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Physico-Chemical Studies Of Ternary Chelates In Solution: Stability Constant Of Ternary Chelates Of Cu(II), Ni(II), And Co(II) With N-[Tris (Hydroxymethyl)Methyl]Glycine And Various Biologically Relevant Ligands

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ABSTRACT

Summary. Stability constants of ternary complexes of Cu(II), Ni(II), and Co(II) metal ions with N-[tris(hydroxymethyl)methyl]glycine(tricine) and some aliphatic carboxylic acids(succinic, oxalic, malic, maleic, and tartaric), aromatic carboxylic acids(5-sulfosalicylic, salicylic, and phthalic), and hydroxamic acids(acetohydroxamic acid(Aha), benzohydroxamic acid(Bha), and salicylhydroxamic acid(Sham)) were determined using potentiometric technique at 298.15K and $0.10 mol\cdot dm^{-3}(NaNO_3)$ ionic strength. The stability of the ternary complex is also discussed in relation to that of the binary complexes of secondary ligands. Evaluation of the effect of temperature and ionic strength of the medium on the stability of the ternary system Cu(II)-tricine-the other ligands has been studied. The thermodynamic parameters(ΔG, ΔH, and ΔS) were studied and discussed. The stability constant of the above-mentioned ternary system has been investigated in(dioxane+water) solution. Confirmation of the ternary complexes in solution has been carried out using differential pulse polarography(DPP), square wave voltammetry, conductometric measurements, and UV-visible spectroscopic measurements.

KEYWORDS

Binary and ternary complexes;
Carboxylic acids;
Hydroxamic acids;
Potentiometric studies;
Stability constants;
Tricine;
Thermodynamics.

INTRODUCTION

Buffers are compounds that undergo reversible protonations and, thus, aid in maintaining the pH of a solution. This is particularly important in biological reactions that are often sensitive to small changes in pH.The use of buffers can present problems, however, because the buffer is often present in relatively high concentrations and can interact with substrate, enzyme or metals in the reaction.

Inorganic and organic buffer used in environmental studies involving trace-metal-ligand speciation may complex a number of trace metal[1-7]. Thus, the degree to which they bind must be determined for their use in speciation studies.

Over the last 30 years a variety of buffers that are suitable for biological systems have been developed. Some of the criteria used for these buffers have included good solubility in water, low membrane permeability, minimum salt effect, low ion effect, good stability and high purity[8]. These characteristics were important in the development of a series of zwitterionic, amino-containing, buffers by Good et al. in 1966[8]. Among the Good family of buffers, we have investigated an ampholyte N-[tris(hydroxymethyl)methyl]glycine; tricine, a derivative of the simple amino acids, glycine. Tricine has proved quit useful biological buffer[9] of pH range 7.2-8.5 which has been used in animal tissue culture[10], in fluorescent dye reagent to analyze cells in urine and one measurement of small masses of protein with bicinchaninic acid[11,12]. Bates et al.[13] prepared tricine buffer of pH=7.407 which matches closely that of human blood. Indeed, the stability constants of the binary[14-17] and ternary[18-20] complexes of tricinate have been determined over the years. Recently, stabilities of binary and ternary complexes involving tricine and some selected α-amino acids have been reported by us[21] using potentiometric technique.

The use tricine as a buffer substance in biochemical studies, which are normally carried out under multiligand conditions and which often also contain metal ions, shows the need to consider also the formation of mixed ligand complexes involving tricinate as a second ligand. Therefore we studied as an example the ternary systems with some aliphatic and aromatic carboxylic acids as well as hydroxamic acid, as these systems mimic many biological reactions. The present investigation is an extension of our earlier work on solution studies on the biological buffers[22-27].

EXPERIMENTAL

Materials and solutions

N-[tris(hydroxymethyl)methyl]glycine(tricine), acetohydroxamic acid and benzohydroxamic acid were Sigma products. Salicylhydroxamic acid was purchased in pure form from nasr pharmaceutical chemicals co., Egypt. phthalic acid, salicylic acid, 5-sulfosalicylic acid, succinic acid, oxalic acid, malic acid, maleic acid, and tartaric acid were analytical-grade(Aldrich or Merck) products. The metal salts were provided by BDH as nitrate or chlorides. Stock solutions of the metal salts were prepared in deionized water, and the metal concentration was obtained by standard analytical methods[28]. A carbonate-free sodiumhydroxide(titrant, prepared in 0.1 $mol\cdot dm^{-3}$ $NaNO_3$ solution) was standardized potentiometrically with KH phthalate(Merck AG). A nitric acid solution($\approx 0.03 mol\cdot dm^{-3}$) was prepared and used after standardization. Sodium hydroxide, nitric acid, and sodium nitrate were from Merck p.a.

Apparatus and procedure

Potentiometric pH titrations were performed using a model SM 702 metrohm automatic titrator with a combined pH glass electrode equipped with a 665 dosimat and a magnetic stirrer. The accuracy of the instrument was(±0.001) pH unit. The electrode system was calibrated in terms of hydrogen ion concentrations instead of activities. It is to be assumed that the activity coefficient is constant, an assumption usually justified by working in a medium of a constant ionic strength ($0.10 mol\cdot dm^{-3}$ $NaNO_3$)[29]. The electrode system was calibrated by periodic titrations of HNO_3(or NaOH) solution($0.10 mol\cdot dm^{-3}$ in $NaNO_3$) with a standard NaOH(or HNO_3) solution. Thus, all constants determined in this work are concentration constants.

The following solutions were prepared(total volume 50 cm^3) and titrated potentiometrically against a standard CO_2-free NaOH($0.10\ mol\cdot dm^{-3}$): 0.003 $mol\cdot dm^{-3}$ HNO_3+0.1 $mol\cdot dm^{-3}$ $NaNO_3$ **(a)** solution a+0.001 $mol\cdot dm^{-3}$ tricine **(b)** solution b+0.001$moldm^{-3}$ M(II) **(c)** solution a+0.001$mol\cdot dm^{-3}$ the other ligands studied **(d)** solution d+0.001$mol\cdot dm^{-3}$ M(II) **(e)** solution a+0.001$mol\cdot dm^{-3}$ tricine+0.001$mol\cdot dm^{-3}$ the other ligands studied+0.001$mol\cdot dm^{-3}$ M(II) **(f)**. Each solution was thermostated at the required temperature with an accuracy of(±0.1)K, where the solutions were left to stand for about 15min before titration. A magnetic stirrer was used during all titrations. The pH-metric titrations were carried out at the desired temperature in a purified nitrogen atmosphere. The titration was repeated at least four times for each titration curve.

The pH titrations were terminated when either the pH readings became unstable, showing a downward drift. In all cases, no calculations have been performed beyond the precipitation point; hence, the hydroxyl species likely to be formed after this point could not be studied. The initial estimates of the stability constants of the binary and ternary complexes formed in solution have been determined using the Irving and Rossotti formula[30].

Initial estimates of the stability constants of the binary and ternary complexes formed in solution have been refined with the clinp 2.1 computer program[31,32]. Standard deviations were also evaluated for the corresponding equilibrium constants. The concentration distribution of various complex species existing in solution as a function of pH was obtained using the SPECIES program[33].

The pH meter readings have been corrected in accordance with the method described by Douheret[34]. Thus, if the pH meter is standardized using queous solution, the meter reading $pH_{(R)}$ obtained in a partially aqueous medium differs by an amount δ from the corrected reading pH^* which is referred to the standard state in the partially aqueous solvent($pH^*=pH_{(R)}-\delta$). In a typical experiment, a sample volume $50cm^{-3}$ containing 0.003 $mol\cdot dm^{-3}$ HNO_3 in the presence of 10%, 30% and 50% (w/w) of dioxane **(a)** 0.003$mol\cdot dm^{-3}$ HNO_3+0.001 $mol\cdot dm^{-3}$ tricine in the presence of 10%, 30% and 50% (w/w)of dioxane **(b)** 0.003$mol\cdot dm^{-3}$ HNO_3+0.001 $mol\cdot dm^{-3}$ tricine+0.001$mol\cdot dm^{-3}$ M(II) in the presence of 10%, 30% and 50%(w/w) of dioxane **(c)** 0.003 $mol\cdot dm^{-3}$ HNO_3+0.001$mol\cdot dm^{-3}$ the other ligands studied in the presence of 10%, 30% and 50%(w/w) of dioxane **(d)** 0.003$mol\cdot dm^{-3}$ HNO_3+0.001$mol\cdot dm^{-3}$ the other ligands studied+0.001$mol\cdot dm^{-3}$ M(II) in the presence of 10%, 30% and 50%(w/w) of dioxane **(e)** 0.003 $mol\cdot dm^{-3}$ HNO_3+0.001$mol\cdot dm^{-3}$ tricine+0.001 $mol\cdot dm^{-3}$ the other ligands studied+0.001$mol\cdot dm^{-3}$ M(II) in the presence of 10%, 30% and 50%(w/w) of dioxane **(f)** was used. The ionic strength of the studied solutions was adjusted at 0.10$mol\cdot dm^{-3}$ using a $NaNO_3$ solution and titrated individually against 0.10$moldm^{-3}$ NaOH, prepared in the ionic medium used for the test solution.

Electrochemical measurements

Square wave voltammetry, and differential pulse voltammetry measurements were collected using an EG and G princeton applied research, potentiostat/galvanostat model 263 with a single compartment voltammetric cell equipped with a glassy carbon(GC) working electrode (area=0.1963cm^2) embedded in a resin, a Pt-wire counter electrode, and an Ag/AgCl reference electrode. The scan rate was 36.6$mV\cdot s^{-1}$ from(+250 to -300)mV, the frequency was 20Hz, the pulse height was 25 mV, and the scan increment was 2.0mV.

The solutions were prepared(total volume 25cm^3) and purged with nitrogen for 180s. The ionic strength of the studied solutions was adjusted to that of the 0.1$mol\cdot dm^{-3}$ $NaNO_3$ solution.

Conductometric measurements

Conductometric titrations were followed with a SUNTEX conductivity meter SC-170.

The following mixture was titrated conductometrically against a 0.10$mo\cdot dm^{-3}$ NaOH solution: 0.01$mol\cdot dm^{-3}$ Cu(II)(10cm^3)+0.01$mol\cdot dm^{-3}$ Salicylhydroxamic acid(10cm^3)+0.01$mol\cdot dm^{-3}$ tricine(10cm^3).

Spectrophotometric measurements

Electronic spectra were recorded using a Perkin-Elmer lambda 2 spectrophotometer.

RESULTS AND DISCUSSION

Representative potentiometric titration curves obtained according to sequence described in the experimental part are shown in figure 1 for the tricine-Bha-Ni(II)-system.

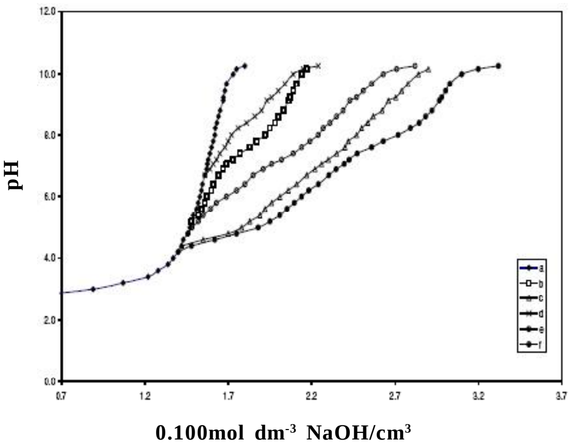
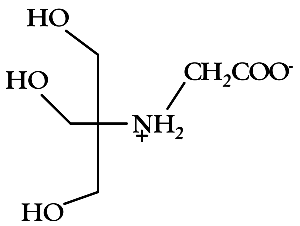


Figure 1. Potentiometric titration curves for the Ni(II)–tricine–bha system at 298.15K and I=0.1mol dm^{-3} $NaNO_3$.(a) 0.003mol dm^{-3} HNO_3+0.1mol dm^{-3}($NaNO_3$);(b) solution a+0.001mol dm^{-3} tricine;(c) solution b+0.001mol dm^{-3} Ni(II);(d) solution a+0.001mol dm^{-3} bha;(e) solution d+mol dm^{-3} Ni(II);(f) solution a+0.001mol dm^{-3} tricine+ 0.001mol dm^{-3} bha+0.001mol dm^{-3} Ni(II).



SCHEME 1

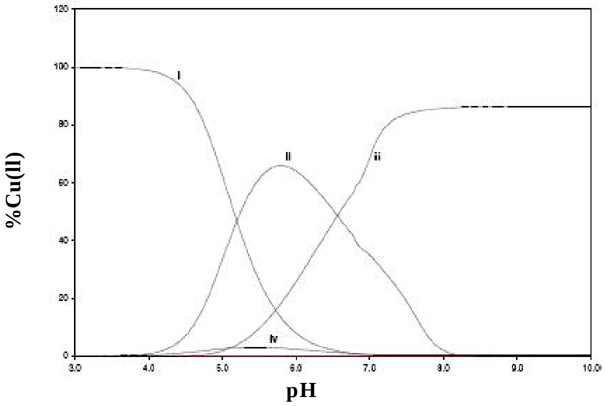


Figure 2 : Concentration distribution of various species as a function of pH in the Cu(II)-sham-tricine system at 298.15K and I=0.1mol·dm^{-3} NaNO$_3$. (i) Cu(II);(ii)Sham-Cu(II); (iii)Sham-Tricine-Cu(II); (iv) Tricine-Cu(II).

Protonation constants

Tricine is a zwitterionic amino acid, whose structure is shown in SCHEME 1. the first protonation constant(pK_{a1}) is due to the carboxylic group, the second one is related to a proton on the amino group(pK_{a2}). At afirst attempt, we intended to determine both protonation constants of tricine. It was not possible to determine the exact value of pK_{a1} but it was verified at pH 3.0 the carboxylic group was already deprotonated. The value of the pK_{a2} was obtained potentiometrically from curves(a) and (b)(Figure 1). The details regarding the potentiometric method were reported in the experimental section. The value of pK_{a2} obtained(8.06) in this work agrees well with the literature values[9].

The protonation constants of aliphatic carbxylic acids, aromatic carboxylic acids and hydroxamic acids have also been determined potentiometrically from curves(a) and(d)(Figure 2) at 298.15K and I=0.10mol·dm^{-3} NaNO$_3$ to obtain values using the experimental procedures as used in the study of binary and ternary systems, and are in agreement with data found in Ref. [35].

Binary systems

Potentiometric pH titrations of Cu(II), Co(II), and Ni(II) were performed at 1:1 metal/ligandmolar ratios. Analysis of the complexed ligands curves(c) and (e) as shown in figure 1, indicates that the addition of metal ion to the free ligand solutions shifts the buffer region of the ligand to lower pH values. This shows that complex formation reaction precede by releasing of protons from such ligands.

The stability constants of 1:1 binary complexes of the ligands studied, already report in Ref.[35,36], have been determined at 298.15K and I=0.10mol·dm^{-3} NaNO$_3$ to obtain values using the same experimental procedures, are in agreement with data found in the literature.

Ternary systems

When a solution contains two different ligands and a metal ion, there may exist equilibria in which either(i) both the ligands may combine with the metal ion simultaneously or(ii) the two ligands may be combined one by one at different pH.

As is evident from the titration curves in the present study, the addition of two ligands is stepwise. It was deduced that tricine acts a primary ligand in the ternary complexes involving aliphatic carboxylic acids and hydroxamic acids, whereas it behaves as a secondary ligand in ternary systems containing aromatic carboxylic acids and Cu-sham-tricine system; that is, the formation of ternary complex takes place according to the following equilibria(charges are omitted for clarity).

$$\mathbf{M+A \quad MA \rightleftharpoons} \qquad \mathbf{(1)}$$

$$\mathbf{MA + L \quad MAL \rightleftharpoons} \qquad \mathbf{(2)}$$

$$\mathbf{K_{MAL}^{MA} = \frac{[MAl]}{[MA][L]}} \qquad \mathbf{(3)}$$

where A represents primary ligand and L represents the secondary ligand.

The overall stability constant β_{MAL}^{M} may be represented by Eq.(4)

$$\mathbf{M+A+L \rightleftharpoons MAL} \qquad \mathbf{(4)}$$

$$\beta_{MAL}^{M} = \frac{[MAL]}{[M][A][L]}$$

$$= K_{MAL}^{MA} \times K_{MA}^{M}$$

Careful consideration of all presented data(TABLE 1) reveals that the stability constants of ternary metal(II) complexes with the ligands studied follow the order

TABLE 1 : Stability constants of 1:1:1 ternary complexes of tricine with other ligand studied at 298.15K, I=0.1mol dm^{-3} ($NaNO_3$)

Ligands	$\log K^{MA}_{MAL}$			$\log \beta^{M}_{MAL}$			$\Delta \log K$		
	Cu^{II}	Ni^{II}	Co^{II}	Cu^{II}	Ni^{II}	Co^{II}	Cu^{II}	Ni^{II}	Co^{II}
Phthalic	7.85±0.03	6.70±0.06	5.12±0.04	11.33	9.96	8.12	0.18	0.56	0.52
Salicylic	7.70±0.04	6.57±0.02	4.93±0.05	18.33	15.22	12.15	0.03	0.43	0.33
5-Sulfosalicylic	7.38±0.05	6.44±0.06	4.86±0.02	16.89	12.79	11.02	-0.28	0.30	0.25
Succinic	5.36±0.04	4.76±0.04	3.97±0.03	13.03	10.90	8.57	2.16	1.64	1.01
Malic	5.21±0.06	4.31±0.06	3.74±0.05	12.88	10.45	8.34	0.07	-0.29	0.61
Maleic	5.13±0.02	4.26±0.05	3.44±0.02	12.80	10.40	8.04	1.06	0.56	0.42
Tartaric	5.02±0.05	4.14±0.02	3.39±0.04	12.69	10.28	7.99	-0.14	-0.54	0.22
Oxalic	4.95±0.03	4.01±0.08	3.13±0.03	12.62	10.15	7.73	0.35	0.55	0.02
Sham	7.81±0.02	6.35±0.05	6.21±0.06	20.87	12.49	10.81	0.14	0.33	-0.38
Aha	7.65±0.06	5.88±0.03	5.63±0.03	15.32	12.02	10.23	-0.38	0.18	0.70
Bha	7.42±0.02	5.37±0.06	5.07±0.02	15.09	11.51	9.67	-0.21	0.32	0.32

Co(II)<Ni(II)<Cu(II), which is in accordance with Irving-Williams order[37].

The complex stability of the same metal ion ternary complexes containing aliphatic and aromatic acids follows the order:

Phthalic>salicylic>5-sulfosalicylic>succinic>malic> maleic>tartaric>oxalic acid.

The higher stability of phthalic acid complex than salicylic acid may be explained[38] as follows: since the carboxylate oxygen is not directly bound to the benzene nucleus, it therefore adjusts sterochemically more easily than the phenolate oxygen which is directly attached to the benzene nucleus. The coulombic repulsion between the end oxygens will be more when both O,O donor atoms are phenolic oxygens than when they are carboxylic oxygens.

The relative stabilities of the ternary complexes of salicylic and 5-sulfosalicylic acid follow this relative basicities. The lower stability of the complexes involving 5-sulfosalicylic acid may be ascribed to the presence of the electron withdrawing sulfonic group.

With respect to aliphatic acids, the order of stabilities of their mixed-ligand complexes is in accord with the basicities(pKa_1+pKa_2) of the ligands. It is well know that the increase in basicity of a ligand increase the stability of its metal complexes.

The observed order of stability of ternary systems with respect to the ligand hydroxamic acid is Sham.Aha. Bha. The increased stability of the salicylhydroxamate ternary complexes relative to those of the other ligands may be ascribed to an additional interaction of the phenolic group with the metal ion.

The relative stability of the ternary, as compared to that of the corresponding binary complexes, can be quantitatively expressed in different ways. A review of those methods[39] has shown that, for a variety of reasons, the most suitable comparison is in stabilities of the ternary complexes in terms of ΔlogK as defined by Eq.(5)

$$\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{MA} \qquad (5)$$

In general, positive ΔlogK values for the systems indicated favored formation of the M(A)(L) ternary complexes over the corresponding binary ones. This can be ascribed to interligand interactions or some cooperatively between the primary and secondary ligands such as H-bond formation.

The equilibrium concentration distribution diagrams of various complex species provide a useful picture of metal ions binding in the biological system. In order to indicate the main features observed in the species distribution plots in these system, the speciation diagram obtained for Cu(II)-Sham-tricine system is shown in figure 2. The concentration distribution of various complex species existing in solution as a function of pH was obtained using the SPECIES program[40].

The values of $\log K^{Cu(A)}_{Cu(A)(L)}$, at different temperature (TABLE 2), shows that the stability constants of the complexes decrease with increasing temperature. This behavior can be mainly ascribed to the thermal hydrolysis of the metal complexes[41].

The thermodynamic quantities(ΔG, ΔH, and ΔS) associated with the formation of 1:1:1 ternary complexes in the systems Cu(II)-tricine-ligands studied were also

TABLE 2 : Thermodynamic quantities associated with the interaction of metal ion with the ligands at a 1:1:1molar ratio, I=0.10mol dm^{-3} NaNO$_3$

Ligands	T/K	log $K^{Cu(A)}_{Cu(A)(L)}$	-ΔG kJ?mol^{-1}	-ΔH kJ?mol^{-1}	ΔS J?mol^{-1}?K^{-1}
Phthalic	298.15	7.85±0.03	44.81	12.7	192.9
	310.15	7.80±0.05	46.32		190.3
	318.15	7.75±0.03	47.21		188.3
	328.15	7.66±0.02	48.15		185.4
Salicylic	298.15	7.70±0.04	43.96	15.7	200.1
	310.15	7.64±0.04	45.36		196.9
	318.15	7.57±0.03	46.11		194.3
	328.15	7.51±0.08	47.20		191.7
5-Sulfosalicylic	298.15	7.38±0.05	42.13	10.1	175.2
	310.15	7.28±0.02	43.23		172.0
	318.15	7.18±0.03	43.74		169.2
	328.15	7.15±0.06	44.92		167.7
Succinic	298.15	5.36±0.04	30.60	12.7	145.2
	310.15	5.30±0.03	31.46		142.4
	318.15	5.26±0.02	32.02		140.6
	328.15	5.17±0.05	32.50		137.7
Malic	298.15	5.21±0.06	29.74	10.7	135.6
	310.15	5.17±0.08	30.70		133.5
	318.15	5.13±0.04	31.25		131.9
	328.15	5.05±0.03	31.73		129.3
maleic	298.15	5.13±0.02	29.29	13.6	143.9
	310.15	5.05±0.08	29.99		140.5
	318.15	4.99±0.04	30.40		138.3
	328.15	4.94±0.03	31.06		136.1
Tartaric	298.15	5.02±0.05	28.66	12.9	139.4
	310.15	4.96±0.07	29.44		136.5
	318.15	4.91±0.02	29.91		134.6
	328.15	4.83±0.03	30.37		131.9
Oxalic	298.15	4.95±0.03	28.26	14.9	144.8
	310.15	4.85±0.08	28.80		141.0
	318.15	4.80±0.03	29.24		138.7
	328.15	4.74±0.06	29.78		136.2
Sham	298.15	7.81±0.02	44.59	15.9	202.9
	310.15	7.73±0.03	45.90		199.3
	318.15	7.67±0.04	46.72		196.8
	328.15	7.58±0.07	47.63		193.6
Aha	298.15	7.65±0.06	43.67	13.5	191.7
	310.15	7.54±0.03	44.78		187.9
	318.15	7.49±0.02	45.63		185.9
	328.15	7.43±0.06	46.68		183.4
Bha	298.15	7.42±0.02	42.36	17.5	200.8
	310.15	7.36±0.05	43.69		197.3
	318.15	7.32±0.07	44.57		195.1
	328.15	7.28±0.03	45.74		192.7

calculated at the constant ionic strength I=0.1mol·dm^{-3} NaNO$_3$.

The free energy change ΔG can be calculated from the equation:

$$\Delta G^0 = -2.303\ TR \log K \qquad (6)$$

Similar to the previous potentiometric studies, the enthalpy change ΔH can be determined by using temperature dependence method[42-44]. In this case, ΔH can be calculated from the straight line slope[45](which equal to-ΔH/2.303R) obtained by plotting logK against the reciprocal of absolute temperature(1/T) as shown in figure 3. Then, the standard entropy change ΔS can be calculated from Eq.(7):

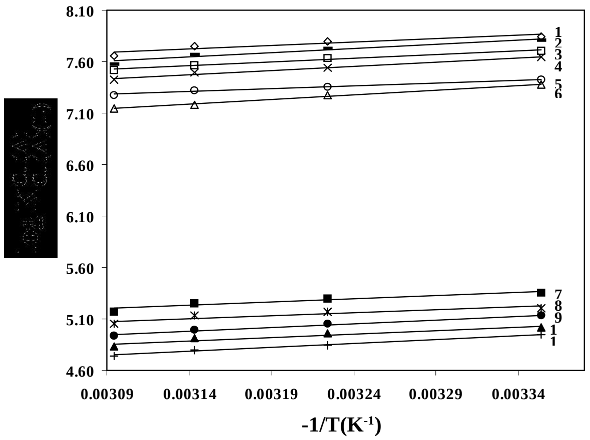


Figure 3 : Plot of versus $\log K^{(A)}_{Cu(A)(L)}$ -1/T at I=0.1 moldm^{-3}NaNO$_3$ (1) Phthalic acid; (2) Sham; (3) Salicylic acid; (4) Aha; (5) Bha; (6) 5-Sulfosalicylic acid; (7) Succinic acid;(8) Malic acid;(9) Maleic acids;(10) Tartaric acid;(11) Oxalic acid.

$$\Delta S = (\Delta H - \Delta G)/T \qquad (7)$$

The overall free energy change, and the enthalpy and entropy changes are reported in TABLE 2. The negative free energy change(ΔG) in each case indicates that the chelation is spontaneous. Furthermore, ΔG becomes more negative with decrease in temperature suggesting an increase in the extent of complex formation at lower temperatures. The strong ternary complexes are evidenced by the large magnitude of stability constants and the exothermic nature of H. The change in entropy upon complexation is related both to changes in the mode of vibration of particles in the system. A positive Δ*S* term, hence the reactions entropy favored. The ternary systems Cu(II)-tricine-the other ligands were chosen for studying the effect of ionic strength on the stability 1:1:1 ternary complexes. $\log K^{MA}_{MAL}$ values were determined at the ionic strengths 0.06, 0.10, 0.15, 0.20 and 0.25mol.dm^{-3}(TABLE 3). Linear plots were obtained when $\log K^{MA}_{MAL}$ values were plotted against I$^{1/2}$ (Figure 4) or I$^{1/2}$(1+2)$^{1/2}$ in accordance with the Debye–Hückel equation[41].

$$\log K = \log K^0 + \frac{A\Delta Z^2 I^{1/2}}{1+I^{1/2}} \qquad (8)$$

TABLE 3 : Stability constants of Cu(II)-tricine-other ligands studied at different ionic strength ($NaNO_3$) and at 298.15K

Ligands	I /mol·dm^{-3}					
	0	0.06	0.1	0.15	0.2	0.25
Phthalic	8.22±0.03	7.91±0.05	7.85±0.03	7.77±0.03	7.74±0.05	7.69±0.03
salicylic	8.04±0.04	7.79±0.02	7.70±0.04	7.66±0.06	7.61±0.02	7.56±0.03
5-sulfosalicylic	7.65±0.04	7.44±0.02	7.38±0.05	7.28±0.02	7.21±0.02	7.17±0.06
succinic	5.66±0.06	5.41±0.02	5.36±0.04	5.27±0.04	5.21±0.03	5.16±0.02
malic	5.52±0.03	5.32±0.03	5.21±0.06	5.16±0.06	5.11±0.05	5.04±0.05
maleic	5.40±0.04	5.2±0.04	5.13±0.02	5.08±0.02	5.01±0.04	4.97±0.02
tartaric	5.27±0.02	5.07±0.05	5.02±0.05	4.97±0.03	4.89±0.04	4.82±0.03
oxalic	5.22±0.03	5.01±0.03	4.95±0.03	4.87±0.02	4.81±0.06	4.76±0.02
Sham	8.1±0.02	7.86±0.04	7.81±0.02	7.73±0.05	7.69±0.02	7.61±0.02
Aha	7.91±0.04	7.72±0.03	7.65±0.06	7.58±0.02	7.53±0.02	7.48±0.06
Bha	7.75±0.02	7.53±0.04	7.42±0.02	7.37±0.02	7.32±0.06	7.25±0.03

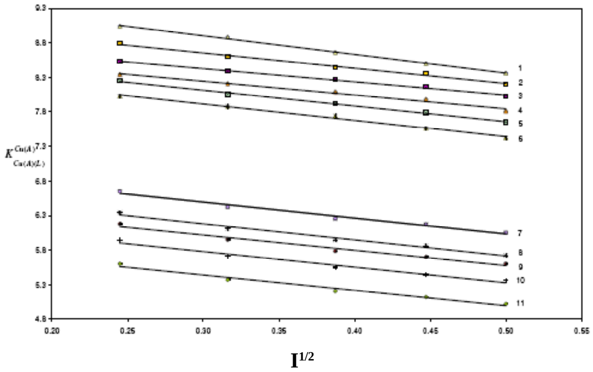


Figure 4 : Plot of versus $\log K^{(A)}_{Cu(A)(L)}$ $I^{1/2}$ at 298.15K

(1) Phthalic acid; (2) Sham; (3) Salicylic acid; (4) Aha; (5) Bha; (6) 5-Sulfosalicylic acid; (7) Succinic acid;(8) Malic acid;(9) Maleic acids;(10) Tartaric acid;(11) Oxalic acid.

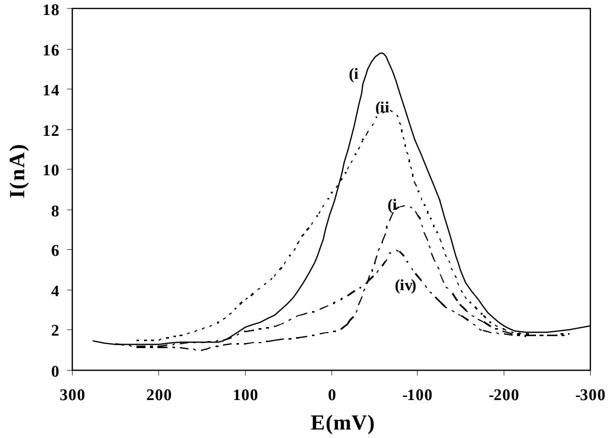


Figure 5 : Differential pulse polarograms for the Cu(II)-Sham-tircine system at I=0.1mol·dm^{-3} $NaNO_3$, pH=6.5, at 298.15K

(i) 0.001mol·dm^{-3} Cu(II); (ii) 0.001mol·dm^{-3} Cu(II)+0.001 mol·dm^{-3} tircine; (iii) 0.001mol·dm^{-3}Cu(II)+0.001mol·dm^{-3} Sham; (iv) 0.001mol·dm^{-3}Cu(II)+0.001mol·dm^{-3}tircine+ 0.001mol·dm^{-3} sham.

where K^0 is the stability constant at infinite dilution; A is the Debye–Huckel constant; I is the ionic strength; ΔZ^2 is the difference in sums of the squares of charges on product and reactant species.

Thermodynamic equilibrium constants(at I=0.00) were determined by extrapolation to zero ionic strength.

Considering that it is by now well established that the 'effective' or 'equivalent solution' dielectric constants in proteins[46] or active site cavities of enzymes[47,48] are reduced compared to that in bulk water, i.e., that the activity of water is deceased[49] due to the presence of aliphatic and aromatic amino acid side chains at the protein-water interface, one has to ask: To what extent are metal ion complex equilibria affected by these effects? Estimates for the effective dielectric constants in such locations range from about 30 to 70[46,47] compared with the approximately 80 of bulk water; hence, by employing aqueous solutions that contain about 20-50 1,4-dioxane, one may expect to simulate to some degree the situation in active site cavities[50]. The dielectric constants of the two indicated mixed solvents are about 60 and 35, respectively[50-52]. Consequently, investigation of stability constant of ternary system Cu(II)-tricine-other ligands studied in water-dioxane mixture is of biological significance.

The dielectric constant[53], hydrogen bonding, solvent basicity, dispersion forces, and proton-solvent interaction effects are commonly recognized as influencing factors in the ionization constant of a ligand in partial aqueous medium[54] and consequently the stability of a M-ligand complex. It was found that the $\log K^{MA}_{MAL}$ values increase as the amount of dioxane increases(i.e., the dielectric constant value decreases)(TABLE 4); thus,

TABLE 4 : Stability constants of the ternary system Cu(II)-tricine-other ligands studied in(water+dioxane) mixture at 298.15K, I=0.1mol·dm^{-3} NaNO$_3$

ligands	w/w %			
	00	10	30	50
Phthalic	7.85±0.03	7.91±0.04	7.95±0.02	8.07±0.03
Salicylic	7.70±0.04	7.76±0.05	7.81±0.05	7.87±0.02
5-Sulfosalicylic	7.38±0.05	7.42±0.03	7.48±0.02	7.56±0.06
Succinic	5.36±0.04	5.41±0.05	5.49±0.04	5.55±0.02
Malic	5.21±0.06	5.32±0.02	5.41±0.08	5.53±0.04
Maleic	5.13±0.02	5.18±0.04	5.29±0.02	5.37±0.06
Tartaric	5.02±0.05	5.13±0.05	5.21±0.04	5.33±0.08
Oxalic	4.95±0.03	5.01±0.02	5.14±0.08	5.29±0.02
Sham	7.81±0.02	7.88±0.08	7.93±0.02	8.01±0.04
Aha	7.65±0.06	7.72±0.03	7.79±0.02	7.81±0.03
Bha	7.42±0.02	7.51±0.08	7.62±0.03	7.76±0.04

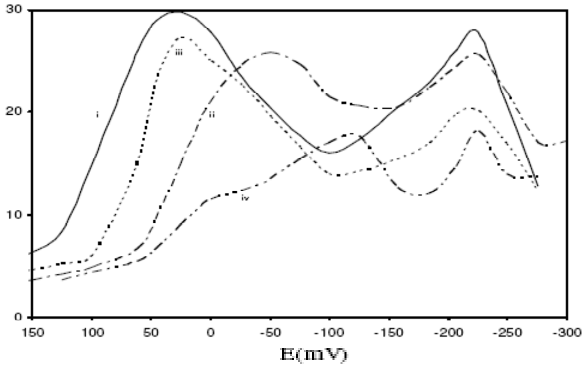


Figure 6 : Square wave polarograms for the the Cu(II)-Sham-tircine system at I=0.1 mol·dm^{-3} NaNO$_3$, pH=6.5, at 298.15K. (i) 0.001mol·dm^{-3} Cu(II); (ii) 0.001mol·dm^{-3} Cu(II)+ 0.001mol·dm^{-3} tircine; (iii) 0.001mol·dm^{-3} Cu(II)+0.001mol·dm^{-3} swqham; (iv) 0.001mol·dm^{-3} Cu(II)+0.001mol·dm^{-3} tircine+0.001 mol·dm^{-3} Sham.

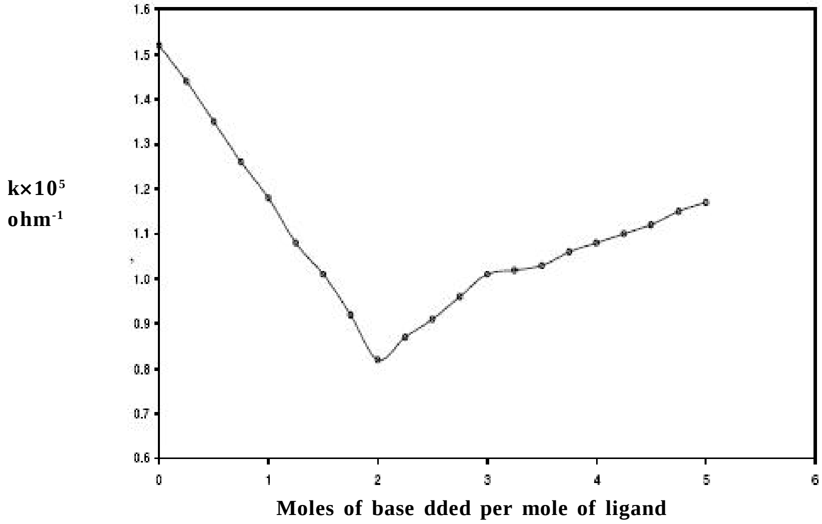


Figure 7 : Conductometric titration of the Cu^{II}–Sham-tricine system, at I=0.1mol·dm^{-3} NaNO$_3$, and 298.15K

the dielectric constant plays an important role in the determination of these values.

Confirmation of the ternary complexes of the type Cu(II)-Sham-tricine in solution has been carried out using differential pulse polarography(DPP), square wave voltammetry (SWV), conductometric, and spectrophotometric measurements.

Representative differential pulse polarogram for the system Cu(II)-sham-tricine is given in figure 5. The differential pulse polarograms of the Cu(II) solution shown one cathodic peak at E_p=-68mV. This peak may be described as a result of the reduction of Cu(II) to Cu(in two-electron-transfer process) at the glassy carbon electrode.

The addition of primary or secondary ligands caused a slight shift of the cathodic of the binary and ternary complexes in solution.

The most interesting observation during the square wave voltammetric reduction of the Cu(II)-sham-tricine ternary system is the discrimination of the two individual one-electron steps of Cu(II/I) and Cu(I/0) couples. Figure 6 shows the square wave voltammogram for 1× 10^{-3}mol·dm^{-3} Cu(II) in the absence and in the presence of primary and secondary ligands in the above-mentioned ternary complexes. By addition of primary and secondary ligands, a more electronegative peak was observed. The new peaks confirm the formation of ternary Cu(II)-sham-tricine in solution.

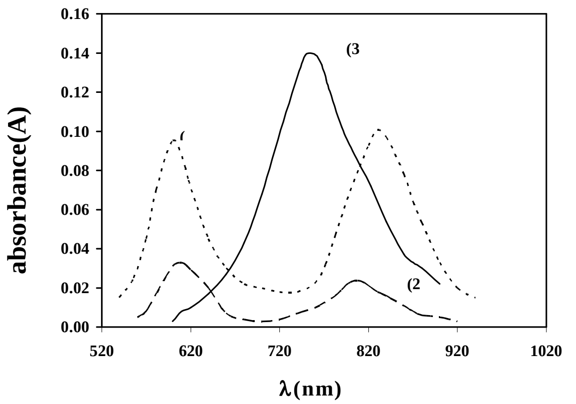


Figure 8 : Visible absorbance spectra for the Cu(II)-tircine-succinic acid system at I=0.1 mol·dm^{-3} NaNO$_3$ and at 298.15K (1) 1×10^{-3}mol·dm^{-3} Cu(II)+1×10^{-3}mol·dm^{-3} tircine; (2) 1×10^{-3}mol·dm^{-3} Cu(II)+1×10^{-3}mol·dm^{-3} succinic acid; (3) 1×10^{-3}mol·dm^{-3} Cu(II)+110^{-3}mol·dm^{-3} tircine+1×10^{-3}mol dm^{-3} succinic acid

The conductometric titration curve for the ternary complex of Cu(II) with sham and tricine(Figure 7) shows an initial decrease and an inflection at a=2. This probably corresponds to the neutralization of H$^+$ ions originating from the formation of the Cu(II)-sham binary complex. In the 3≥a≥2 range, the conductance increases slightly due to the formation of a ternary complex associated with the release of a H$^+$ ion from tricine. Beyond a=3, the conductance increases appreciably due to the presence of an excess of NaOH.

Figure 8 shows the visible absorption spectra of the binary and ternary Cu(II) systems at given pH values. The spectra of the ternary systems are quite different from those of the binary systems, emphasizing the formation of the former in solution.

Evidence for the structure of isolated solid ternary complexes needs further study(e.g. Xray crystal structure determination), which must be considered in the future.

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