Potentiometric studies on ternary complexes involving some divalent transition metal ions, gallic acid and biologically abundant aliphatic dicarboxylic acids in aqueous solutions

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ABSTRACT

Formation of binary and ternary complexes of the divalent transition metal ions, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Zn$^{2+}$ with gallic acid and the biologically important aliphatic dicarboxylic acids (adipic, succinic, malic, malonic, maleic, tartaric and oxalic acids) were investigated by means of the potentiometric technique at 25°C and I = 0.10 mol dm$^{-3}$ NaNO$_3$. The acid-base properties of the ligands were investigated and discussed. The acidity constants of gallic acid and aliphatic dicarboxylic acids were determined and used for determining the stability constants of the binary and ternary complexes formed in the aqueous medium under the above experimental conditions. The formation of the different 1:1 and 1:2 binary complexes and 1:1:1 ternary complexes are inferred from the corresponding potentiometric pH-metric titration curves. The ternary complex formation was found to occur in a stepwise manner. The stability constants of these binary and ternary systems were calculated. The values of $\Delta \log K$, percentage of relative stabilization (%R.S.) and log X were evaluated and discussed. The concentration distribution of the various complex species formed in solution was evaluated and discussed. The mode of chelation of ternary complexes formed was ascertained by conductivity measurements.

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1. Introduction

Gallic acid is commonly used in the pharmaceutical industry because many in vivo and in vitro studies in humans, animals, and cell culture have provided evidence for cytotoxicity against cancer cells, without harming healthy cells (Elvira et al., 2006). Gallic acid exists in two forms as the free molecule and as part of tannins. Pure gallic acid is a colorless crystalline organic powder. Green tea is the most abundant source of tea phenolics, mostly in the form of simple hydroxybenzoic acids and propyl gallate and its catechin derivatives (epigallocatechin-3-gallate, epigallocatechin, epicatechin-3-gallate, and epicatechin). One of the most common moieties in the structure of tea phenolics, besides hydroxyl groups, is the gallic acid moiety. Green tea catechins and phenolic acids have been shown to demonstrate profound biochemical and pharmacological activities including...
antioxidant activities, modulation of carcinogen metabolism, and inhibition of cell proliferation (Barbosa, 2007; Chiu-Lan et al., 2007; Cook et al., 1995; Hurrell et al., 1999; Jittawattan and Sirithon, 2008; Kuroda and Hara, 1999; Min et al., 2002; Misao et al., 2007; Rajalakshmi and Narasimban, 1996). Extracts derived from green tea have the potential to reduce the oxidation of food products and extend their shelf life. The antioxidant action was shown to be dependent on the ability of their constituent phenolic compounds to scavenge free radicals and to chelate and the metal ion chelating ability of polyphenols is related to the presence of ortho-dihydroxy polyphenols, i.e., molecules bearing catechol or galloyl groups metals (Moran et al., 1997; Morck et al., 1983). Coordination of metal ions by gallic acid may be desirable in view of potential clinical significance (Ziano and Roberts, 1977). Aliphatic carboxylic acids are biologically abundant and important and versatile binding ligands (Inezedy, 1976).

As a continuation of our research program oriented to study the binary and ternary complexes of biologically active ligands (Radalla, 2010; Radalla and Khalil, 1998; Radalla et al., 1997, 2009a, 2009b, 2009c, 2013, 2014), the formation of binary and ternary complexes of the divalent transition metal ions, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Zn$^{2+}$ with gallic acid and the biologically important aliphatic dicarboxylic acids (adipic, succinic, malic, malonic, maleic, tartaric and oxalic acids) was investigated by means of the potentiometric and conductometric techniques at 25 °C and ionic strength used in the investigation. A computer program (GLEE, glass electrode evaluation (Gans and O'Sullivan, 2000) has been used to calibrate the glass electrode by means of a strong acid-strong base titration under the same temperature and ionic strength used in the investigation. This program provides an estimate of the carbonate contamination of the base, the pseudo-Nernstian standard potential and slope of the electrode, and optionally, the concentration of the base and pKw. The autoprotolysis of water (H$_2$O = H$^+$ + OH$^-$, K$_w$) at 25 °C and ionic strength of 0.1 mol dm$^{-3}$ of NaNO$_3$ were (1.05 × 10$^{-14}$ ± 1.01 × 10$^{-16}$ or pK$_w$ = 13.97 ± 0.01), (1.05 × 10$^{-14}$ ± 1.02 × 10$^{-16}$ or pK$_w$ = 13.98 ± 0.01) and (1.04 × 10$^{-14}$ ± 1.0 × 10$^{-16}$ or pK$_w$ = 13.99 ± 0.01) which averaged to (1.06 × 10$^{-14}$ ± 1.00 × 10$^{-16}$ or pK$_w$ = 13.97 ± 0.02). The combination electrode involves the use of a 3 M KCl salt bridge between the internal reference and the external solution. This salt bridge reduces the 4junction potential, but it does not become zero (Longhi et al., 1990). This potential varies from one solution to another, and this variability increases the uncertainty of the measured pH with respect to that obtained by the other methods. For this reason, the reported accuracy cannot be better than (0.02 pH/pKa units).

The investigated solutions were prepared (total volume 50 cm$^3$) and titrated potentiometrically against standard CO$_2$-free NaOH (0.20 mol dm$^{-3}$) solution. A stream of nitrogen was passed throughout the course of the experiment in order to exclude the adverse effect of atmospheric carbon dioxide. Magnetic stirring was used during all titrations. The ligand concentrations were varied in the range 1 × 10$^{-3}$–6 × 10$^{-3}$ mol dm$^{-3}$. Three to four different metal-to-ligand ratios for binary systems and 1:1:1 and 1:2:2 (metal:primary ligand:secondary ligand) ratios for the ternary systems were used in the investigation. The initial estimates of the ionization constants of the ligands and the stability constants of binary and ternary complexes were calculated by adopting Irving and Rossotti technique (Irving and Rossotti, 1953, 1954). Part of information required for determining the metal complex stability constants is the acid dissociation constant (pKa). Therefore, the pKa values were calculated from Eq. (1) where $\beta$ is the proton-ligand formation constant of the ligand and $n_H$ is the average number of protons associated per mole of ligand at several pH values.

$$\bar{n}_H = \beta[H^+] \{1 + \beta[H^+]\}^{-1}$$  \hspace{1cm} (1)

Eq. (2) was used for calculation of the $n_H$ values from the titration curves corresponding to solutions 1, 2, and 4, where $y$ is the number of dissociable protons ($y = 2$ in case of all ligands studied).

$$n_H = \frac{yC_L + [(V_S - V_b)\sigma(V_a - V_s)]C_b}{V_s} (C_L)^{-1}$$ \hspace{1cm} (2)
$V_a$, $V_b$, and $V_e$ are the volumes of NaOH consumed to reach the same pH values in curves 1, 2, and 4, respectively. $C_b$ and $C_L$ are the concentrations of NaOH and ligand, respectively, and $V_o$ is the original volume (50 cm$^3$). Titration curves 2, 4, and 5 (Fig. 2) were used to calculate the stability constants of the binary metal complexes of gallic acid and dicarboxylic acids, respectively.

The average number of ligand molecules ($n_b$) coordinated to the metal ion and the free ligand exponent ($P_L$) at several pH values were calculated according to Eqs. (3) and (4), where $V_c$ and $V_e$ are the volumes of NaOH consumed to reach the same pH values in curves 3 and 5, respectively.

\[
n_b = \frac{|(V_e - V_b)\alpha_0(C_b + C_L(y - F_b))|}{(V_a + V_b)\alpha_0(C_L - n_bC_M)} \tag{3}
\]

\[
P_L = \log \left( \frac{\sum_{y=0}^{y=1} \alpha_0 \beta_y^P \frac{1}{\beta_y^P} V_a + (V_c + V_f)Y}{V_b} \right) \tag{4}
\]

$C_b$ is the concentration of HNO$_3$, and $C_M$ is the initial concentration of the metal ion used. $\beta_y^P$ represents the proton-ligand dissociation constants of the ligands, and $B$ is the pH value. $n_b$ values were available from the determination of the proton-ligand formation constant. It is worth mentioning that the values of $n_b$ exceed 1.5 indicating the formation of both 1:1 and 1:2 binary complexes.

On the other hand, the titration curves c and f were used to calculate the number of secondary ligands attached to one binary 1:1 MA complex molecule ($n_{mix}$) for a mixed ligand ternary complex. The equation used for the calculation of $n_{mix}$ (Eq. (5)) was the same as that reported elsewhere (Khalil et al, 1997), where $C_b$ is the concentration of the binary complex involving the primary ligand, which equals the concentration of $M^{2+}$ used, $C_L$ is the concentration of the secondary ligand, $y$ is the number of dissociable protons per molecule of the secondary ligand, and $V_t$ is the volume of NaOH consumed to reach the same pH values in curve 6.

\[
n_{mix} = \left( \frac{V_t - V_e)\alpha_0(C_b + C_L(y - F_b))}{(V_a + V_c + V_f)\alpha_0CM} \right) \tag{5}
\]

In this case, the $n_{mix}$ values are the average number of protons associated with the secondary ligand at different pH values. The $n_{mix}$ values do not exceed unity indicating that only one secondary ligand molecule combines with the complex MA, forming a 1:1:1 MAG ternary complex. The free secondary ligand exponent, $P_{mix}$, was calculated from the obtained values of $n_{mix}$ using Eq. (6) where $\beta_y^H$ are the proton-ligand dissociation constants of the secondary ligand.

\[
P_{mix} = \log \left( \frac{\sum_{y=0}^{y=1} \alpha_0 \beta_y^H \frac{1}{\beta_y^H} V_a + (V_c + V_f)\alpha_0C_L - n_{mix}C_M}{V_o} \right) \tag{6}
\]

All other terms have the same meaning as defined above.

The equilibrium constants were refined with a computer program based on unweighted linear least-squares fit. About 100 to 120 experimental data points were available for evaluation in each system. The titration was repeated at least four times for each titration curve. The complexes are quite stable up to high pH values.

Regarding formation of hydroxyl species in case of binary and ternary systems investigated, two factors affect the presence of hydroxo-complexes. First, the ligand-to-metal
ratio used. Second, the choice of pH range for calculations of the stability constant values which depend on pHs at which the different complexes start to form (in our investigations, complexes started to form at pH values below 3 for 1:1 and 1:1:1 ratios which is low value and this pH values are also dependent in turn on ligand-to-metal ratios used and get more lower as the ratios increase). Also, high ligand-to-metal ratios were used for binary and ternary complex systems purposely to suppress hydrolysis of the formed complexes. Also, in the case of Zn (II) ions, ZnCl₂ is used as Cl⁻ ions compete with OH⁻ and thus suppress hydrolysis of Zn-complexes at low pHs. According to the above mentioned reasons, hydroxo-complexes were neglected in our choice of the model for our calculations for all the investigated metal ions. In all cases, no calculations have been performed beyond the precipitation point; hence, the hydroxo species likely to be formed after this point could not be studied.

A summary of the experimental details, for the potentiometric measurements, is given in Table 1.

2.3. Conductometric measurements

Conductometric titrations of ternary complexes in solution were followed with a HANNA conductivity meter HI-98304. The conductivity cell is a reliable pocket-sized instrument with quick and accurate readings of conductivity and TDS. The cell is from Hanna Instruments, USA model HI-98304 with a conductivity range up to 2000 μS cm⁻¹ and an automatic temperature sensor (0⁻50 °C).

The following mixture was titrated conductometrically against 0.20 mol dm⁻³ NaOH solution: 1·10⁻² mol dm⁻³ metal (II) ion (10 cm³) + 1·10⁻² mol dm⁻³ dicarboxylic acid (10 cm³) + 1·10⁻² mol dm⁻³ gallic acid (10 cm³).

3. Results and discussion

3.1. Dissociation constants of the free ligands

The structural formulas of the investigated ligands are given in Chart 1. The proton dissociation constants of the ligands investigated have been determined in aqueous medium at 25 °C and [I] = 0.10 mol dm⁻³ (NaNO₃). Gallic acid (H₄G) is expected to have four ionization constants relevant to the following ionization steps (Fazary et al., 2009; Fouzia, 1997) as shown in Eqs. (7)–(10):

Fig. 3 – Concentration distribution curves as a function of pH calculated for Cu²⁺ + Tartaric acid + Gallic acid system in the ratio 1:2:2 at 25 °C, I = 0.10 mol dm⁻³ (NaNO₃). C_{Cu²⁺} = 4·10⁻⁴ mol dm⁻³ and C_{ligand} = 1·10⁻³ mol dm⁻³.

### Table 1 – Summary of experimental parameters for the potentiometric measurements.

<table>
<thead>
<tr>
<th>System</th>
<th>Dissociation processes of ligands: gallic acid and aliphatic dicarboxylic acids (adipic, succinic, malic, malonic, maleic, tartaric and oxalic acids). Adipic/succinic/malic/malonic/maleic/tartaric/oxalic acids, gallic acid with Cu²⁺, Ni²⁺, Zn²⁺ and Co²⁺ in aqueous media.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary</td>
<td>Ligand range (from 1 · 10⁻³ to 4 · 10⁻³ mol dm⁻³), metal/ligand ratios ranging from 1:1 to 1:2.5 for binary systems and 1:1:1 and 1:2.5:2.5 for ternary systems.</td>
</tr>
<tr>
<td>Ternary:</td>
<td>0.10 mol dm⁻³ supporting electrolyte (NaNO₃). pH-metric titration of 50 cm³ samples in the range 2 to 11.5. SM 702 Metrohm automatic titrator with a combined pH glass electrode equipped with a 665 dosimat and a magnetic stirrer (Switzerland). By titrating HNO₃ solution (0.10 mol dm⁻³) against a standard NaOH solution at the same temperature and ionic strength as the solution under study.</td>
</tr>
<tr>
<td>Solution composition</td>
<td>Ligand range (from 1 · 10⁻³ to 4 · 10⁻³ mol dm⁻³), metal/ligand ratios ranging from 1:1 to 1:2.5 for binary systems and 1:1:1 and 1:2.5:2.5 for ternary systems.</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>0.10 mol dm⁻³ supporting electrolyte (NaNO₃). pH-metric titration of 50 cm³ samples in the range 2 to 11.5. SM 702 Metrohm automatic titrator with a combined pH glass electrode equipped with a 665 dosimat and a magnetic stirrer (Switzerland). By titrating HNO₃ solution (0.10 mol dm⁻³) against a standard NaOH solution at the same temperature and ionic strength as the solution under study.</td>
</tr>
<tr>
<td>Instrument</td>
<td>0.10 mol dm⁻³ supporting electrolyte (NaNO₃). pH-metric titration of 50 cm³ samples in the range 2 to 11.5. SM 702 Metrohm automatic titrator with a combined pH glass electrode equipped with a 665 dosimat and a magnetic stirrer (Switzerland). By titrating HNO₃ solution (0.10 mol dm⁻³) against a standard NaOH solution at the same temperature and ionic strength as the solution under study.</td>
</tr>
<tr>
<td>Calibration</td>
<td>0.10 mol dm⁻³ supporting electrolyte (NaNO₃). pH-metric titration of 50 cm³ samples in the range 2 to 11.5. SM 702 Metrohm automatic titrator with a combined pH glass electrode equipped with a 665 dosimat and a magnetic stirrer (Switzerland). By titrating HNO₃ solution (0.10 mol dm⁻³) against a standard NaOH solution at the same temperature and ionic strength as the solution under study.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method of calculation</th>
<th>computer program based on unweighted linear least-squares fit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>nₐₜ</td>
<td>Method of calculation computer program based on unweighted linear least-squares fit.</td>
</tr>
<tr>
<td>nₛₜ</td>
<td>Method of calculation computer program based on unweighted linear least-squares fit.</td>
</tr>
</tbody>
</table>

Method of calculation computer program based on unweighted linear least-squares fit.

a Number of titration points per titration.

b Number of titrations per titration curve.
The first ionization proton is assigned to the carboxylic group (COOH), and the rest are assigned to the hydroxyl groups (OH) of gallic acid molecule. The proton dissociation steps involved in the potentiometric pH-metric titration in the pH range 2–11 of gallic acid can be represented as follows:

\[ \text{H}_4\text{G} = \text{H}_3\text{G}^- + \text{H}^+ \]  \hspace{1cm} (7)

\[ \text{H}_3\text{G}^- = \text{H}_2\text{G}_2^+ + \text{H}^+ \]  \hspace{1cm} (8)

\[ \text{H}_2\text{G}_2^+ = \text{HG}_3^- + \text{H}^+ \]  \hspace{1cm} (9)

\[ \text{HG}_3^- = \text{G}_4^- + \text{H}^+ \]  \hspace{1cm} (10)

The first ionization proton is assigned to the carboxylic group (COOH), and the rest are assigned to the hydroxyl groups (OH) of gallic acid molecule. The proton dissociation steps involved in the potentiometric pH-metric titration in the pH range 2–11 of gallic acid can be represented as follows:

The first and the second ionization constants of gallic acid were determined potentiometrically in aqueous solutions, under the experimental conditions \((t = 25^\circ \text{C}, I = 0.1 \text{ mol dm}^{-3} \text{NaNO}_3)\). The values obtained (Table 2) agreed quite well with previously reported ones (Fazary et al., 2009; Fouzia, 1997; Martell and Smith, 1976). The third and fourth dissociations of the protons from hydroxyl groups (OH) of gallic acid take place at higher buffer regions as \(\text{pH} \geq 11.5\) (Inezedy, 1976; Martell and Smith, 1976); therefore, these two dissociation constant values (\(\text{pK}_{3a}\) and \(\text{pK}_{4a}\)) could not be determined by the potentiometric method and were not used in the calculations.

The concentration distribution diagram of gallic acid (Fig. 1) shows that the gallic acid forms the \(\text{H}_3\text{G}^-\) species up to pH 6.0. Above pH 6.0, the concentration of this species decreases, and \(\text{H}_2\text{G}_2^+\) species, starts to form and reaches its maximum concentration of 99% at pH > 10.0. The \(\text{H}_2\text{G}^-\) and \(\text{H}_2\text{G}_2^+\) species are predominant in the pH range of 4–10.

### 3.2. Binary metal complex systems

Potentiometric pH-metric titrations of Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\), and Zn\(^{2+}\) metal ions with the investigated ligands were performed according to the procedures described in the experimental section. A representative set of potentiometric pH-metric titration curves for the Cu\(^{2+}\)- tartaric acid + gallic acid system are displayed in Fig. 2. Analyses of the complexed ligands curves indicate that the addition of metal ion to the free ligand solutions shifts the buffer regions of the ligands to lower pH values (curves 3 and 5). This shows that complex formation reactions proceed by releasing of protons from such ligands as shown for gallic acid Eqs. (11) and (12) and carboxylic acids Eqs. (13) and (14):

\[ \text{M}^{2+} + \text{H}_4\text{G} = \text{M(HG)}^- + 3\text{H}^+ \]  \hspace{1cm} (11)

\[ \text{M(HG)}^- + \text{H}_4\text{G} = \text{M(HG)}_2^- + 3\text{H}^+ \]  \hspace{1cm} (12)

\[ \text{M}^{2+} + \text{H}_2\text{A} = \text{MA} + 2\text{H}^+ \]  \hspace{1cm} (13)

\[ \text{MA} + \text{H}_2\text{A} = \text{MA}_2^2^- + 2\text{H} \]  \hspace{1cm} (14)

The binary complexes observed for gallic acid begin to form in the pH range of 3.5–8.2. With respect to the titration curves of the binary metal ion/carboxylic acid complexes, one may deduce that these complexes start to form in the pH range 2.8–4.3. These values obtained from the appearance of a divergence of the binary complex titration curves from that of the free ligands. The stability constants of 1:1 and 1:2 binary complexes of gallic acid have been determined in an aqueous medium at \(25^\circ \text{C}\) and \(I = 0.10 \text{ mol dm}^{-3} \text{NaNO}_3\) (Tables 3–6). The stability constants of 1:1 and 1:2 binary complexes of investigated aliphatic dicarboxylic acids were determined in aqueous medium at \(25^\circ \text{C}\) and \(I = 0.10 \text{ mol dm}^{-3} \text{NaNO}_3\) (Tables 3–6). It is observed that the stability constants of the different 1:2 metal-ligand complexes are lower than the corresponding 1:1 systems (Tables 3–6), as expected from the statistical considerations (Martin and Prados, 1974). This is the normal trend in neutral ligands where the enthalpy is more favorable for a 1:1 species (exothermic) as compared to a 1:2 species and thus, for stepwise coordination in the binary complexes of the investigated ligands, the entropy contribution to the free energy change becomes less favorable from one coordination step to the next.
Examination of the stability constants of the binary complexes (Tables 3-6) reveals the following:

a) Stabilities of the 1:1 binary complexes for all investigated ligands are higher than the corresponding 1:2 binary ones.

b) Normal 1:1 and 1:2 binary complexes of gallic acid are formed with all the metal ions studied.

c) The order of stability of the 1:1 binary complexes of all investigated ligands with respect to the divalent transition metal ions studied follows the Irving–Williams series Zn < Cu > Ni > Co (Irving and Williams, 1948).

d) Stabilities of the 1:1 binary metal-complexes of aliphatic dicarboxylic acids follows their basicities (pK_{a1} + pK_{a2}).

### 3.3. Formation of ternary complexes

For the formation of the ternary complexes of the selected bivalent metal ions in presence of gallic acid (secondary ligand = G) and aliphatic dicarboxylic acid (primary ligand = A), the following equilibria may be considered Eqs. (15) and (16)):
Stability constants for Zn\(^{2+}\) binary and ternary complexes in aqueous media at 25.0 ± 0.1 °C and I = 0.1 mol dm\(^{-3}\) NaNO\(_3\),

<table>
<thead>
<tr>
<th>Ligands</th>
<th>pK(_a)s of Ligands</th>
<th>K(_{MAG})</th>
<th>K(_{MA})</th>
<th>(\Delta) log K</th>
<th>% R.S.</th>
<th>log X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid</td>
<td>4.12 ± 0.01</td>
<td>6.75 ± 0.01</td>
<td>15.08</td>
<td>1.49</td>
<td>15.28</td>
<td>7.51</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>3.84 ± 0.04</td>
<td>2.29 ± 0.04</td>
<td>13.30</td>
<td>1.35</td>
<td>13.85</td>
<td>6.10</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>3.20 ± 0.02</td>
<td>–</td>
<td>17.57</td>
<td>1.20</td>
<td>17.31</td>
<td>5.81</td>
</tr>
<tr>
<td>Malic acid</td>
<td>6.80 ± 0.05</td>
<td>10.95 ± 0.02</td>
<td>15.60</td>
<td>1.03</td>
<td>15.56</td>
<td>5.61</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>4.82 ± 0.05</td>
<td>3.77 ± 0.05</td>
<td>10.78 ± 0.01</td>
<td>1.50</td>
<td>10.56</td>
<td>5.21</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>4.08 ± 0.05</td>
<td>2.82 ± 0.05</td>
<td>14.78</td>
<td>0.50</td>
<td>9.74</td>
<td>6.16</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>6.96 ± 0.03</td>
<td>5.70 ± 0.03</td>
<td>17.59</td>
<td>0.88</td>
<td>9.02</td>
<td>6.02</td>
</tr>
<tr>
<td></td>
<td>4.66 ± 0.02</td>
<td>4.06 ± 0.02</td>
<td>15.09</td>
<td>0.68</td>
<td>6.97</td>
<td>4.86</td>
</tr>
</tbody>
</table>

Here complex formation is considered to take place in a stepwise manner. Therefore, it is assumed that, in the presence of both ligands, the aliphatic dicarboxylic acid (A) interacts first with the metal ion forming a 1:1 MA binary complex which is then followed by the interaction of the algalic acid (G), i.e., stepwise manner. The overall stability constant \(\beta\)\(^M\) may be represented by Eq. (17):

\[
\text{M} + \text{A} = \text{MA}, \quad K_{MA} = \frac{[\text{MA}]}{[\text{M}] [\text{A}]} \quad (15)
\]

\[
\text{MA} + \text{G} = \text{MAG}, \quad K_{MAG} = \frac{[\text{MAG}]}{[\text{MA}] [\text{G}]} \quad (16)
\]

The \(\beta\)\(^M\) constant expresses the stability of the mixed-ligand species; it does not represent the binding strength between G and M\(^{2+}\) ions directly in the presence of A. This effect is much better reflected by the equilibrium constant, \(K_{MA} K_{MAG}\) calculated according to Eq. (18):

\[
\log K_{MA} = \log \beta_{MA} - \log K_{MA} \quad (18)
\]

This latter reaction constant (the reaction is shown as in eq. (11)) indicates how tightly G is bound to the simple MA binary complex.

Based on the ternary complexes stability constant values, the following conclusions could be drawn:

<table>
<thead>
<tr>
<th>System</th>
<th>log (K_1)</th>
<th>log (K_2)</th>
<th>log (K_{MAG})</th>
<th>log (\beta_{MAG})</th>
<th>(\Delta) log K</th>
<th>% R.S.</th>
<th>log X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid (G)</td>
<td>8.90 ± 0.01</td>
<td>5.50 ± 0.01</td>
<td>12.71</td>
<td>1.17</td>
<td>14.62</td>
<td>6.10</td>
<td></td>
</tr>
<tr>
<td>Adipic acid</td>
<td>3.54 ± 0.04</td>
<td>2.28 ± 0.04</td>
<td>9.17 ± 0.03</td>
<td>12.23</td>
<td>10.64</td>
<td>4.95</td>
<td></td>
</tr>
<tr>
<td>Succinic acid</td>
<td>3.17 ± 0.02</td>
<td>–</td>
<td>9.06 ± 0.02</td>
<td>12.23</td>
<td>10.64</td>
<td>4.95</td>
<td></td>
</tr>
<tr>
<td>Malic acid</td>
<td>4.63 ± 0.05</td>
<td>–</td>
<td>8.89 ± 0.02</td>
<td>13.52</td>
<td>11.12</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Maleic acid</td>
<td>3.93 ± 0.05</td>
<td>2.92 ± 0.05</td>
<td>8.72 ± 0.02</td>
<td>12.65</td>
<td>9.00</td>
<td>4.95</td>
<td></td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>3.68 ± 0.05</td>
<td>2.82 ± 0.05</td>
<td>8.64 ± 0.03</td>
<td>12.32</td>
<td>8.00</td>
<td>4.64</td>
<td></td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>4.67 ± 0.03</td>
<td>3.88 ± 0.03</td>
<td>8.56 ± 0.02</td>
<td>13.23</td>
<td>7.00</td>
<td>4.41</td>
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</tr>
<tr>
<td></td>
<td>3.46 ± 0.02</td>
<td>2.96 ± 0.02</td>
<td>8.38 ± 0.02</td>
<td>11.84</td>
<td>4.75</td>
<td>3.76</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System</th>
<th>log (K_1)</th>
<th>log (K_2)</th>
<th>log (K_{MAG})</th>
<th>log (\beta_{MAG})</th>
<th>(\Delta) log K</th>
<th>% R.S.</th>
<th>log X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid (G)</td>
<td>8.56 ± 0.01</td>
<td>5.83 ± 0.01</td>
<td>13.87</td>
<td>1.90</td>
<td>22.19</td>
<td>7.59</td>
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<tr>
<td>Adipic acid</td>
<td>3.41 ± 0.02</td>
<td>2.35 ± 0.02</td>
<td>10.46 ± 0.02</td>
<td>13.87</td>
<td>17.09</td>
<td>6.26</td>
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</tr>
<tr>
<td>Succinic acid</td>
<td>3.06 ± 0.02</td>
<td>–</td>
<td>10.34 ± 0.03</td>
<td>13.40</td>
<td>20.79</td>
<td>6.07</td>
<td></td>
</tr>
<tr>
<td>Malic acid</td>
<td>3.18 ± 0.02</td>
<td>–</td>
<td>10.19 ± 0.02</td>
<td>13.37</td>
<td>19.04</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Maleic acid</td>
<td>2.98 ± 0.03</td>
<td>2.33 ± 0.04</td>
<td>10.02 ± 0.01</td>
<td>13.00</td>
<td>16.70</td>
<td>6.03</td>
<td></td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>3.40 ± 0.05</td>
<td>2.45 ± 0.05</td>
<td>9.95 ± 0.03</td>
<td>13.35</td>
<td>16.24</td>
<td>6.26</td>
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</tr>
<tr>
<td>Oxalic acid</td>
<td>3.81 ± 0.03</td>
<td>2.75 ± 0.03</td>
<td>9.88 ± 0.02</td>
<td>13.69</td>
<td>15.42</td>
<td>6.13</td>
<td></td>
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<tr>
<td></td>
<td>3.03 ± 0.02</td>
<td>2.47 ± 0.02</td>
<td>9.68 ± 0.02</td>
<td>12.71</td>
<td>13.08</td>
<td>5.53</td>
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</tr>
</tbody>
</table>
Table 6—Stability constants for Co²⁺ binary and ternary complexes in aqueous media at 25.0 ± 0.1 °C and I = 0.1 mol dm⁻³ NaNO₃.

<table>
<thead>
<tr>
<th>System</th>
<th>log K₁</th>
<th>log K₂</th>
<th>log KMA₂</th>
<th>log KMG₂</th>
<th>Δ log K</th>
<th>% R.S.</th>
<th>log X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid (G)</td>
<td>7.25 ± 0.01</td>
<td>4.75 ± 0.01</td>
<td>7.99 ± 0.01</td>
<td>11.3</td>
<td>0.74</td>
<td>10.21</td>
<td>5.10</td>
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<tr>
<td>Adipic acid</td>
<td>3.31 ± 0.02</td>
<td>2.19 ± 0.02</td>
<td>7.88 ± 0.03</td>
<td>10.85</td>
<td>0.63</td>
<td>8.69</td>
<td>—</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>2.97 ± 0.02</td>
<td>—</td>
<td>7.73 ± 0.02</td>
<td>10.75</td>
<td>0.48</td>
<td>6.62</td>
<td>—</td>
</tr>
<tr>
<td>Malic acid</td>
<td>3.12 ± 0.05</td>
<td>—</td>
<td>7.54 ± 0.01</td>
<td>10.48</td>
<td>0.29</td>
<td>4.00</td>
<td>3.74</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>2.94 ± 0.03</td>
<td>2.28 ± 0.03</td>
<td>7.45 ± 0.03</td>
<td>10.53</td>
<td>0.20</td>
<td>2.76</td>
<td>3.70</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>3.15 ± 0.03</td>
<td>2.37 ± 0.03</td>
<td>7.38 ± 0.03</td>
<td>10.43</td>
<td>0.13</td>
<td>1.79</td>
<td>3.44</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>2.88 ± 0.02</td>
<td>2.38 ± 0.02</td>
<td>7.17 ± 0.02</td>
<td>10.05</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

(a) Stabilities of ternary complexes with respect to the aliphatic dicarboxylic acids follow the order: adipic > succinic > maleic > malonic > tartaric > oxalic; this behavior can be explained in terms of the decrease in basicity of the aliphatic dicarboxylic acids in the same direction.

(b) The complex stability of the ternary complexes with respect to the metal ion present follows the Irving–Williams series.

(c) The stabilities of the ternary complexes are higher than the 1:1 binary complexes of the corresponding aliphatic dicarboxylic acid or gallic acid for all systems studied; this behavior can be attributed to some cooperative interactions between the carboxylic acid and gallic acid in the ternary complex such as H-bond formation.

Different methods are used to estimate the formation and the relative stability of the different ternary complexes formed in solution (Martin and Prados, 1974). In most cases, the relative stability of the mixed-ligand species [MAG] is expressed in terms of the Δ log K parameter (the constant due to the equilibrium [MA] + [MG] = [MAG] + [M]), which is a way to characterize the tendency toward formation of mixed-ligand complexes.

\[ \Delta \log K = \log K_{\text{MAG}}^{\text{b}} - \log K_{\text{MAG}}^{\text{c}} \]  
\[ \text{(19)} \]

The Δ log K expresses the effect of the bounded primary ligand (A) towards an incoming secondary ligand (G). The positive Δ log K values obtained (Tables 3–6) for ternary systems indicate favored formation of the ternary complexes over the corresponding binary ones. This can be ascribed to interligand interactions or some cooperation between the primary and secondary ligands such as H-bond formation.

Another parameter, percent relative stabilization (% R.S.), to quantify stability of a ternary complex is defined by Eq. (19) as:

\[ \% \text{ R.S.} = \left( \frac{\log K_{\text{MAG}}^{\text{b}} - \log K_{\text{MAG}}^{\text{c}}}{\log K_{\text{MAG}}^{\text{c}}} \right) \times 100 \]  
\[ \text{(20)} \]

and its values obtained (Tables 3–6) agree well with the Δ log K values. A third parameter known as log X, is frequently used to characterize the stability of ternary or mixed-ligand complexes. It measures the tendency of 1 mol each of the binary complexes MA₂ and MG₂ to disproportionate forming 2 mol of MAG as follows Eq. (21):

\[ \text{MA}_2 + \text{MG}_2 \rightleftharpoons 2\text{MAG}, \quad X = \frac{[\text{MAG}]^2}{[\text{MA}_2][\text{MG}_2]} \]  
\[ \text{(21)} \]

It is therefore calculated according to Eq. (21):

\[ \log X = 2 \log \beta_{\text{MAG}} - (\log \beta_{\text{MA}_2} + \log \beta_{\text{MG}_2}) \]  
\[ \text{(22)} \]

The value of the constant log X expected on statistical ground is 4. Whenever it deviates from this value, it must be the result of interligand electronic and/or steric interactions (Laurie and James, 1983). The log X values were calculated (Tables 3–6) and the results showed that the values are always greater than the statistically expected ones.

Estimation of the concentration distribution of various complex species in solution provides a useful picture of metal ion binding in biological systems. A species distribution diagram obtained for Cu²⁺ + tartaric acid + gallic acid systems (Fig. 3), shows that the formation of CuA₂ starts at pH < 3, reaches a maximum concentration (30% total Cu²⁺) at pH 4.0 and decreases to a minimum when MA₂ becomes predominant. Above pH 4.0, CuA₂ is predominant. Above pH 6.0, CuHG species starts to form. The maximum concentration of Cu(HG)₂ is less than 5% total Cu²⁺ in solution and is omitted from the curve. Beyond pH 8.0, CuA(HG) ternary species starts to form on the expense of CuHG binary species. The concentration distribution of various complex species existing in solution as a function of pH was obtained using the SPECIES program (Gans and Vacca, 1974).

3.4. Conductometric measurements

The conductometric titrations have been investigated to indicate the complexion behavior of ternary systems studied in solution. The conductometric titration curve for the ternary complex of Cu²⁺ with gallic acid and malic acid is displayed in Fig. 4. The titration curve shows an initial decrease and an inflection at a = 2 (a = moles of base added per mole of ligand), which probably corresponds to the neutralization of H⁺ ions resulting from the formation of the Cu²⁺ + malic acid binary complex. Between 2 < a < 4, the conductance increases slightly due to the formation of the ternary complex and is associated with the release of two protons from the secondary ligand (gallic acid). Beyond a = 4, the conductance increases more uniformly due to excess NaOH.

4. Conclusion

This study offers an intensive investigation on stoichiometries and stabilities associated with binary and ternary complex systems studied in aqueous solutions. The complexion
behavior of Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, and Co$^{2+}$ with gallic acid and the biologically abundant aliphatic dicarboxylic acids shows the formation of ternary complexes in a stepwise manner in aqueous media. The complex formation equilibria were investigated to ascertain the composition and to determine the stability constants of the formed binary and ternary complexes. The concentration distribution diagrams of ligands and different binary and ternary complexes formed were evaluated. The potentiometric technique was used to obtain reliable formation constant values for different complexes formed and to validate the speciation models for both the ligands and complexes studied. The mode of chelation of the ternary complexes was ascertained by conductometric titration technique. The ternary complexes formed may have interesting biological activity and more research work need to be conducted by biologists.

References


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