CHAPTER - II

DETERMINATION OF STABILITY CONSTANTS
OF TERNARY COMPLEXES OF Hg(II)
The studies on complex formation of CH$_3$Hg$^+$ and C$_6$H$_3$Hg$^+$ with eight substituted quinolines, 2,2'-dipyridyl and 1,10 orthophenanthroline have been reported by Anderrg, (1-4) and potentiometric studies on thioacid mercury (II) systems for a few thioacids was conducted by Dubey and coworkers (5-7) Khokhalova, A.I. et al. have performed potentiometric and pH metric studies on mercury ions with some monocarboxylic acid anions (8) and pH metric and calorimetric studies of mercury (II) complexes with N,N-dimethylethylenediamine and N,N-diethylethylenediamine have been conducted by Ahmed, A.K.S. and coworkers (9) However very little is reported on potentiometric studies of mixed ligand complexes of mercury (II).

Following MAL type mixed ligand systems have been studied:

A, (i) Hg(II)-en/amine  
(ii) Hg(II)Cl-en/amine.

B, (i) Hg(II)-en/amino acid  
(ii) Hg(II) Cl-en/amino acid
C.  
(i)  \( \text{Hg(II)} - \text{en/thioacid} \)  
(ii)  \( \text{Hg(II)} \text{Cl-en/thioacid} \)

D.  
(i)  \( \text{PhHg}^+ - \text{en-amino acid} \).

In the above mixed ligand systems (A, B and C) ethylenediamine was considered as the primary ligand and an amine i.e. ethylenediamine, 2-aminoethanol; aminoacid, i.e. Glycine, L-lysine, L-histidine, DL-alanine, Glutamic acid L-cysteine; thioacid i.e. thioglycolic as the secondary ligand. For system (D) only two aminoacids i.e. glycine and L-lysine were taken as the secondary ligands. The primary complex formation on mixing metal and primary ligand leads to formation of 1:1 MA or HACl type of complex species. Thus initially with ethylenediamine and mercury salt the primary complex formation can be expressed as:

\[
\text{Hg}^{2+} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow \left[ \text{Hg(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \right]^{2+}
\]

\[
\text{HgCl}_2 + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightleftharpoons \left[ \text{Cl-Hg(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \right]^{+}
\]

The reaction mixture containing 1:1 MA or HACl complex and secondary ligand is then titrated with standard alkali.
The increase in pH of mixed ligand systems on titrating with alkali leads to gradual ionisation of the secondary ligand and the ionised secondary ligand then complexes with MA or MAGl to yield MAL mixed ligand complex. On the basis of measurement of pH of the reaction mixture and amount of protons titrated the stability constants of the mixed ligand complexes are determined. With the help of stabilities determined at two different temperatures viz., 30°C and 45°C ± 0.01°C at 0.1 M ionic strength (with respect to KNO₃). The thermodynamic parameters namely entropy change $\Delta S^0$, enthalpy change $\Delta H^0$, and free energy change $\Delta F^0$ were calculated.

The titrations have been carried out employing Bjerrum-Calvin's(10) pH titration technique which was modified by Irving and Rossotti.(11)

**EXPERIMENTAL**

**Materials:**

The details regarding materials used the methods of preparation of standard solutions, along with experimental set up and instrumentation are mentioned below:
(1) **Potassium hydroxide solution:**

(0.2M) carbon dioxide free potassium hydroxide solution was prepared by dissolving the requisite amount of (AR, BDH) alkali in redistilled water in a well corked pyrex measuring flask. The solution was standardised by titrating it against standard solution of oxalic acid, using phenolphthalein as indicator. A fresh solution of potassium hydroxide was always used in all the experiments.

(2) **Nitric acid solution:**

(0.1M) solution of nitric acid was prepared by dissolving required volume of AR quality reagent in 500 ml flask. The exact strength was determined by titrating it against standard alkali solution.

(3) **Potassium nitrate solution:**

(0.5M) solution was prepared by weighing 25.25 g of sample (AR, BDH make) and dissolving in 500 ml of redistilled water.
4. Primary complex solutions:

(a) $\text{Hg(en)(NO}_3\text{)}_2$ solution: 0.01M primary complex solution was prepared by mixing 50 ml each of 0.05M ethylenediamine and $\text{Hg(NO}_3\text{)}_2$ solution and raising the volume to 250 ml. Mercuric nitrate solution was prepared by dissolving requisite amount in 100 ml of redistilled water and standardising by titrating against standard solution of potassium chloride using diphenyl-carbazone as indicator. (12)

(b) $\text{HgCl}_2$: en solution: 0.1M primary complex solution was prepared by mixing 50 ml each of 0.05M ethylenediamine and $\text{HgCl}_2$ solutions and raising the volume to 250 ml.

(c) $\text{PhHg(en)NO}_3$ solution: Phenylmercury nitrate (0.3396 gms) was weighed accurately and a paste of it made hot water. The required amount of ethylenediamine (0.0601 gms) in 50 ml of hot water was added slowly in small amounts with constant stirring. Phenylmercury nitrate dissolved slowly in presence of amine and then the volume of the
solution was raised to the required mark.

5. **Ligand Solutions**:

The ligands were obtained from various chemical companies i.e.

(a) Amines:

(i) Ethylenediamine (99.0% Sarabahi M.Chem.)

(ii) 2-aminoethanol (Riedel-De-Haenag,Seelse-Hannover).

(b) Amino acids:

(i) Glycine (99.5% BDH,Glaxo laboratories India)

(ii) L-Lysine hydrochloride (Kyowa biochemicals, Japan).

(iii) L-histidine hydrochloride (BDH,England)

(iv) Di-Alanine (BDH, England).

(v) Glutamic acid (99% E.Merck,India)

(vi) L-cysteine hydrochloride (SD's laboratories India).

(c) Thioacid:

(i) Thio glycolic acid (97% Sarabahi chemicals).

All the amines were purified by redistillation and other reagents were used without further purification. The
ligand solutions i.e. amines, amino acids and thioacid (0.01M) were prepared by dissolving the required amounts in redistilled water. Only freshly prepared ligand solutions were used in pH titrations leading to evaluation of stability constants.

Solvent:

(a) Water: Redistilled water free from carbon dioxide was obtained by redistilling the distilled water containing alkali permanganate. Further dissolution of carbon dioxide in this was prevented by connecting a potassium hydroxide trap to the receiver of the distillate during distillation. Finally nitrogen gas was passed through water before using.

(b) Ethanol: Ethanol obtained from Bengal chemicals was purified by redistillation.(13)

INSTRUMENTS

1. pH-meter and other accessories: All the pH measurements were carried out on a Techniwal pH meter model (CL-46) having glass calomel electrode assembly operating at 220 volts, stabilised on AC mains. The
pH meter was calibrated at two pH values viz 4.00 and 9.20 using buffer tablets (Sarabahi M. Chemicals). Before calibration of the pH indicator scale, the temperature compensation knob was adjusted to the temperature at which the actual experiment was carried out. The pH meter was always standardised before commencing a new titration.

2. Thermostat arrangement: All the experiments were carried out at a controlled temperature. This was done by using an electronically maintained thermostat (Toshniwal India Ltd.) having regulating accuracy of ± 0.1°C. During the course of titrations the titration cell was kept in the thermostat, so that the titrations could be performed at a desired temperature.

3. Titration cell and inert atmosphere: The titration cell was coming beaker filled with solution in/where dipped glass and calomel electrodes, microburette tip and glass bent tube for passing nitrogen gas. The alkali was added from the microburette.
For titrations the following three solutions were prepared:

A. $\text{KNO}_3(0.5M)$ 10.0 ml + $\text{HNO}_3(0.1M)$ 5.0 ml

B. $\text{KNO}_3(0.5M)$ 10.0 ml + $\text{HNO}_3(0.1M)$ 5.0 ml + Secondary ligand (0.01 M) 10.0 ml.

C. $\text{KNO}_3(0.5M)$ 10.0 ml + $\text{HNO}_3(0.1M)$ 5.0 ml + Secondary ligand (0.1 M) 10.0 ml + Primary complex solution (0.01 M) 10.0 ml*.

The total volume in all cases was raised to 50 ml each containing 10% ethanol. The solutions were titrated with a standard solution of alkali at two different temperatures i.e. 30°C and 45°C. The solutions were kept for at least thirty minutes in a thermostat in order to allow them to attain a requisite temperature and then titrated separately. After the measured addition of alkali the solution was stirred and pH noted. Titration curves were

* The MA type $\text{Hg(en)(NO}_3)_2$ and $\text{Hg(en)Cl}$ primary complexes were assumed to be formed on mixing equal volumes of equimolecular mercury salt and ethylenediamine solutions.
obtained by plotting the volume of alkali added against pH of the solutions for reaction mixtures A, B and C.

**Calculation of proton-ligand stability constants.**

The horizontal distances between acid titration curve (A) and ligand titration curve (B) obtained at different pH values were used for calculating the average number of protons attached to ligand i.e. $\bar{n}H$ using the following equation:

$$\bar{n}H = \frac{YTCL_0 - (N_0 + E_0)(V_2 - V_1)}{(V_0 + V_1)}$$

Where:

- $\bar{n}H$ = Average number of protons attached per ligand ion
- $Y$ = Number of dissociable or replaceable protons attached to the ligand.
- $TCL_0$ = The total concentration of the ligand
- $N_0$ = Concentration of the alkali
- $E_0$ = Total concentration of free acid.
- $V_2$ = Volume of alkali needed to reach specified pH for reaction mixture (B).
- $V_1$ = Volume of alkali needed to reach specified pH for reaction mixture (A).
\[ V_0 = \text{Total volume of the reaction mixture.} \]

The calculated values of \( \bar{n} \) have been plotted against \( \text{pH} \) and the curves so formed, called as formation curves for the proton-ligand or protonation curves. Logarithmic protonation constants (\( \text{pK} \)) of various ligands were evaluated from the formation curves by interpolation at half \( \bar{n} \) values. The experimental values of protonation constants were found corresponding to the literature values of proton-ligand stability constants as reported by Smith and Martell.\(^{(14)}\)

C. \textbf{Calculation of metal-ligand stability constants.}

The average number of ligand molecules bound to the metal ion, \( \bar{n} \) have been calculated by measuring the horizontal distance between the ligand titration curve (\( B \)) and metal ligand complex curve (\( C \)) i.e. \( (V_3 - V_2) \) at different \( \text{pH} \) values. The displacement between these two is a measure of complex formation and the horizontal difference gives the amount of alkali required for the titration of protons liberated by the formation of metal complex at corresponding \( \text{pH} \) values. The average number of ligands attached to per metal ion have been evaluated by the following equation :-
\[
\bar{n} = \frac{(V_0 + E_0) (V_3 - V_2)}{(V_0 + V_1)(\bar{m}H \times TCM_0)}
\]

Where,

- \(\bar{n}\) = Average number of ligands attached per metal ion.
- \(N_0\) = Normality of alkali
- \(E_0\) = Total concentration of free acid
- \(V_3\) = Volume of alkali required to attain the same pH in the curve (C) i.e. (acid + primary complex solution + secondary ligand).
- \(V_2\) = Volume of alkali required to attain the same pH in the curve (B) i.e. (acid + secondary ligand).
- \(V_1\) = Volume of alkali required to attain same pH in curve (A) i.e. (acid).
- \(V_0\) = Total volume of the reaction mixture.
- \(TCM_0\) = Total concentration of primary complex.
- \(\bar{m}H\) = Average number of protons bound to free ligand molecule (which is not complex bound).

Since primary complex remains mainly undissociated in the range of combination of secondary ligand it has been considered that the secondary ligand combines with the primary complex (\(\text{MA}\)) just as it does with \([\text{M(aq)}]^{n+}\) in simple systems and hence the concentration of primary complex (\(\text{MA}\)) equals to its initial concentration.
The third and the last function is \( pL = -\log L \), where \( L \) is the free ligand concentration. This function was calculated from the following equation:

\[
\text{pL} = \log \frac{K_1(H^+) + K_1 K_2(\overline{H})^2 + K_1 \ldots \ldots \ldots \ldots \ldots K_n(H^+)x(v_0+v_3)}{TCL_0 - \overline{\alpha} x TCM_0} (v_0)
\]

Where \( K_1, K_2, \ldots, K_n \) represent the successive protonation constants of the ligands and \( (H^+) \) is the hydrogen ion concentration, \( TCL_0, TCM_0, \overline{\alpha}, v_0 \) and \( v_3 \) etc. have usual meaning as described earlier.

Finally, the calculated values of \( \overline{\alpha} \) were plotted against \( pL \) values and the formation curves so obtained are graphically represented in Figures. The step stability constants were evaluated by interpolation at half \( \overline{\alpha} \) values (Bjerrum’s half \( \overline{\alpha} \) method).

**RESULTS AND DISCUSSION**

(A) \( \text{Hg(II)/Hg(II)Cl-en/en-2amath mixed ligand systems} \):

The potentiometric titration curve dealing with the above systems are given in Figures 1–3. The
secondary ligands viz. en and 2amath are completely protonated in reaction mixtures in presence of strong acid and on titrating with alkali they are deprotonated according to the following equations.

\[
\begin{align*}
&\text{enH}_2^+ \xrightleftharpoons{PK_1} \text{enH}^+ + \text{H}^+ \\
&\text{enH}^+ \xrightleftharpoons{PK_2} \text{en}^+ + \text{H}^+ \\
&\text{2amath}^+ \xrightleftharpoons{PK_1} \text{2amath} + \text{H}^+
\end{align*}
\]

The protonation constant values of en and 2amath have already been reported by Smith and Martell (loc cit). The \( pK_1 \) and \( pK_2 \) values for en are 9.89 and 7.08 respectively and \( pK_1 \) for 2amath is 9.55. When their reaction mixture containing the MA/MACl complex and secondary ligand in the ratio of 1:1 is titrated with alkali the deprotonation of protonated amines starts and with increase in pH the concentration of free secondary ligand increases which then combines with primary 1:1 MA and MACl complexes to form MAL complexes according to the equation given below:

\[
\begin{align*}
&\text{Hg(II)-en} + \text{en} \rightarrow \text{Hg(II)-en-en} \\
&\text{Cl-Hg-en} + \text{en} \rightarrow \text{Cl-Hg-en-en}
\end{align*}
\]
The values on step stability constants and other thermodynamic parameters i.e. $\Delta F^0$, $\Delta H^0$, and $\Delta S^0$ are given in Table I. A perusal of the table indicates that $\log^{\text{MAD}}_{\text{MIA}}$ values are higher than corresponding values of $\log^{\text{MAD}}_{\text{MACL}}$. It may be attributed to the fact that in the former case a four coordinated species is formed from two coordinated species and in the latter case the four coordinated species is formed from a three coordinated species. A perusal of the table shows that whereas the enthalpy change is positive indicating that complex formation is unfavourable, the entropy changes are also positive and are of much greater magnitude as compared to the unfavourable enthalpy change. The overall free energy change for the complex formation is therefore mainly due to favourable entropy term.
<table>
<thead>
<tr>
<th>MAL System</th>
<th>30°C Log $^{\text{ML}}_{\text{MA}}$</th>
<th>30°C $-\Delta F^0$ kcal/mole</th>
<th>45°C Log $^{\text{ML}}_{\text{MA}}$</th>
<th>45°C $-\Delta F^0$ kcal/mole</th>
<th>$\Delta H^0$ Kcal/mole</th>
<th>$\Delta S^0$ cal/degree/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(II)-(en)(en)</td>
<td>9.10</td>
<td>12.62</td>
<td>9.53</td>
<td>13.87</td>
<td>12.65</td>
<td>83.40</td>
</tr>
<tr>
<td>Hg(II)(en)(zamath)</td>
<td>4.13</td>
<td>5.75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MAL System</th>
<th>30°C Log $^{\text{ML}}_{\text{MA}}$</th>
<th>30°C $-\Delta F^0$ Kcal/mol</th>
<th>45°C Log $^{\text{ML}}_{\text{MA}}$</th>
<th>45°C $-\Delta F^0$ Kcal/mol</th>
<th>$\Delta H^0$ Kcal/mol</th>
<th>$\Delta S^0$ cal/degree/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(II)(en)(en)</td>
<td>6.67</td>
<td>9.25</td>
<td>7.15</td>
<td>10.40</td>
<td>14.18</td>
<td>77.33</td>
</tr>
<tr>
<td>Hg(II)(en)(zamath)</td>
<td>3.28</td>
<td>4.55</td>
<td>3.47</td>
<td>5.05</td>
<td>5.99</td>
<td>33.47</td>
</tr>
</tbody>
</table>

TABLE - I
METAL LIGAND STABILITY CONSTANTS OF 1:1:1 TERNARY MERCURY(II) COMPLEXES
IONIC STRENGTH $\mu = 0.1 \text{M (KNO}_3\text{)}$
Hg(II)/Hg(II)Cl-en-amine acid systems:

For studying mixed ligand complexes with amino acids, the amino acids which have been used as secondary ligands in these systems are: glycine, L-lysine hydrochloride, L-histidine hydrochloride, DL-alanine, glutamic acid and cysteine. Figures (5–10) deal with the pH titration curves of the above systems. The formation curves for metal ligand stability constants are given in figures (11–14). The proton ligand equilibria of the various amino acids stated above occur as follows:

**Glycine:**

\[
\begin{align*}
\text{NH}_2 & \\
\text{CH}_2\text{COO}^- & \xrightleftharpoons{\text{PK}_1} \text{NH}_2^+ \\
\text{CH}_2\text{COOH} & \ + \ H^+
\end{align*}
\]

**L-lysine**

\[
\begin{align*}
\text{NH}_2 & \\
\text{CH}_2(\text{CH}_2)_4\text{COO}^- & \xrightleftharpoons{\text{PK}_1} \text{NH}_2(\text{CH}_2)_2\text{COO}^- \\
\text{CH}_2\text{COOH} & \ + \ H^+
\end{align*}
\]
The protonation constant values of above amino acids have already been reported by Smith and Martell (Loc.cit).
The values are as follows:

Glycine (pK$_1$ = 9.57, pK$_2$ = 2.36)

Alanine (pK$_1$ = 9.69, pK$_2$ = 2.30)

L-lysine (pK$_1$ = 10.69, pK$_2$ = 9.08, pK$_3$ = 2.04)

L-histidine (pK$_1$ = 9.08, pK$_2$ = 6.02, pK$_3$ = 1.70)

Glutamic acid (pK$_1$ = 9.59, pK$_2$ = 4.30, pK$_3$ = 2.18)

L-cysteine (pK$_1$ = 10.29, pK$_2$ = 8.15, pK$_3$ = 1.88)

The acid solution containing metal ion and secondary ligand i.e. glycine, L-lysine, L-histidine, Dl-alanine, glutamic acid and cysteine in the ratio of 1:1:1 could be considered to be comprised of (1:1) amine mercury complex and amino acid and when such a solution is titrated with alkali the gradual deprotonation of amino acids takes place. This leads to progressive formation of mixed ligand metal complexes as represented by the equation.

\[
\begin{align*}
\text{Hg}^{2+} + A & \rightleftharpoons [\text{HGA}]^{2+} \\
\text{HgCl}_2 + A & \rightleftharpoons [\text{HgACL}]^+ \\
\end{align*}
\]
Where $A$ is the primary neutral ligand ethylenediamine and $L^-$ is the secondary ligand i.e. an amino acid ion. L-lysine, L-histidine and L-cysteine were used as their hydrochloride salts and while calculating $\bar{n}$ and $\tilde{n}$ values the volume of alkali used for the neutralisation of hydrochloride was subtracted from the actual volume of alkali used. The results obtained on step stability constants and thermodynamic parameters are given in tables IIA and IIB. A perusal of the tables indicate that $\log K_{\text{HgA}}^{\text{MAL}}$ are generally lower than the $\log K_{\text{HgA}}^{\text{MAL}}$ values. However, for some secondary ligands especially for L-lysine and L-cysteine, $\log K_{\text{HgA}}^{\text{MAL}}$ values are higher than the corresponding $\log K_{\text{HgA}}^{\text{MAL}}$ values, which may be due to the formation of HgACL complex through an additional equilibrium.

Table II B also shows that for mixed ligand complexes of L-lysine, complex formation is both enthalpy and entropy favoured. For L-histidine and L-cysteine complexes the enthalpy change is favourable (\( \Delta H = -9.71, -47.06 \) respectively) but entropy change is unfavourable (\( \Delta S = -11.32 \) and \(-125.34 \) respectively). However, enthalpy change being of greater magnitude overrides the unfavourable entropy term and hence the complex formation is enthalpy oriented. For all other systems except, Hg(II)(en)(glu) (Table IA) system in which complex formation is both enthalpy and entropy favoured, the enthalpy change values are positive (unfavourable) but entropy change values are also positive (favourable). In these cases therefore the favourable enthalpy term determines the favourable free energy change for complex formation.
**TABLE IIIA**

METAL LIGAND STABILITY CONSTANTS OF 1:1:1 TERNARY MERCURY(II) COMPLEXES IONIC STRENGTH \( \mu = 0.1 \text{M} (\text{KNO}_3) \)

<table>
<thead>
<tr>
<th>MAL System</th>
<th>30°C</th>
<th>45°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log ( \text{MAL} )</td>
<td>( -\Delta F^0 ) kOal/mole</td>
<td>Log ( K )</td>
</tr>
<tr>
<td>Hg(II)(en)(gly)</td>
<td>6.51</td>
<td>9.03</td>
<td>7.07</td>
</tr>
<tr>
<td>Hg(II)(en)(lys)</td>
<td>3.90</td>
<td>5.41</td>
<td>4.57</td>
</tr>
<tr>
<td>Hg(II)(en)(hist)</td>
<td>4.04</td>
<td>5.60</td>
<td>4.98</td>
</tr>
<tr>
<td>Hg(II)(en)(alan)</td>
<td>6.67</td>
<td>9.25</td>
<td>7.38</td>
</tr>
<tr>
<td>Hg(II)(en)(glu)</td>
<td>6.90</td>
<td>9.57</td>
<td>6.75</td>
</tr>
<tr>
<td>Hg(II)(en)(cyst)</td>
<td>4.30</td>
<td>5.96</td>
<td>4.49</td>
</tr>
<tr>
<td>MAL System</td>
<td>$30^\circ C$</td>
<td>$45^\circ C$</td>
<td>$30^\circ C$</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td></td>
<td>Log$_{MACl}$</td>
<td>$\Delta F^0$</td>
<td>log K</td>
</tr>
<tr>
<td>Hg(II)(en)(gly)</td>
<td>5.39</td>
<td>7.47</td>
<td>5.67</td>
</tr>
<tr>
<td>Hg(II)(en)(lys)</td>
<td>6.30</td>
<td>8.74</td>
<td>6.15</td>
</tr>
<tr>
<td>Hg(II)(en)(hist)</td>
<td>4.53</td>
<td>6.28</td>
<td>4.20</td>
</tr>
<tr>
<td>Hg(II)(en)(alan)</td>
<td>5.50</td>
<td>7.63</td>
<td>5.93</td>
</tr>
<tr>
<td>Hg(II)(en)(glu)</td>
<td>5.74</td>
<td>7.96</td>
<td>5.89</td>
</tr>
<tr>
<td>Hg(II)(en)(cyst)</td>
<td>6.55</td>
<td>9.08</td>
<td>4.95</td>
</tr>
</tbody>
</table>
The proton ligand equilibria of thio glycolic acid occurs as follows:

\[
\begin{align*}
\text{HSCH}_2\text{COOH} & \rightleftharpoons pK_2(10.67) \quad \text{HSCH}_2\text{COO}^- + H^+ \\
\text{HSCH}_2\text{COO}^- & \rightleftharpoons pK_1(3.67) \quad \text{SCCH}_2\text{COO}^-
\end{align*}
\]

The gradual deprotonation of thio glycolic acid leads to progressive formation of MAL complexes involving the equilibria -

\[
\begin{align*}
[Hg\text{en}]^{2+} + (\text{SCCH}_2\text{CO}_2)^2- & \rightleftharpoons [Hg\text{en}\cdot\text{SCCH}_2\text{CO}_2] \\
[Hg\text{Cl} : \text{en}]^+ + (\text{SCCH}_2\text{CO}_2)^2- & \rightleftharpoons [Hg\text{en}\cdot\text{SCCH}_2\text{CO}_2]
\end{align*}
\]

The pH titration curves for the above systems are given in figure(15) and the formation curves are given in figure(16). From the formation curves it has been observed that 1:1:1 MAL complexes are formed. The results on step stability constants along with thermodynamic parameters at 0.1M ionic strength are given in Table III. The results indicate that \( \log K_{MAL}^{NACL} \) values are higher than \( \log K_{MAL}^{NACL} \) values, which may
be due to formation of higher coordinated species Hg\[\text{ALCl}\] through an additional equilibrium. The free energies of these complexes have more negative values at higher temperature and also the entropy change accompanying the complex formation is positive and are of higher magnitude as compared to enthalpy change values. As a result of this the entropy term strongly favours the complex formation.

**PhHg\(^{+}\) : ethylenediamine : glycine : L-lysine mixed ligand systems:**

Equilibrium studies on amino acid phenylmercury nitrate mixed ligand complexes of the type \(\text{MAL}\) (Where \(A = \text{ethylenediamine}, \) and \(L = \text{glycine}, \) L-lysine) have been conducted at two temperatures viz. 30 and 45\(^\circ\)C at 0.1M ionic strength (with respect to KNO\(_3\)). Figures 17, 18 deal with the pH titration curves of the above systems and figure 19 represent the formation curves of these systems. The step stability constants along with thermodynamic parameters \(\Delta r^0, \) \(\Delta H^0, \) \(\Delta S^0\) are given in Table IV. A perusal of the table shows that the stabilities of these complexes are very low as compared to similar Hg(II) complexes. The higher entropy change values favour the complex formation.
### Table III

**Metal Liquid Stability Constants of 1:1:1 Ternary Hg(II) Complexes**

**Ionic Strength \( \mu = 0.1 \text{M (KNO}_3 \text{)} \)**

<table>
<thead>
<tr>
<th>MAL system</th>
<th>30°C</th>
<th>45°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LogK</td>
<td>(-\Delta F^0) kcal/mole</td>
<td>LogK</td>
</tr>
<tr>
<td>Hg(II)(en)(TGA)</td>
<td>5.90 Log(_{\text{MAL}}) 8.18</td>
<td>6.22</td>
<td>9.05</td>
</tr>
<tr>
<td>Hg(II)(en)(TGA)</td>
<td>6.35 Log(_{\text{MAG}}) 8.80</td>
<td>6.56</td>
<td>9.55</td>
</tr>
</tbody>
</table>
### Table - IV

**Metal Ligand Stability Constants of 1:1:1 Ternary PhHg⁺ Complexes**

**Ionic Strength 0.1M (KNO₃)**

<table>
<thead>
<tr>
<th>MAL System</th>
<th>LogK</th>
<th>$-\Delta F^o$ Kcal/mole</th>
<th>LogK</th>
<th>$-\Delta F^o$ Kcal/mole</th>
<th>$\Delta H^o$ Kcal/mole</th>
<th>$30°C$ $\Delta s^o$ cal/deg/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhHg(en)(gly)</td>
<td>3.02</td>
<td>4.19</td>
<td>3.20</td>
<td>4.66</td>
<td>5.29</td>
<td>31.28</td>
</tr>
<tr>
<td>PhHg(en)(lys)</td>
<td>3.11</td>
<td>4.31</td>
<td>3.63</td>
<td>5.28</td>
<td>15.29</td>
<td>64.68</td>
</tr>
<tr>
<td>REFERENCES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>---------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>Author(s)</td>
<td>Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>--------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>