(pH),\ C_L/C_M = 5$

[d] $\log B_{1H} = \log K^*_{1H} + pK_{a_1}$

[e] $\log B_1 = \log B_{1H} + \log K^*_{K_{a_1}} + pK_{a_1}$

[f] $\log B_2 = \log K^*_2 + \log B_{1H} + pK_{a_1} + 2\,pK_{a_2}$

[g] $\log B_{OH} = \log K^*_{OH} + \log B_1 + 2\,pK_w = \log K^-_{OH} + \log B_2 - pK_{a_2} + 2\,pK_W$

where $(pH)_{0i}$ represent the pH values for corresponding solutions, m is the number of metal ions bound in the chelate and q is the number of protons liberated during complexation. The results obtained reveal no evidence for the presence of any dinuclear complex in solution under the experimental conditions. The stoichiometry of the Hg(II)-*hyna* complexes was further verified by the method of continuous variation. In solutions having $C_0 = C_M + C_L = 5 \cdot 10^{-3}\,\mathrm{mol\,dm^{-3}}$ at $pH = 3$, the maximum of the Job plot corresponds to a component ratio of 1 : 1 (metal to ligand). At pH 5.5 a component ratio of 1 : 2 was confirmed. The calculated values of the molar absorptivities, equilibrium constants and stability constants of the various Hg(II)-*hyna* complexes are given in Table 2.

According to the results of this work, the formation of a Hg*L* complex which possesses greater stability and higher molar absorptivity was undertaken as a suitable base for the spectrophotometric determination of mercury(II) under optimum conditions. At pH 4.5–5.0 the system conformed Beer's law up to a concentration of $36.1\,\mathrm{\mu g\,ml^{-1}}$ of Hg(II). The molar absorptivity of the complex at 325 nm was $0.8 \cdot 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$. A Ringbom plot showed an optimal working range for the determination of Hg(II) of $6–28.5\,\mathrm{\mu g\,ml^{-1}}$. The Sandell's sensitivity of the reaction of Hg(II) was found to be $6.2 \cdot 10^{-3}\,\mathrm{\mu g\,cm^{-2}}$. The reproducibility of the method was checked by analyzing two series of solutions (ten determinations for each) having mercury(II) concentrations of 10 and 25 $\mu g\,ml^{-1}$. The relative standard deviations were found to be 0.8 and 0.5%, respectively.

Effect of Diverse Ions

To determine the effect of diverse ions on the determination of mercury, solutions were prepared containing 0.5 mg of Hg(II) and varying concentrations of the ions to be tested. Mercury(II) was then determined as HgL under optimum conditions as described in the given procedure. The results of this work indicate that the presence of 20 mg of Li^+, Na^+, K^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, SO_4^{2-}, SCN^-, NO_3^-, ClO_4^-, CN^-, Cl^-, Br^-, and F^- has no effect on the procedure. The determination of Hg(II) was also possible in presence of Zn^{2+}, Cd^{2+}, Cr^{3+}, or $H_2PO_4^-$ (6.0 mg) and Al^{3+} (3 mg). Under our experimental conditions it was observed that mercury(II) could be determined in the presence of appreciable amounts of cyanide or fluoride ions (~ 50-fold excess). Interference from large amounts of Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zr^{4+}, Mo^{6+}, Ru^{3+}, Rh^{3+}, Pt^{2+}, Os^{8+}, Ir^{4+}, Pt^{2+}, Tl^{3+}, La^{3+}, U^{6+}, Ce^{4+} (up to 15 mg) could be eliminated by adding ammonium fluoride solution (~ 50-fold excess) as a masking agent. Samples containing less than 2 mg of Fe^{3+} could be easily tolerated in the presence of F^- ions.

Substitution Equilibria in the System: Mercury(II)-2-Hydroxynicotinic Acid (hyna)-Thiosalicylic Acid (tsa)

At *pH* ~ 5.5 the spectra of solutions containing equimolar amounts of Hg(II) and *hyna* exhibit an absorption band at 325 nm due to the formation of the non-charged complex species HgL. The 1 : 1 binary complex of mercury(II) with *tsa* possesses an absorption peak at 330 nm. The solutions containing equimolar concentrations of *hyna* and *tsa* give an intense absorption band at 345 nm when mixed with Hg(II) solution which is presumably due to the formation of a mixed-ligand complex of Hg(II) with *hyna* and *tsa*. The absorbance of the solution of the ternary system was measured as a function of *pH*, the maximum absorbance of the ternary complex was attained at *pH* 4.8–6.5. Further measurements on the system were carried out at *pH* 6. The solution spectra of the ternary system containing Hg(II), *hyna* and *tsa* in a molar ratio of 1 : 1 : 1 and also the spectra of Hg(II) complexes with *hyna* or *tsa* in 50% (v/v) ethanol with reagent blank as reference are given in Fig. 4.

At *pH* 6.0, the Job's plot of continuous variation gives a ratio of 1 : 1 metal to ligand for the complex of Hg(II) with *hyna* at 345 nm in equimolar solutions with a constant excess of *tsa*. The plots show also a ratio of 1 : 1 Hg(II) : *tsa* (at *pH* 6) in the presence of a constant excess of *hyna*, so the over-all Hg(II)-*hyna*-*tsa* complex has a 1 : 1 : 1 composition at the *pH* studied.

The formation of the mixed complex was investigated in dependence on the acidity of the medium in equimolar solutions or in a solution containing an excess of the two ligands. The solution spectra at the *pH* range 2.5–6.5 indicate the formation of at least two complex species depending on the *pH* of the medium and the concentration of components. For solutions containing equimolar concentrations of components, the absorbance versus *pH* graphs at 345 nm indicate the existence of two basic equilibria that are sufficiently separated. The analysis of the two rising parts of these graphs within the *pH* ranges 2–4 and 4.5–6.0 were carried out under the assumption that the Hg(II)-thiosalicylate complex (HgX) is converted at $pH \sim 5$ to the mixed complex HgXL according to the following scheme:

$$\mathrm{Hg}^{2+} + X\mathrm{H}_2 \rightleftharpoons \mathrm{Hg}X + 2\,\mathrm{H}^+ , \tag{8}$$

$$\mathrm{Hg}X(\varepsilon_\mathrm{I}) + L\mathrm{H}_2 \rightleftharpoons [\mathrm{Hg}XL]^{2-}\ (\varepsilon_\mathrm{II}) + 2\,\mathrm{H}^+ , \tag{9}$$

$X\mathrm{H}_2$ symbolizing the molecular form of *tsa*.

This assumption is based on the fact that the mono-thiosalicylate complex of Hg(II) is the most stable complex in solution at the pH range studied. Eq. (9) represents a transition of the Hg-*tsa* complex to a complex containing the competing ligand *hyna*. The transformation (B) was used for the estimation of the value of the molar absorptivity (ε_II) of the HgXL ternary complex from a limit on the $C_{M/A}$ ordinate,

$$C_{M/A} = 1/\varepsilon_\mathrm{II} + (A - \varepsilon_\mathrm{I} C_M)\,[\mathrm{H}]^q Z/A\, {}^*K_{(i)}\varepsilon_\mathrm{II} C_L , \tag{B}$$

where

$$Z = 1 + K_{a_2}/[\mathrm{H}].$$

The transformation was linear assuming the splitting of two protons ($q = 2$) from *hyna* ($L\mathrm{H}_2$) during the formation of the ternary complex. The number of liberated

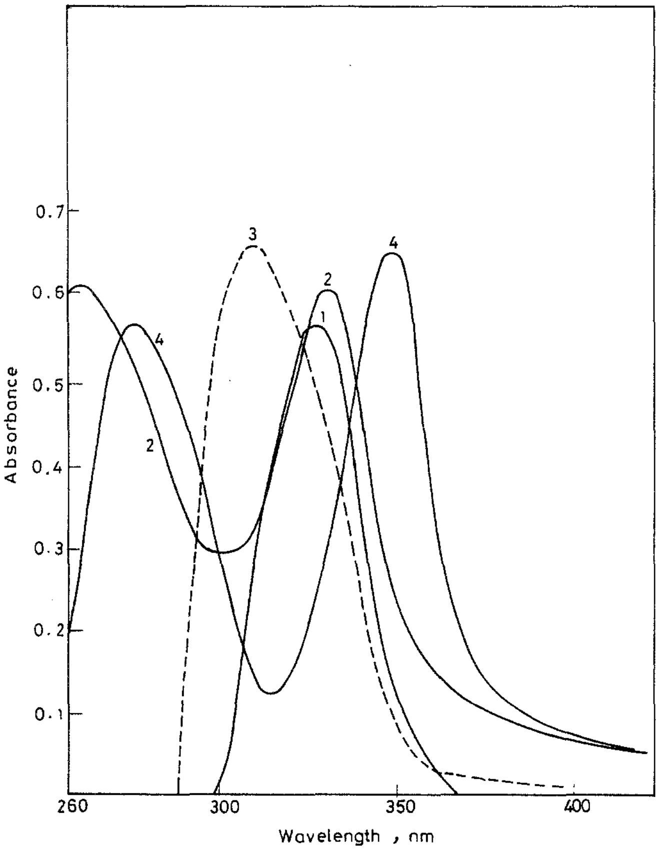


Fig. 4. The absorption spectra of binary and ternary complexes of mercury(II) with *hyna* and *tsa*: $pH = 6$; (*1*) 1 : 1 Hg-*hyna*; (*2*) 1 : 1 Hg-*tsa*; (*3*) 1 : 2 Hg-*tsa*; (*4*) 1 : 1 : 1 Hg-*hyna*-*tsa* complex

protons (q) was also given by slopes of logarithmic straight lines according to Eq. (C):

$$\log[(A - \varepsilon_I C_M)Z/(\varepsilon_{II} C_M - A)] = qpH + \log C_L + \log {}^*K_{(i)} . \qquad \text{(C)}$$

The analysis of the absorbance versus pH graphs for solutions of the Hg-*tsa-hyna* ternary system containing variable amounts of the two ligands (each present in excess) using transformations (D)–(F) confirmed the existence of equilibrium (10) provided that the ratio *hyna*:*tsa* is 2:1 or higher,

$$\mathrm{Hg}X_2^{2-} + LH_2 \rightleftharpoons \mathrm{Hg}XL^{2-} + X\mathrm{H}^- + \mathrm{H}^+ , \qquad (10)$$

$$C_{M/A} = 1/\varepsilon_1 + \frac{{}^*K_{(ii)}(A - A_{0\,2})(C_L)}{\varepsilon_1 A[\mathrm{H}]^q C'_X} , \qquad \text{(D)}$$

$$C_{M/A} = 1/\varepsilon_2 - \frac{[\mathrm{H}]^q (C'_X)(A_{0\,1} - A)}{{}^*K_{(ii)} \varepsilon_2 A \, C'_L} , \qquad \text{(E)}$$

$$\log(A_{0\,1} - A)/(A - A_{0\,2}) = qpH + \log {}^*K_{(ii)} - \log C'_X + \log C'_L , \qquad \text{(F)}$$

where

$$A_{0\,1} = \varepsilon_1 C_M ; \qquad A_{0\,2} = \varepsilon_2 C_M ,$$

$$C'_X = C_X - \{n(A - A_{0\,2}) + (A_{0\,1} - A)\}(\varepsilon_1 - \varepsilon_2)^{-1} ,$$

$$C'_L = C_L - (A_{0\,1} - A)(\varepsilon_1 - \varepsilon_2)^{-1} .$$

The transformations (D) and (E) or their modified forms (D′) and (E′) correspond to typical equations of the straight line type,

$$A = A_{0\,1} - \frac{{}^*K_{(ii)}(A - A_{0\,2})C'_L}{[\mathrm{H}]^q C'_x} , \qquad \text{(D}'\text{)}$$

$$A = A_{0\,2} + \frac{[\mathrm{H}]^q C'_X (A_{0\,1} - A)}{{}^*K_{(ii)} C'_L} . \qquad \text{(E}'\text{)}$$

As mentioned before, if $C_{M/A}$ or A is plotted against the variable right side, a straight line is obtained for the true exponent (q) being inserted. The number of protons released during the equilibrium reaction is checked from the slope of the particular straight line resulting from the logarithmic plot according to Eq. (F). On the other hand, if the concentration of *hyna* in solutions of the ternary system is not sufficiently high with respect to *tsa*, transition of the Hg(*tsa*)$_2$ complex to the Hg-*tsa-hyna* 1:1:1 ternary complex according to Eq. (8) is not accomplished. The absorbance-pH plots under these conditions coincide with those obtained in absence of *hyna*.

Analysis of the Absorbance Versus Concentration Plots in Solutions of the Ternary System

The absorbance plots against one particular ligand concentration, while keeping the others constant, are examined. Substitution equilibria including ternary complex formation may be interpreted by the analysis of these plots. In the presence of a constant excess of *tsa*, at pH 6, the plot $A = \mathrm{f}(C_L)$ (Fig. 5 a) was analyzed for variable concentrations of *hyna* according to Eqs. (G) and (H) assuming the existence of Eq. (10),

$$C_M/A = 1/\varepsilon_2 + \frac{[\mathrm{H}]^q}{{}^*K_{(\mathrm{iii})}\,\varepsilon_2}\;\frac{(A-\varepsilon_1 C_M)}{A\left[C_L - n\dfrac{A-A_{01}}{\varepsilon_2-\varepsilon_1}\right]^n}, \qquad \text{(G)}$$

$$\log\frac{(A-\varepsilon_1 C_M)}{(\varepsilon_2 C_M - A)} = n\log\left(C_L - n\frac{A-\varepsilon_1 C_M}{\varepsilon_2-\varepsilon_1}\right) - \log C_X + qpH + \log{}^*K_{(\mathrm{iii})}, \qquad \text{(H)}$$

where n is the number of molecules of the competing ligand *hyna*.

The transformation (G) is linear only for $n = 1$. The molar absorptivity ε_2 corresponds to the ternary complex Hg-*tsa-hyna*, whereas ε_1 corresponds to the binary thiosalicylate complex of mercury ($\mathrm{Hg}X_2$). Transformations (G) and (H) are advantageously used for interpretation of concentration dependences of the absorbance in solutions containing variable concentrations of the ligand or of the second complexing agent. Assuming the initial complex to be $\mathrm{Hg}(tsa)_2$, the value

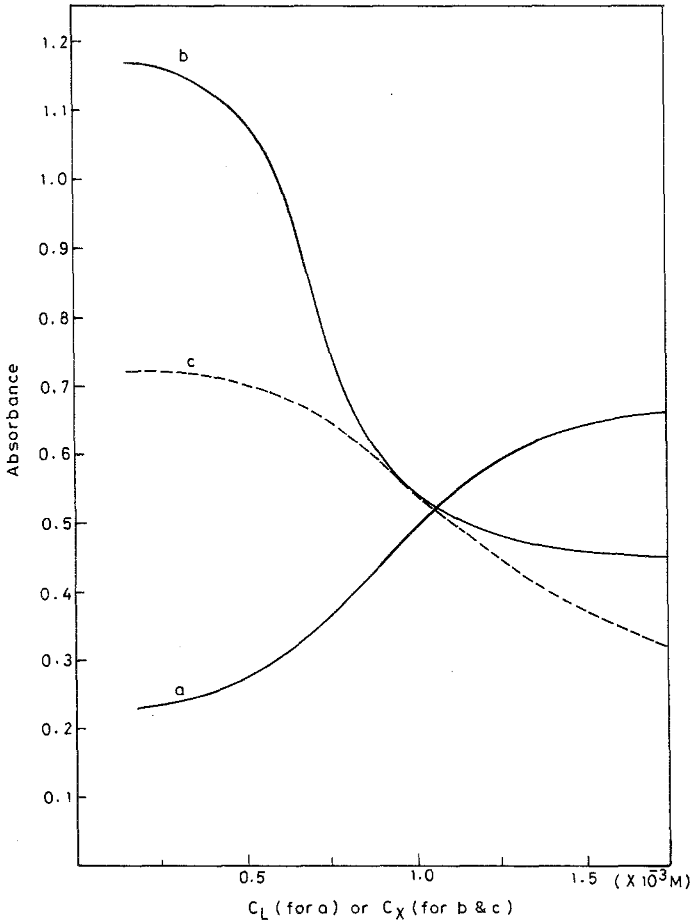


Fig. 5. Substitution equilibria in the ternary system: concentration plots at pH 6, $\lambda = 340$ nm; (*a*) $A = \mathrm{f}(C_L)$, $C_M = 2.5 \cdot 10^{-4}$ mol dm^{-3}, $C_X = 5 \cdot 10^{-4}$ mol dm^{-3}; (*b*) $A = \mathrm{f}(C_X)$, $C_M = 2.5 \cdot 10^{-4}$ mol dm^{-3}, $C_L = 5 \cdot 10^{-4}$ mol dm^{-3}; (*c*) $A = \mathrm{f}(C_X)$, $C_M = C_L = 2.5 \cdot 10^{-4}$ mol dm^{-3}

of the equilibrium constant of Eq. (10) was found in a good agreement with that calculated under a similar assumption from the absorbance-*pH* graphs with constant *hyna* and *tsa* concentrations.

Similarly an equilibrium of the type (11) was realized in solutions with a constant excess of *hyna* and with a variable concentration of thiosalicylate at *pH* 5.5–6,

$$\mathrm{Hg}L_2^{2-} + X\mathrm{H}^- \rightleftharpoons \mathrm{Hg}LX^{2-} + L^{2-} + \mathrm{H}^+ . \qquad (11)$$

With increasing concentration of *tsa* an exponential decrease of the absorbance of the Hg-*hyna* complex was observed (cf. Fig. 5, curve b). Values of ε_2 obtained from horizontal parts of absorbance plots $A = \mathrm{f}(C_X)$ are lower than those determined by means of the absorbance versus *pH* graphs and of the plots $A = \mathrm{f}(C_L)$. Transition of $\mathrm{Hg}L_2^{2-}$ complex according to Eq. (11) was proved by the analysis of the graph $A = \mathrm{f}(C_X)$ at *pH* 6 in solutions with a constant excess of *hyna*. The linear transformation of the descending part of the graph show that only one molecule of *tsa* is coordinated at this *pH*. The logarithmic analysis of this part of the curve yields a straight line with a slope approaching unity.

For solutions containing variable concentration of *tsa* and having a Hg(II) : *hyna* ratio of 1 : 1, (Fig. 5, curve c), the increase of *tsa* concentration leads to gradual transition of the Hg(*tsa*)(*hyna*) complex to the bis-thiosalicylate complex $\mathrm{Hg}(tsa)_2$. In contrast with the spectra of the 1 : 1 : 1 (Hg : *hyna* : *tsa*) ternary complex the solution spectra in presence of a component ratio of 1 : 1 : 5 display an absorption band at 310 nm characterizing the $\mathrm{Hg}(tsa)_2$ complex and a very weak absorption at 345 nm.

The formation of the Hg(*tsa*)(*hyna*) ternary complex has also been ascertained by examining the equilibrium reaction (12) spectrophotometrically as described elsewhere [18],

$$\mathrm{Hg}X_2 + \mathrm{Hg}L_2 \rightleftharpoons 2\,\mathrm{Hg}XL . \qquad (12)$$

The solution spectra of binary and ternary complex species of Hg(II) with *tsa* and *hyna* at variable molar fractions of the two ligands are recorded at *pH* ~ 6. The equilibrium constant $K^*_{(\mathrm{iv})}$ for reaction (12) was calculated by using Eq. (L),

$$^*K_{(\mathrm{iv})} = \frac{4\,\alpha_{11}^2}{(1-\alpha_{11})^2 - (1 - R/1 + R)^2}, \qquad (\mathrm{L})$$

where $R = C_{MX2}/C_{ML2}$ and the ratio $\alpha_{11} = [MXL]/C_M$ (the mole fraction of the metal ion present as MXL). Values of α_{11} were calculated for each point in the vicinity of $R = 1$ and then plotted versus log R. The equilibrium constant was calculated for each point and log $^*K_{(\mathrm{iv})}$ was averaged for all points.

The various equilibria set in solution of the Hg-*tsa*-*hyna* ternary system and the corresponding equilibrium constants and the stability constant of the 1 : 1 : 1 mixed-ligand complex calculated for various transitions are given in Table 3.

Table 3. Mean values of equilibrium, stability constant and molar absorptivity of the ternary mercury complex (MXL) with *tsa* and *hyna*; $I = 0.1\,\text{mol}\,\text{dm}^{-1}$ ($NaClO_4$), 20°C, 50% (v/v) ethanol

	Equilibrium	Constant	log constant	Conditions	Molar absorptivity $1\,\text{mol}^{-1}\,\text{cm}^{-1}$
(i)	$[MXL][H]^2/[MX][H_2L]$	$K^*_{(i)}$	−6.79	$A = f(pH)$, $C_M = C_X = C_L$	$0.7 \cdot 10^4$
(ii)	$[MXL][HX][H]/[MX_2][H_2L]$	$K^*_{(ii)}$	−6.57	$A = f(pH)$, $C_M : C_X : C_L\,(1:3:5)$	
(iii)	$[MXL][HX][H]/[MX_2][H_2L]$	$K^*_{(iii)}$	−5.9	$A = f(C_L)$, $pH = 6.0$, $C_X = 5 \cdot 10^{-4}$	
(iv)	$[MXL]^2/[MX_2][ML_2]$	$K^*_{(iv)}$	6.74	$A = f(C_L/C_X)$, $pH = 6.0$	
	$[MXL]/[M][X][L]$	B	21.4[a]	$A = f(pH)$, $C_M : C_X : C_L\,(1:1:1)$	
			21.28[b]	$A = f(pH)$, $C_M : C_X : C_L\,(1:3:5)$	
			21.65[c]	$A = f(C_L)$, $pH = 6.0$, $C_X = 5 \cdot 10^{-4}$	
			21.67[d]	$A = f(C_L/C_X)$	
	Average		21.50		

[a] $\log B = \log K^*_{(i)} + \log B_{MX} + pK_{a_1L} + pK_{a_2L}$

[b] $\log B = \log K^*_{(ii)} + \log B_{MX_2} - pK_{a_2(X)} + pK_{a_1(L)} + pK_{a_2(L)}$

[c] $\log B = \log K^*_{(iii)} + \log B_{MX_2} - pK_{a_2(X)} + pK_{a_1(L)} + pK_{a_2(L)}$

[d] $\log B = \frac{1}{2}\log K^*_{(iv)} + \frac{1}{2}\log B_{MX_2} + \frac{1}{2}\log B_{ML_2}$

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