STABILITY CONSTANT OF SOME METAL ION OF COMPLEXES (4-AMINO HIPPURIC ACID) IN AQUEOUS SOLUTIONS

Yaha A.Majid*, Bassima M.Sarhane and Nada A.Al-Najjar***

*Department of Chemistry , College of Science for women University of Baghdad.
**Department of Chemistry , College of Education. Ibn-Al-haitham, University of Baghdad.

Abstract

Measurement of stabilility constant of complexes formed by (4-Amino hippuric acid) (4Aha) with (Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+} and La^{3+}) ions , have been performed. The bidendate ligand (4AhaA) has a hardness parameter (α) of (0.216) and a softness parameter (β) of (0.06).

Bonding in these complexes occur most probably through oxygen atom of the carboxylate ion and the lone pair electrons of the amide nitrogen atom.

Introduction

Amino acid have been used as complexing ragents with various metal ions(1-6). Therefore , determination of stability constants of amino acid complexes is highly encouraging. Anumber of measurements of stability constant of amino acid complexes have been reported by potentiometric technique, such as , L-Aspargine and L-Glutamine with La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Y^{3+} by Tewari and Shrivastava(7).Tyrosine , tryptophane and glcine derivatives with copper(II)(8-10) , and also the stability constant of Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes with [(glycylamino methyl)] phosphinic acid have been reported(11).

In this paper we are interested mainly in measuring the stability constants of complexes formed by (4-Amino hippuric acid) (4Aha) with selected metal ions , also to apply pearsons hard-soft acid-base postulate to explain the behaviour of this ligand in terms of Mesonos parameters(12).

Experimental

1-Reagents

The (4-Amino hippuric acid)(4Aha) were used as (B.D.H) analar grade. Standared solutions of metal nitrate were prepared from analar reagents, dissolved in distilled water. Carbonate free alkali solution in the distilled water were standardized against pure potassium hydrogen phthalate(13).

2-Apparatus and procedure :.

pH-measurements were carried out with Philips pH-meter. The pH-meter was standardized before each run against buffer solutions of known complexes, it is necessary to find out the acid dissociation constant of the ligand by titrating the ligand with standard alkali, then titrating mixtures of the ligand and metal ions following the procedure given in previous papers(13).

Results and Calculation

The acid dissociation constant of (4Aha) was calculated the detailed calculation can be seen in Table(1). Titration of the mixtures of (metal ion–ligand) with alkali solution can be seen in Fig. (1) which indicate clearly the formation of complexes in solution.

In order to determine stability constants of metal complexes, two functions must be calculated, the concentration of the free chelating species (L^-) and the degree of formation (n^-) which is defined as the average of ligand species bound per atom of metal ion . Concentration of free ligand in solution were calculated by equation previously used with thorium-glycinate(13) of the form:

$$\log\left[L^-\right]=\left(pH-pK_a\right)+\log\left[(L)_T-(KOH)_T\right] \quad .... (1)$$

An expression for the degree of formation (n^-) was used of the form :.

$$n^{-} = \frac{[L]_T - \left[\frac{H^{+}+1}{K_a}\right]\left[L^{-}\right]}{[M]_T} \quad H \text{ .... } (2)$$

Where $[L]_T$, $[L^-]$, $[M]_T$ are concentration of total ligands, free ligands and total metal ion respectively. For the present systems the reported stability conctants β_1, β_2 and β_3 were computed using the well known J.Bjerum summation equation with $[L^-]$ and $[n^-]$ calculated at different pH values from equation (1) and (2) respectively

$$\left[\sum_{n_o}^{n=n_{max}} \left[n^{-} - n\right]\right]\beta_n\left[L^{-}\right] = 0 \text{ .... } (3)$$

It can be shown after simple approximation that equation (3) may be written for the present system as :.

$$n^{-}\frac{1}{\beta_3} + \left(n^{-}-1\right)\left[L^{-}\right]\frac{\beta_1}{\beta_3} + \left(n^{-}-2\right)\left[L^{-}\right]^2\frac{\beta_2}{\beta_3} = \left(3-n^{-}\right)\left[L^{-}\right] \text{ .... } (4)$$

Where β_1,β_2,β_3 are the corresponding stability constants equation (4) , this equation could be simplified as

$$c + ax + by = z \text{ .... } (5)$$

where

$$x = \frac{\left(n^{-}-1\right)\left[L^{-}\right]}{n^{-}},$$

$$y = \frac{\left(n^{-}-2\right)\left[L^{-}\right]^2}{n^{-}},$$

$$z = \frac{\left(3-n^{-}\right)\left[L^{-}\right]^3}{n^{-}}$$

:.

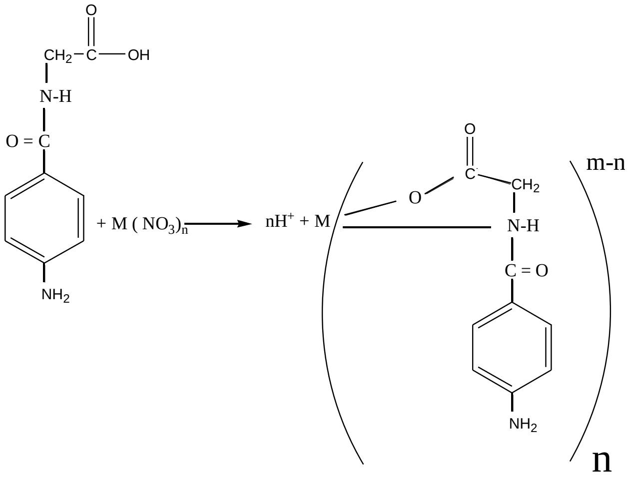
All being experimentally determined functions and

$$a = \frac{\beta_1}{\beta_2}, \quad b = \frac{\beta_2}{\beta_3}, \quad c = \frac{1}{\beta_3}$$

In each system, the function x, y and z were calculated from the experimental data and where fitted to aeggression equation using Carmemors' rule for solving such equation with a special computer program. Typical titration results are summarized in Table (2 and 3). Stability constants of melal-(4Aha) complexes and hardness-softness parameter of the ligand (4Aha) are calculated using Misonos' equation[12] Results are shown in Table (4)

Discussion

The decrease in the pH value of solution of (4Aha) when a neutral salt solution of metal ions were added is aclear indication of complex formation , the chemical equation representing the equilibrium could be written as follows :.



As indicated from the above figure. Bonding may occur through oxygen atom of the carboxylate ion and the lone pair electrons of the amide nitrogen atom.

However, calculation of acidity as can be seen in Table (1) (K_a= 8.25×10^{-7}) indicate that (4Aha) behaves as an acid. It is reasonable to expect a correlation between the stability of the complex and the acidic dissociation constant of the conjugate acid of the ligand.

$$n\,HL + M^{+m} \Leftrightarrow [ML_n]^{m-n} + nH^{+}$$

Considering the case of (4Aha) the association with metal ions takes the following route :

$$n(4AHA) + M^{+m} \Leftrightarrow \left[M(4AHA)_n\right]^{m-n} + nH^{+}$$

Where $[M(4Aha)_n]^{m-n}$ represents metal-4-amino hippuric acid complex.

Hardness-Softness Parameters

In the assestment of stability constants of complexes Misono[12] introduced an equation of the from

$$pK = -\log K = \alpha X + \beta Y + \gamma$$

Where K is the instability constant of the ligand, X and Y are parameters of metal ion , α and β are those of the ligand, the parameter (γ) is characteristic of the ligand and is used to adjust the pK so that all lie on the same scale. The Y parameter is considered to be ameasure of softness and may be calculated from atomic parameters including the radius of the ion. It correlates nicely with ideas on hardness and softness, hard ion have values below (2.8) while soft ions have values greater than (3.2) and border lines species are (2.8-3.2).

The analogous ligand parameter β like wise shows the expected increase in values from hard to soft species : $OH^- = 0.40$, $NH_3 = 1$, $Cl^- = 2.4$, $Br^- = 5.58$, $I^- = 7.17$, $S_2O_3^{-2} = 12.4$, softness parameter (β) of (4Aha) ligand under investigation has a value of (0.06) a value comparable to (0.04) of 2,4-dihydroxyacetophenone[14] , the α and X parameters' were interpreted by Misano as hardness parameters' of ligand and metal ion respectively. The X is closely related to the electronegativity of the ion and measures the tendency of the metal ion to accept electrons from the ligand. Calculated hardness parameter (α) for (4Aha) was found to be (0.216) a value comparable to (0.230) of the pyrocaticol[14]. Values of α, β and γ of the (4Aha)ligand were calculated by solving three Mesono type equations for three different metal ions using Table (4).

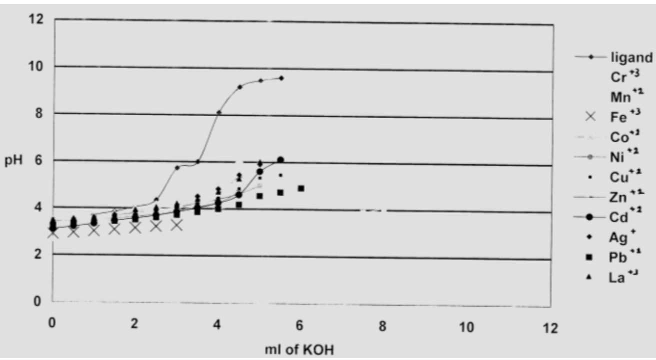


Fig. (1) : Representative titration curves

Table (1)
Determination 0f the dissociation constant of (4-Amino hippuric acid) (20 ml) (0.025 M) of (4Aha) + (27.5 ml) of distilled water . μ = 0.1 , temp : 25 Cº

ml KOH 0.085 M	PH	Stoichiometric [HL]	Stoichiometric [B]	$[HL]_T$ $[HL]_T = [HL] – [B]$	[OH]	$\frac{[HL]_T + [OH]}{[B] - [OH]}$	$pK_a = pH + \log \frac{[HL]_T + [OH]}{[B] - [OH]}$
٠	٣,٣٩	٠,٠١٠٥	٠	٠,٠١٠٥	2.45×10^{-11}	٠	
٠,٥	٣,٤٩	٠,٠١٠٤	8.854×10^{-4}	9.515×10^{-3}	3.09×10^{-11}	١٠٧,٥	٤,٥٢
١	٣,٧٠	٠,٠١٠٣	1.753×10^{-3}	8.547×10^{-3}	5.01×10^{-11}	٤,٨٨	٤,٣٩
١,٥	٣,٨٦	٠,٠١٠٢	2.602×10^{-3}	7.594×10^{-3}	7.24×10^{-11}	١,٢٢	٣,٩٥
٢	٤,٠٦	٠,٠١٠١	3.434×10^{-3}	6.666×10^{-3}	1.23×10^{-10}	١,٩٤٣	٤,٣٨
٢,٥	٤,٣٦	٠,٠١	4.25×10^{-3}	5.750×10^{-3}	2.29×10^{-10}	١,٣٥٢	٤,٤٩
٣	٥,٧٣	9.901×10^{-3}	5.049×10^{-3}	4.851×10^{-3}	5.37×10^{-9}	٠,٩٦١	٥,٧١
٣,٥	٦	9.804×10^{-3}	5.833×10^{-3}	3.971×10^{-3}	1×10^{-8}	٠,٦٨	٥,٨٣
٤	٨,١	9.708×10^{-3}	6.602×10^{-3}	3.106×10^{-3}	1.26×10^{-6}	٠,٤٧	٧,٧٧
٤,٥	٩,٢	9.615×10^{-3}	7.356×10^{-3}	2.25×10^{-3}	1.58×10^{-5}	٠,٣١	٨,٦٩
٥	٩,٤٨	9.524×10^{-3}	8.095×10^{-3}	1.42×10^{-3}	3.02×10^{-5}	٠,١٨	٨,٧٤
٥,٥	٩,٦	9.434×10^{-3}	8.821×10^{-3}	0.613×10^{-3}	3.98×10^{-5}	٠,٠٧	٨,٤٥
							$pK_a = 6.08$ $K_a = 8.25\times10^{-7}$

Table (2)

Titraion of 30ml (0.25) (4AHA) + 5ml (0.05M) $M(NO_3)_n$ solution with (0.085M) KOH solution ,

μ = 0.1, temp = 25C° , Vol = 47.5ml

ml KOH 0.085M	pH										
	Cr^{+3}	Mn^{+2}	Fe^{+3}	Co^{+2}	Ni^{+2}	Cu^{+2}	Zn^{+2}	Cd^{2+}	Ag^{+}	Pb^{+2}	La^{+3}
٠	٢,٦٦	٣,٤٥	٢,٩٠	٣,٣٧	٣,٤٩	٣,٣٦	٣,٤٤	٣,١	٣,٢٣	٣,٢٣	٣,٤٦
٠,٥	٢,٦٨	٣,٥٣	٢,٩٥	٣,٤٦	٣,٥١	٣,٤٣	٣,٥٣	٣,٢١	٣,٣٨	٣,٣٣	٣,٥٤
١	٢,٧٤	٣,٦٣	٣,٠٢	٣,٤٩	٣,٥٩	٣,٥٢	٣,٦٢	٣,٣٣	3.48	٣,٣٦	٣,٦٢
١,٥	٢,٨١	٣,٧٤	٣,٠٩	٣,٥٧	٣,٦٩	٣,٦٢	٣,٧٤	٣,٤٦	٣,٦٤	٣,٤٤	٣,٧٤
٢	٢,٨٨	٣,٨٧	٣,١٦	٣,٦٥	٣,٨	٣,٧٤	٣,٨٨	٣,٥٨	٣,٧٣	٣,٥١	٣,٩٤
٢,٥	٢,٩٦	٤	٣,٢٣	٣,٧٥	٣,٩١	٣,٨٨	٤,٠٢	٣,٧	٣,٩٢	٣,٦١	٤,٠٥
٣	٣,٠٢	٤,١٤	٣,٢٩	٣,٩	٤,٠٦	٤	٤,١٨	٣,٨٦	٤,٠٤	٣,٧٢	٤,٢١
٣,٥	٣,١١	٤,٣٢	PPT	٤,٠٨	٤,٢٢	٤,٢١	٤,٣٨	٤,٠٤	٤,٥٢	٣,٨٦	٤,٤١
٤	٣,١٩	٤,٦١		٤,٢٦	٤,٤١	٤,٤٦	٤,٧١	٤,٢٥	٤,٨٤	٣,٩٩	٤,٧٢
٤,٥	٣,٢٥	٤,٩٨		٤,٧١	٤,٦٤	٤,٨٦	٥,٣٦	٤,٦	٥,٤٥	٤,١٨	٥,٢٨
٥	٣,٣٧	٦,١١		PPT	٤,٩٩	٥,٣٣	٥,٩٤	٥,٦	٥,٩	٤,٥٦	٦,٠٢
٥,٥	٣,٤٨	PPT			PPT	٥,٤٦	PPT	٦,١١	PPT	٤,٧٢	PPT
٦	٣,٦					PPT		PPT		٤,٩	
٦,٥	٣,٧٤									PPT	
٧	٣,٩١										
٧,٥	٤,٠٨										
٨	٤,٣١										
٨,٥	٤,٥٨										
	PPT										

Table (3)
Titraion of (0.025M) (4Aha) and (0.05M) $Ni(NO_3)_2$ solution with (0.085M) KOH solution , μ = 0.1 , temp = 25Cº

ml KOH 0.085M	pH	$[H^+]$	$[M]_T$	$[L]_T$	$[KOH]_T$	$\frac{[H^+]}{K_a}$	$[L^-]$	n^-
٠	٣,٤٩	3.24×10^{-4}	5.26×10^{-3}	٠,٠١٥٧٨٩	٠,٠٨٥	٣٩٤,٦٣		
٠,٥	٣,٥١	3.09×10^{-4}	5.21×10^{-3}	٠,٠١٥٦٢٥	8.85×10^{-4}	٣٧٦,٨٧	3.97×10^{-5}	٠,١١٩٧
١	٣,٥٩	2.57×10^{-4}	5.15×10^{-3}	٠,٠١٥٤٦٤	1.75×10^{-3}	٣١٣,٤٦	4.44×10^{-5}	٠,٢٩١٦
١,٥	٣,٦٩	2.04×10^{-4}	5.10×10^{-3}	٠,٠١٥٣٠٦	2.6×10^{-3}	٢٤٨,٩٩	5.18×10^{-5}	٠,٤٦٢١
٢	٣,٨	1.58×10^{-4}	5.05×10^{-3}	٠,٠١٥١٥	3.43×10^{-3}	١٩٣,٢٨	6.15×10^{-5}	٠,٦٣٤٠
٢,٥	٣,٩١	1.23×10^{-4}	5×10^{-3}	٠,٠١٥	4.25×10^{-3}	١٥٠,٠٣	7.27×10^{-5}	٠,٨٠٤
٣	٤,٠٦	8.71×10^{-5}	4.95×10^{-3}	٠,٠١٤٨٥١٤	5.05×10^{-3}	١٠٦,٢٢	9.36×10^{-5}	٠,٩٧٢٩
٣,٥	٤,٢٢	6.03×10^{-5}	4.9×10^{-3}	٠,٠١٤٧٠٥٨	5.83×10^{-3}	٧٣,٤٨	1.23×10^{-4}	١,١٣١٦
٤	٤,٤١	3.89×10^{-5}	4.85×10^{-3}	٠,٠١٤٥٦٣١	6.6×10^{-3}	٤٧,٤٤	1.7×10^{-4}	١,٣٠٤٨
٤,٥	٤,٦٤	2.29×10^{-5}	4.81×10^{-3}	٠,٠١٤٤٢٣	7.35×10^{-3}	٢٧,٩٤	2.57×10^{-4}	١,٤٥٢٣
٥	٤,٩٩	1.02×10^{-5}	4.76×10^{-3}	٠,٠١٤٢٨٩٧	8.09×10^{-3}	١٢,٤٨	5.04×10^{-4}	١,٥٧٣٩
٥,٥	٥,٣	5.01×10^{-6}	4.72×10^{-3}	٠,٠١٤١٥٠٩	8.82×10^{-3}	٦,١١	8.85×10^{-4}	١,٦٦٤٩
	PPT							

Table (4)

Misano metal-(4Aha)parameters calculated according to the equation log K = αX +βY +γ where K being the first association constant

Metal Ion	β_1	β_2	Metal parameters*	
			X	Y
Cr^{+3}	1.25×10^{9}	6.87×10^{10}	٨,٣٩	٢,٧
Mn^{+2}	2.25×10^{5}		٤,٢	٣,٠٣
Fe^{+3}	4.75×10^{6}	6.27×10^{10}	٨,٤٦	٢,٠٦
Co^{+2}	6.64×10^{5}		٤,٣٩	٢,٥٩
Ni^{+2}	4.11×10^{5}		٤,٧٣	٢,٨٢
Cu^{+2}	4.88×10^{5}	1.35×10^{7}	٥,٣١	٢,٨
Zn^{+2}	1.01×10^{6}		٤,٥٢	٢,٣٤
Cd^{+2}	9.09×10^{5}	2.65×10^{6}	٤,٨٨	٣,٠٤
Ag^{+}	3.64×10^{5}		٤,٨	٣,٩٩
Pb^{+2}	1.38×10^{6}		٣,٨٩	٣,٥٨
La^{+3}	2.28×10^{5}		٥,٠٢	١,٤٧
****Ligand parameters**			α	٠,٢١٦
			β	٠,٠٦
			γ	٤,٧

* X : is related to the electronegativity of the ion and obtained from the equation :

$$(10\,X)^{1/2} = X^{o}_{m} + (I_n)^{1/2}$$

Where X^{o}_{m} is the electronegativity of the metal taken from Gordy and Thomas[15] and (I_n) is the ionization energy .

Y : is calculated by an equation

$$Y = 10\left(\frac{I_n}{I_{n+1}}\right)\left(\frac{ri}{n^{1/2}}\right)$$

Where ri is the ions radius of meral ion and (n) is the formal charge .

** Values of ligand 's parameters where calculated using the least squares solution of an over determined system of linear equations to derive the normal equation[16] .

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الخلاصة

فـي هـذا البحـث تـم تعيـين ثابـت التفكك للحـامض -4 Amino hippuric acid)(4Aha) في درجـة (25C°) وثوابت الأستقرارية للمعقدات التي يكونها مع أيونات Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}) La^{3+}, Pb^{2+}, Ag^{+}, Cd^{2+}, Zn^{+2}, Cu^{2+}, Ni^{2+}) فـي المحاليـل المائيـة . ان هـذا الليكانـد يتصـرف وكأنـه ثنـائي المخلـب ويكـون مـع معظـم الفلـزات معقـدات ثابتـة بنسـبة (١:١) (فلـز – ليكانـد) . كمـا حسـبت معاملات الصـلادة والليونـة لليكاند وقد وجد أن قيمـة معامل الصـــلادة (α) تســاوي (٠,٢١٦) وان معامــل الليونـــة (β) تساوي (٠,٠٦) .