

Investigation of Magnesium (II), Calcium (II) and Barium (II) Complexes in Aqueous Solution

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دراسة توصيلية لمتراكبات المغنيسيوم والكالسيوم والباريوم الثنائي في المحلول المائي

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تم تعيين ثوابت التجمع الأيوني (K_A) لأيونات فلز المغنيسيوم والكالسيوم والباريوم مع ليجندات السكسينات والمالات والطرترات، وذلك باستخدام طريقة التوصيل في الماء عند درجة حرارة 25-40°م. عند تحليل نتائج التوصيل بطريقة شيدلوفسكي الاستقرائية، وجد أن قيم K_A تميل لأن تقل مع حجم الكاتيون بالتسلسل: الكالسيوم < الباريوم لكل الأملاح تحت الدراسة باستثناء أملاح المغنيسيوم، في حين أن قيم K_A تتزايد لليجندات بالتسلسل: السكسينات > المالات > الطرترات. وبالنسبة للأملاح قيد الدراسة، فقد تم تعيين ودراسة دوال الديناميكا الحرارية القياسية ΔH° ، ΔS° لعمليات التجمع. وتشير القيم الموجبة لكل من ΔH° و ΔS° في كل الأنظمة إلى أن عمليات التجمع الأيوني هي تفاعلات محببة لتغيرات الانتروبي وغير محببة لتغيرات الأنتالبي في المحلول المائي. أيضا تم تعيين درجة الميل الديناميكي الحراري للفلز β ، ونوقشت دلالتها للتجمع الأيوني لكل الأملاح تحت الدراسة. من الناحية الأخرى، تمت مناقشة نتائج التوصيل المولاري عند تخفيف لانتهائي Λ_0 في ضوء حاصل فالدن.

Keywords: conductivity, association constant, alkaline-earth metal, succinate, malate, tartrate, aqueous solution.

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, ΔH° and ΔS° for the association, were evaluated and discussed. The positive values of both ΔH° and ΔS° 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, β , 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, Λ_o , are discussed on the light of Walden product.

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 ΔG° , ΔH° and ΔS° 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 0.90×10^{-6} , 1.00×10^{-6} , 1.10×10^{-6} and $1.25 \times 10^{-6} \text{ Scm}^{-1}$ 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 $(1.5-6.0) \times 10^{-3} \text{ mol dm}^{-3}$.

Equipment

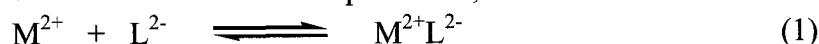
The conductivity measurements were carried out by means of a digital conductivity meter model 72 out fit with an accuracy of $\pm 0.5\%$ in the range $(1 \times 10^{-6} - 1.0) \Omega^{-1}$ using a dip type immersion cell which was calibrated with a cell constant of 1.00 cm^{-1} .

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 $\pm 0.005^\circ\text{C}$. Due correction was made for the specific conductance of the solvent.

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,



Then, the association constants, K_A , were computed from the conductivity data on the basis of the Shedlovsky extrapolation method [12]. This method consists of plotting $(\frac{1}{\Lambda S_{(Z)}})$ vs. $(C\Lambda S_{(Z)} f_{\pm}^2)$

according to the function,

$$\frac{1}{\Lambda S_{(Z)}} = \frac{1}{\Lambda_0} + \frac{C\Lambda S_{(Z)} f_{\pm}^2 K_A}{\Lambda_0^2} \quad (2)$$

where $S_{(Z)} = [\frac{Z}{2} + (1 + (\frac{Z}{2})^2)^{0.5}]^2$ and Z is defined by $Z = \frac{S(C\Lambda)^{0.5}}{\Lambda_0^{1.5}}$.

The values of S and C represent the limiting law slope and the molar concentration of the electrolyte, respectively. Also, f_{\pm}^2 , Λ_0 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 Debye-Hückel equation [14]

$$\log f_{\pm}^2 = -\frac{A\sqrt{\gamma C}}{1 + Ba\sqrt{\gamma C}} \quad (3)$$

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 γ is the degree of dissociation in the mass action equation

$$K_A = \frac{(1 - \gamma)}{C\gamma^2 f_{\pm}^2} \quad (4)$$

where it is assumed that the activity coefficient for the neutral ion-pair is equal to unity. The degree of dissociation γ is correlated with the Shedlovsky function by the equation

$$\gamma = \frac{\Lambda}{\Lambda_0} S(Z) \quad (5)$$

A set of parameters Λ_0 and K_A were calculated from the intercept and slope of the straight line on the plot of $\frac{1}{\Lambda S_{(Z)}} \text{ vs. } \text{CAS}_{(Z)} f_{\pm}^2$. The above procedures [11] were solved by a C2+ Computer program, where an initial value of Λ_0 was calculated from Arrhenius-Ostwald relation [12] [$(S_{(Z)} = f_{\pm} = 1)$ in equation (2)] by the least squares analysis and the iterations were continued until the error in Λ_0 became less than 1×10^{-3} . The values of Λ_0 and K_A are cited in Tables (1 – 3). It is clearly desirable to evaluate the standard enthalpy change, ΔH° , by investigating the K_A over a temperature range using the van't Hoff's isochore

$$\frac{d(\ln K_A)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (6)$$

Then

$$\ln K_A = \frac{-\Delta H^\circ}{RT} + \text{constant} \quad (7)$$

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

$$\Delta G^\circ = -RT \ln K_A \quad (8)$$

Similarly, the standard entropy changes, ΔS° , can be calculated from

$$\Delta S^\circ = \frac{(\Delta H^\circ - \Delta G^\circ)}{T} \quad (9)$$

The values of ΔH° and ΔS° are reported in Table 4.

From Tables (1–3), the limiting molar conductances, Λ_0 , of some alkaline–earth metal salts were found to increase as the size of the cation increases. The results show that conductance of 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 $\Lambda_0 \eta$ [15] share a common characteristic, the $\Lambda_0 \eta$ values for $\text{M}^{2+} \text{L}^{2-}$ decrease with an increase in temperature from 25 to 40°C. This shortage in $\Lambda_0 \eta$ 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

$$\frac{d(\Lambda_0 \eta)}{dT} = 1.05 \frac{d\Lambda_0}{dT} \quad (10)$$

This decrease in $\Lambda_0 \eta$ 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 Λ_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 Λ_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 solvation 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 ΔH° and ΔS° . So, the values of ΔH° and ΔS° 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 ΔS° 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 [17] is given by

$$K_F = \frac{4\pi N_A a^3}{3000} \exp(b), \quad (11)$$

where $b = |Z_1 Z_2| e^2 / aDKT$, N_A is Avogadro's number and a is the ion size parameter which represents the sum of ionic radii ($r_+ + r_-$) evaluated from the slope of the plot of $\log K_A$ vs $1/D$ (Fig.1), and its values are cited in Tables (1 - 3).

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

Metal	T/K	Λ_o Scm ² mol ⁻¹	K_A dm ³ mol ⁻¹	$\Lambda_o \eta$ Scm ² mol ⁻¹ cp	a / A°
Mg	298	111.02	140.72	99.22	4.81
	303	117.88	146.12	94.38	---
	308	124.67	151.84	90.07	---
	313	131.70	158.04	86.39	---
Ca	298	117.12	99.85	104.67	4.87
	303	124.60	104.05	99.76	---
	308	132.12	109.02	95.45	---
	313	139.70	111.69	91.64	---
Ba	298	121.31	49.96	108.41	5.22
	303	129.01	53.04	103.30	---
	308	138.00	54.33	99.71	---
	313	145.93	55.85	95.73	---

Table 2: Conductance Parameters for Malate Salts in Water at Different Temperatures.

Metal	T/K	Λ_o Scm ² mol ⁻¹	K_A dm ³ mol ⁻¹	$\Lambda_o\eta$ Scm ² mol ⁻¹ cp	a / A°
Mg	298	112.22	330.84	100.29	5.68
	303	119.42	342.05	95.62	---
	308	126.32	353.23	91.26	---
	313	133.51	363.91	87.58	---
Ca	298	118.70	456.92	106.08	6.41
	303	126.30	472.02	101.13	---
	308	133.81	485.29	96.68	---
	313	141.66	498.88	92.93	---
Ba	298	122.81	155.21	109.75	6.87
	303	130.62	161.45	104.59	---
	308	139.68	165.19	100.92	---
	313	147.73	168.65	96.91	---

Table 3: Conductance Parameters for Tartrate Salts in Water at Different Temperatures.

Metal	T/K	Λ_o Scm ² mol ⁻¹	K_A dm ³ mol ⁻¹	$\Lambda_o\eta$ Scm ² mol ⁻¹ cp	a / A°
Mg	298	113.03	230.12	101.01	6.11
	303	120.53	237.68	96.51	---
	308	128.04	244.90	92.51	---
	313	135.49	252.35	88.88	---
Ca	298	119.50	630.78	106.80	6.52
	303	127.22	649.85	101.86	---
	308	135.06	670.03	97.58	---
	313	134.12	687.07	87.98	---
Ba	298	123.72	347.12	110.57	6.74
	303	132.04	358.83	105.72	---
	308	141.22	368.13	102.03	---
	313	149.35	377.57	97.97	---

Table 4: Standard Thermodynamic Functions, ΔH° and ΔS° for Various Ligands at 25°C.

Ligand	$\Delta H^\circ/\text{kJ mol}^{-1}$			$\Delta S^\circ/\text{J(kmol)}^{-1}$		
	Mg	Ca	Ba	Mg	Ca	Ba
succinate	6.034	5.972	5.663	61.376	58.315	51.513
malate	4.894	4.502	4.225	64.674	66.037	56.127
tartrate	4.859	4.539	4.363	61.530	68.825	63.275

Table 5: Values of The Thermodynamic Metal Gradient, β , for Metal Salts.

Ligand	$10^3\beta$		
	Mg	Ca	Ba
succinate	479	455	400
malate	543	553	470
tartrate	598	669	616

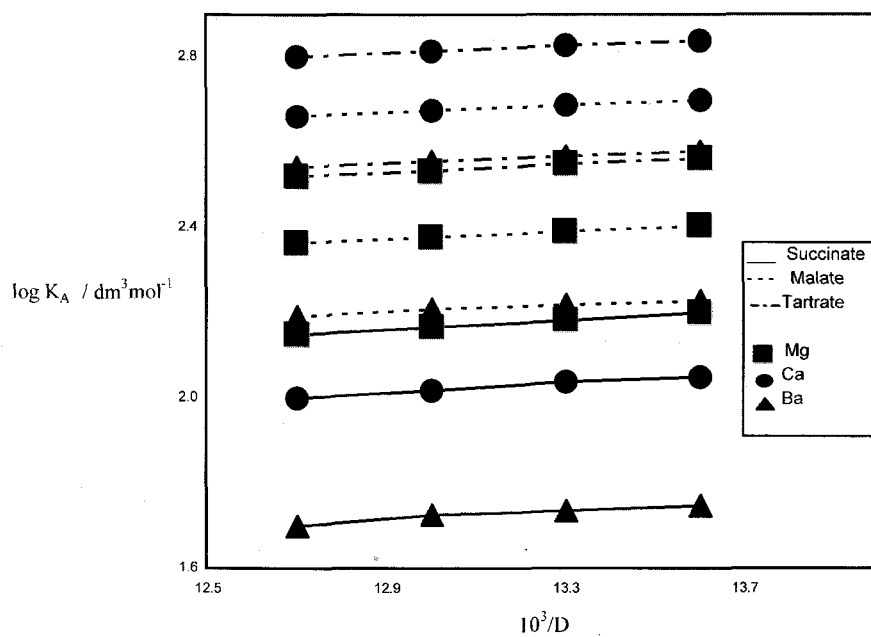


Figure 1: $\log K_A$ vs $1/D$ for the metal salts in aqueous solution at various temperatures.

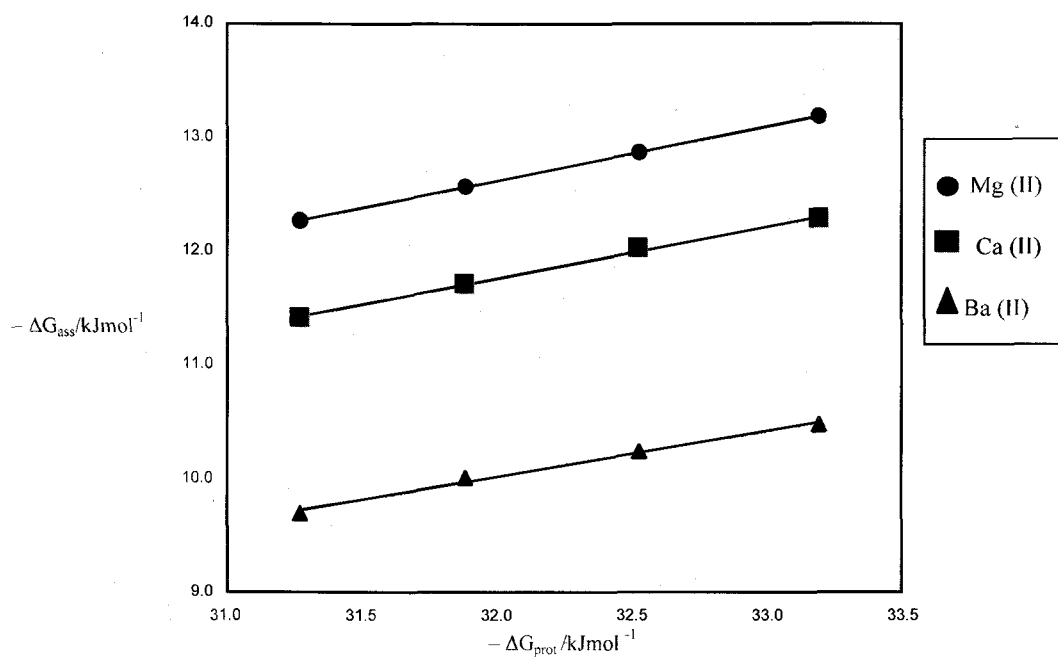


Figure 2: $-\Delta G_{\text{ass.}}$ vs. $-\Delta G_{\text{prot.}}$ plots for the metal (II) succinates at various temperatures.

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 solvation 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 [13] using the following equation whose parameters have their usual significance

$$\log K_{ML} = B \log K_M^{sL} + (\log K_{ML}^\circ - B \log K_M^{sL}^\circ) \quad (12)$$

Eqn. (12) can be replaced by

$$\Delta G_{ass} = \beta \Delta G_{prot} + (\Delta G_{ass}^\circ - \beta \Delta G_{prot}^\circ) \quad (13)$$

where ΔG_{ass} , ΔG_{prot} , ΔG_{ass}° , ΔG_{prot}° and β are the Gibbs energy of the association process at various temperatures, ΔG_{prot} is the Gibbs energy of the protonation process at any temperature, ΔG_{ass}° is the standard Gibbs energy of the complexation process at 25°C, ΔG_{prot}° is the standard Gibbs energy of the protonation process at 25°C and β is the rate of change in the Gibbs energy of association in a series of complexes (the thermodynamic metal gradient) ML at various temperatures [18]. Eqn. (13) can be written as

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

For the salts under investigation, the β values are positive (Table 5) indicating that the change in ΔG_{ass} is directly proportional to ΔG_{prot} . The β 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 ΔG_{ass} against ΔG_{prot} for succinate salts is linear with slope β (Fig.2). On the other hand, the β values decrease in the order tartrate > malate > succinate for the metal ions under study. Consequently, the rate of ΔG_{ass} and ΔG_{prot} is smaller where the association process occurs spontaneously in the order tartrate > malate > succinate.

Conclusions

1. The limiting molar conductance, Λ_∞ , decreases in the order $Ba^{2+} > Ca^{2+} > Mg^{2+}$ for the alkaline-earth metal salts of weak acids in water.
2. Λ_∞ for the ligands increases in the order succinate < malate < tartrate. On the other hand, $\Lambda_\infty \eta$ for ion-pair decreases with an increase in temperature from 25 to 40 °C and this behavior was discussed.
3. The order of K_A is $Mg < Ca > Ba$ for malate and tartrate salts while K_A decreases in the order $Mg > Ca > Ba$ for succinate salts. These trends were explained in view of the thermodynamic functions ΔH° and ΔS° .
4. The plot of $-\Delta G_{ass}$ vs $-\Delta G_{prot}$. (Fig. 2) confirms the interpretation of ion-association process for all the systems under investigation.

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