CONDUCTOMETRIC INVESTIGATION OF MAGNESIUM (II), CALCIUM (II) AND BARIUM (II) COMPLEXES IN AQUEOUS SOLUTION

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Abstract

The ionic association constants, $K_A$, of Mg, Ca and Ba metal ions with succinate, malate and tartrate ligands were conductometrically determined in water at 25–40°C. The conductometric data were analysed by the Shedlovsky extrapolation method. The $K_A$ values tend to decrease with the cation size in the order Ca > Ba for all the salts under study with the exception of Mg salts, whereas the $K_A$ values for the ligands increase in the order succinate < malate < tartrate. For the salts under study, standard thermodynamic functions, $\Delta H^\circ$ and $\Delta S^\circ$ for the association were evaluated and discussed. The positive values of both $\Delta H^\circ$ and $\Delta S^\circ$ in all the systems indicate the ionic association processes are the reactions of unfavorable enthalpy and favorable entropy changes in aqueous solution. The thermodynamic metal gradient, $\beta$, was evaluated and its significance of ion association of all salts under investigation was discussed. On the other hand, the results of limiting molar conductance, $\Lambda_m$, are discussed on the light of Walden product.

Key words: conductivity, association constant, alkaline–earth metal, succinate, malate, tartrate, aqueous solution.

Introduction

Several experimental techniques have been applied to study the thermodynamic and various interactions in electrolytic solutions.1–8 Ion pairing between the metal ions and ligands has usually investigated by means of conductance technique.9–11 However, there were no available cited recent studies in the literature concerning the association of the bivalent cations with bivalent organic ligands. Here, the conductometric technique was applied to study the association of Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ metal ions with some aliphatic bivalent organic ligands (succinate, malate and tartrate) in aqueous solution at 25–40°C. The conductance data were treated using the Shedlovsky extrapolation method.12 These results were discussed in terms of the
association constants and also the approach of linear Gibbs energy relationship, LGER\(^{13}\) can be applied to the association process at various temperatures to discuss the thermodynamic features of metal–ion complexes.

Also, the thermodynamic parameters \(\Delta G^\circ\), \(\Delta H^\circ\) and \(\Delta S^\circ\) were evaluated by investigating the process over a certain temperature range. In addition, Walden product was derived and discussed.

**Experimental**

**Materials**
All the salts used in our study were either Prolabo grade or Merck grade. The conductivity water was redistilled twice and deionized by passing through a column containing mixed resin (anion–cation exchangers). The specific conductances of this conductivity water were 0.90 x 10\(^{-6}\), 1.00 x 10\(^{-6}\), 1.10 x 10\(^{-6}\) and 1.25 x 10\(^{-6}\) Scm\(^{-1}\) at 25, 30, 35 and 40°C, respectively.

**Solutions**
The solutions were made by dissolving the suitable weight of each salt in the conductivity water just before conductivity measurements. The exact molarities of stock solutions were standardized by titration with EDTA. The solutions of any desired concentrations were prepared by using an appropriate dilution. The molar concentrations of the measured solutions were within the range (1.5 – 6.0) x 10\(^{-3}\) mol dm\(^{-3}\).

**Equipment**
The conductivity measurements were carried out by means of a digital conductivity meter model 72 out fit with an accuracy of \(\pm 0.5\%\) in the range (1x10\(^{-6}\) – 1.0) \(\Omega\) \(^{-1}\) using a dip type immersion cell which was calibrated with a cell constant of 1.00 cm\(^{-1}\).

The measurements were done at 25, 30, 35 and 40°C, utilizing a thermostated circulator water bath (LKB Bromma Multitemp.) supplied with a refrigeration unit. The accuracy of the temperature measurements was \(\pm 0.005\)°C. Due correction was made for the specific conductance of the solvent.
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Results and Discussion

Analysis of conductivity data

In our solutions, the association of $M^{2+}$ ($Mg^{2+}$, $Ca^{2+}$ and $Ba^{2+}$) with $L^{2-}$ (succinate, malate and tartrate) ligands is considered for the ionic equilibrium,

$$
L^{2-} + M^{2+} \rightarrow M^{2+}L^{2-}
$$

(1)

Therefore, the association constants, $K_A$, were computed from the conductivity data on the basis of the Shedlovsky extrapolation method. This method consists of plotting $\frac{1}{\Lambda S(Z)}$ vs. $(C\Lambda S(Z) f^2_\pm)$ according to the function,

$$
\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_o} + \frac{C\Lambda S(Z)}{\Lambda_o^2} f^2_\pm K_A
$$

(2)

where $S(Z) = \left[ \frac{Z}{2} + \left( 1 + \left( \frac{Z}{2} \right)^2 \right)^{0.5} \right]^2$

and $Z$ is defined by $Z = \frac{S(C\Lambda)^{0.5}}{\Lambda_o^{1.5}}$ the values of $S$ and $C$ represent the limiting law slope and the molar concentration of the electrolyte, respectively. Also, $f^2_\pm$, $\Lambda_o$ and $K_A$ are a mean molar activity coefficient, a limiting molar conductivity and an association constant, respectively.

The mean molar activity coefficient was calculated by the following Debye – Hückel equation,

$$
\text{Log} \ f^2_\pm = - \frac{\Lambda \sqrt{YC}}{1 + Ba \sqrt{YC}}
$$

(3)

Where $A$ and $B$ are constants, $a$ is the distance of closest approach [ion size parameter which represents the sum of ionic radii ($r_+ + r_-$)] and $\gamma$ is the degree of dissociation in the mass action equation,

$$
K_A = \frac{(1 - \gamma)}{C\gamma^2 f^2_\pm}
$$

(4)
Where it is assumed that the activity coefficient for the neutral ion–pair equals to unity. The degree of dissociation $\gamma$ is correlated with the Shedlovsky function by the equation,

$$\gamma = \frac{\Lambda}{\Lambda_o} S(Z)$$  \hspace{1cm} (5)

A set of parameters $\Lambda_o$ and $K_A$ were calculated from the intercept and slope of the straight line on the plot of $\frac{1}{\Lambda S(Z)}$ vs. $C \Lambda S(Z) f_{\pm}^2$. The above procedures were solved by a C2+ computer program, where an initial value of $\Lambda_o$ was calculated from Arrhenius – Ostwald relation $[(S(Z) = f_{\pm} = 1)$ in equation (2)] by the least squares analysis and the iterations were continued until the error in $\Lambda_o$ became less than $1 \times 10^{-3}$. The values of $\Lambda_o$ and $K_A$ are cited in Tables (1 – 3). It is clearly desirable to evaluate the standard enthalpy change, $\Delta H^o$, by investigating the $K_A$ over a temperature range using the van't Hoff's isochore:

$$\frac{d(\ln K_A)}{dT} = \frac{\Delta H^o}{RT^2}$$  \hspace{1cm} (6)

then,

$$\ln K_A = -\frac{\Delta H^o}{RT} + \text{constant}$$  \hspace{1cm} (7)

Where $\log K_A$ values were plotted against $T^{-1}$, giving a straight line with a slope equals $-\frac{\Delta H^o}{2.303R}$. Thus, the standard enthalpy changes, $\Delta H^o$, can be determined. The standard Gibbs free energy changes, $\Delta G^o$, can be evaluated from

$$\Delta G^o = -RT \ln K_A$$  \hspace{1cm} (8)

Similarly, the standard entropy changes, $\Delta S^o$, can be calculated from,

$$\Delta S^o = \frac{(\Delta H^o - \Delta G^o)}{T}$$  \hspace{1cm} (9)

The values of $\Delta H^o$ and $\Delta S^o$ are reported in Table 4.

From Tables (1 – 3), the limiting molar conductances, $\Lambda_o$, of some alkaline – earth metal salts were found to increase as the size of the cation increases. The results show that conductance of $\text{Mg}^{2+}$ ion is much lower due to greater interaction between the charge on the ion and the dipoles of the adjacent solvent molecules, which leads to a reduction in its mobility. It is generally accepted that larger alkaline – earth metal ions possess an excess mobility in aqueous solution owing to their
ability to break hydrogen bonds in their immediate vicinity and thereby reduce the 
local viscosity. However, the Walden products, $15 \Lambda_o \eta$, share a common 
characteristic, the $\Lambda_o \eta$ values for $M^{2+}L^{2-}$ decrease with an increase in temperature 
from 25 to 40°C. This shortage in $\Lambda_o \eta$ is very low, i.e. 1.05% on going from 25 to 
40°C. So, this trend in the Walden products can be interpreted by the following 
function;

$$\frac{d (\Lambda_o \eta)}{dT} = 1.05 \frac{d \Lambda_o}{dT}$$ (10)

This decrease in $\Lambda_o \eta$ with temperature, which is often found in aqueous solutions 
may be due to a thermal expansion of the solvent sheath, i.e. the expansion of a 
solvated ion, because of the activation of solvent molecules forming the sheath. $^{15-16}$

The $\Lambda_o$ values for the ligands decrease in the order tartrate > malate > succinate, 
i.e., as the number of –OH groups of the ligand increases, the $\Lambda_o$ values increase. 
On the other hand, the $K_A$ values for the malate and tartrate salts are in order of Mg 
< Ca < Ba. This trend may be due to ion–pairing can occur through the immediate 
vicinity of solvent molecules, causing greater association. However, the $K_A$ values 
for the succinate salts decrease in the order Mg > Ca > Ba.

This greater stability of $Mg^{2+}$ ion pairs in comparison with $Ba^{2+}$ is as a result of a 
favorable enthalpy term; the enthalpies (Table 4) increase as the atomic number 
decreases; i.e. in the order Mg > Ca > Ba. It has been found that there is a close 
relationship between the $K_A$ values and the strength of salvation of $M^{2+}$; i.e. the 
weaker $M^{2+}$ is solvated, the stronger the association between $M^{2+}$ and the ligand $L^{2-}$ 
becomes in aqueous solutions and thus causing an increase in both $\Delta H^o$ and $\Delta S^o$. So, 
the values of $\Delta H^o$ and $\Delta S^o$ were found to be positive (Table 4).

As a result of ion – pairing occurs with the hydrated cations, where the solvent is 
more easily arranged around the smallest ions resulting in a decrease in the 
enthalpies as the ion size increases. Consequently, an increase in the disorder of the 
system was found due to the loss of hydration process.

Thus, with smaller cations, the entropy changes will be greater. It is clear that $\Delta S^o$ 
values increase with the increase of the number of the –OH groups of the ligand in the 
order succinate < malate < tartrate.
Similarly, the association of ligands increase in the order succinate < malate < tartrate which may arise from excess hydroxyl groups which are capable to form greater chelation with alkaline – earth metal cations causing greater association in the order tartrate > malate > succinate. Also, the association constants increase as the temperature increase for all the salts under study indicating that all the association processes are endothermic.

Further, the Fuoss equation is given by

$$K_F = \frac{4\pi N_A a^3}{3000} \exp (b),$$

(11)

Where,

$$b = \frac{|Z_1Z_2|e^2}{aDKT}$$

$N_A$ is Avogadro's number and $a$ is the ion size parameter which represents the sum of ionic radii ($r_+ + r_-$) which is evaluated from the slope of the plot of log $K_A$ vs $\frac{1}{D}$ (Fig.1), and its values are cited in Tables (1 – 3).

Eqn. (11) gives the effect of dielectric constant ($D$) of the medium on the ion – pair association constant ($K_F$) of an electrolyte. A linear relationship is observed for all the systems under study from the plot as the Fuoss theory predicted indicating the absence of specific ion-solvent interactions or the absence of preferential salvation of the ions by aqueous solution. This may be attributed to the existence of strong interactions between the cation and anion of the electrolyte. So, this linearity indicates ion – ion interactions.

Besides, another approach can be applied concerning with the linearity between the protonation constants of the derivatives of selected reference compounds and the corresponding stability constants of their derivatives with a metal (Linear Gibbs energy relationship, LGER) which was discussed by Neiboer et al using the following equation whose parameters have their usual significance,

$$\log K_{ML} = B \log K_{MSL} + (\log K_{MLo} - B \log K_{MSLo})$$

(12)

Eqn. (12) can be replaced by,

$$\Delta G_{ass} = \beta \Delta G_{prot} + (\Delta G_{ass}^O - \beta \Delta G_{prot}^O)$$

(13)
where $\Delta G_{\text{ass}}$, $\Delta G_{\text{prot}}$, $\Delta G_{\text{ass}}^0$, $\Delta G_{\text{prot}}^0$ and $\beta$ are the Gibbs energy of the association process at various temperatures, $\Delta G_{\text{prot}}$ is the Gibbs energy of the protonation process at any temperature, $\Delta G_{\text{ass}}^0$ is the standard Gibbs energy of the complexation process at 25°C, $\Delta G_{\text{prot}}^0$ is the standard Gibbs energy of the protonation process at 25°C and $\beta$ is the rate of change in the Gibbs energy of association in a series of complexes (the thermodynamic metal gradient). ML at various temperatures. Eqn. (13) can be written as

$$\Delta G_{\text{ass}} = \beta \Delta G_{\text{prot}} + R \quad (14)$$

For the salts under investigation, the $\beta$ values are positive (Table 5) indicating that the change in $\Delta G_{\text{ass}}$ is directly proportional to $\Delta G_{\text{prot}}$. The $\beta$ values decrease in the order Ba > Ca > Mg for succinate salts confirming that the Gibbs energy for MgL is the lowest, whilst for BaL is the highest. However, there is no obvious trend for the other two ligands. The plot of $\Delta G_{\text{ass}}$ against $\Delta G_{\text{prot}}$ for succinate salts is linear with slope $\beta$ (Fig. 2). On the other hand, the $\beta$ values decrease in the order tartrate > malate > succinate for the metal ions under study. Consequently, the rate of $\Delta G_{\text{ass}}$ and $\Delta G_{\text{prot}}$ is smaller where the association process occurs spontaneously in the order tartrate > malate > succinate.

**Table 1: Conductance Parameters for Succinate Salts in Water at Different Temperatures**

<table>
<thead>
<tr>
<th>Metal</th>
<th>T/K</th>
<th>$\Lambda_a$ Scm$^2$mol$^{-1}$</th>
<th>$K_A$ dm$^3$mol$^{-1}$</th>
<th>$\Lambda_\eta$ Scm$^2$mol$^{-1}$</th>
<th>$\alpha / A^o$</th>
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Table 3: Conductance Parameters for Tartrate Salts in Water at Different Temperatures

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<th>$\Lambda_0$ S cm$^{-2}$ mol$^{-1}$</th>
<th>$\kappa_0$ cm$^{-2}$ mol$^{-1}$</th>
<th>$\Lambda_0\eta$ S cm$^{-2}$ mol$^{-1}$ cp</th>
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Table 5: Values of The Thermodynamic Metal Gradient, $\beta$, for Metal Salts

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CONDUCTOMETRIC INVESTIGATION OF MAGNESIUM (II),

Fig. 1: $\log K_A$ vs $1/D$ for the metal salts in aqueous solution at various temperatures.

Fig. 2: $-\Delta G_{\text{ass}}$ vs. $-\Delta G_{\text{prot}}$ plots for the metal (II) succinates at various temperatures.

References


