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Equilibrium Studies of Binary and Ternary Complexes Involving Tricine and Some Selected α-Amino Acids

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Summary. The formation equilibria for the binary complexes of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Mn^{II}, Pb^{II}, Th^{IV}, UO_2^{II}, and Ce^{III} with tricine and for the ternary complexes involving some α-amino acids (glycine, α-alanine, proline, serine, asparagine, and aspartic acid) were investigated using *pH*-metric technique. The formation of binary and ternary complexes was inferred from the *pH*-metric titration curves. It was deduced that tricine acts as a primary ligand in the ternary complexes involving the monocarboxylic amino acids (glycine, α-alanine, proline, serine, and asparagine), whereas it behaves as a secondary ligand in the ternary systems containing the dicarboxylic aspartic acid. The ternary complex formation was found to take place in a stepwise manner. The stability constants of the complexes formed in aqueous solutions were determined potentiometrically under the experimental conditions ($t = 25°C$, $I = 0.1\ mol\ dm^{-3}$ $NaNO_3$). The order of stability of the ternary complexes in terms of the nature of the amino acids is investigated and discussed. The values of $\Delta \log K$ for the ternary complexes have been evaluated and discussed. Evaluation of the effects of ionic strength and temperature of the medium on the stability of the ternary system M^{II}-tricine-α-alanine ($M^{II} = Co^{II}$, Ni^{II}, and Cu^{II}) has been studied. The thermodynamic parameters were calculated and discussed.

Keywords. Amino acids; Binary and ternary complexes; Stability constants; Tricine.

Introduction

The importance of metal ions in biological systems and the phenomenon of complexation are well recognised. However, an accurate elucidation of the complexation process is apparently complicated in metabolic reactions where a variety of equilibria involving a number of metal ions and ligands coexist. Yet, studies on complexation reactions between biologically important metal ions and donor molecules in vitro are desirable. Complexation equilibria in such systems would be much closer to those existing in metabolic reactions.

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N-[Tris(hydroxymethyl)methyl]glycine, $(HOCH_2)_3CNHCH_2COOH$ (trivial name, tricine), which was first prepared by *Good* [1], has proved quite useful as a buffer of *pH* range 7.2–8.5 in biological research studies [2]. It has also been used as a buffer in animal tissue culture by *Gardner* [3], in fluorescent dye reagent to analyze cells in urine and on measurement of small masses of protein with bicinchaninic acid [4, 5]. *Bates* et al. [6] prepared tricine buffer of $pH = 7.407$ which matches closely that of human blood. The same authors have also determined the two *pK* values for the ampholyte tricine in 50% methanol and have derived some standard thermodynamic parameters by e.m.f. measurements over the temperature range 5–50°C. Recently, *Jumean* and *Qaderi* [7] reported the volumetric behavior of tricine in mixed aqueous solvents.

Scanning the literature survey reveals that solution studies on the binary [8–11] and ternary [12] metal complexes of tricine, using polarographic [8, 9], voltammetric [10], and potentiometric [11, 12] techniques, are scarce.

In connection with our continuing research oriented toward the study of complexation equilibria and the determination of stability constants of binary and ternary complexes of biological importance [13–15], the present work concerns a study of the solution equilibria involved in the formation of binary and ternary metal complexes involving tricine and some selected α-amino acids, as these systems mimic many biological reactions (enzyme – metal ion – buffer interactions).

Results and Discussion

Representative *pH*-metric equilibrium titration curves for the free and metal complexed ligands are depicted in Figs. 1 and 2.

The dissociation constant of cationic tricine, H_2A^+, could not be calculated potentiometrically under the present experimental conditions because of the highly acidic nature of the associated proton. The second proton dissociation constant of tricine, corresponding to the cationic ($\equiv N^+H$) group, was determined potentiometrically from curves (a) and (b) using a computer program based on *Irving* and *Rossotti pH* titration technique [16]. The details regarding the potentiometric method were reported in the experimental section. The value obtained (8.06), at 25°C and $I = 0.10\,\text{mol}\,\text{dm}^{-3}$ $NaNO_3$, is compared with that of glycine (9.76), the lower value of the former may be due to the inductive electron attraction by the hydroxyl oxygens, and it agreed quite well with that previously reported [2], after allowing for changes in experimental conditions as well as methods of calculation.

The acid–base equilibrium of the Zwitter ion form of tricine can be represented as follows in Scheme 1.

The proton dissociation constants of α-amino acids studied have also been determined potentiometrically from curves (a) and (d). The values of pKa_2 for monocarboxylic amino acids, and pKa_2 and pKa_3 for the dicarboxylic aspartic acid, although already reported in Ref. [17], have been redetermined at 25°C and $I = 0.10\,\text{mol}\,\text{dm}^{-3}$ $NaNO_3$ to obtain values using the same experimental procedures as used in the study of binary and ternary systems, and are in agreement with data found in the literature. It is worth mentioning that the pKa_1 values of the amino acids investigated are too low (≤ 2.30) [18], and exist only in strongly acidic

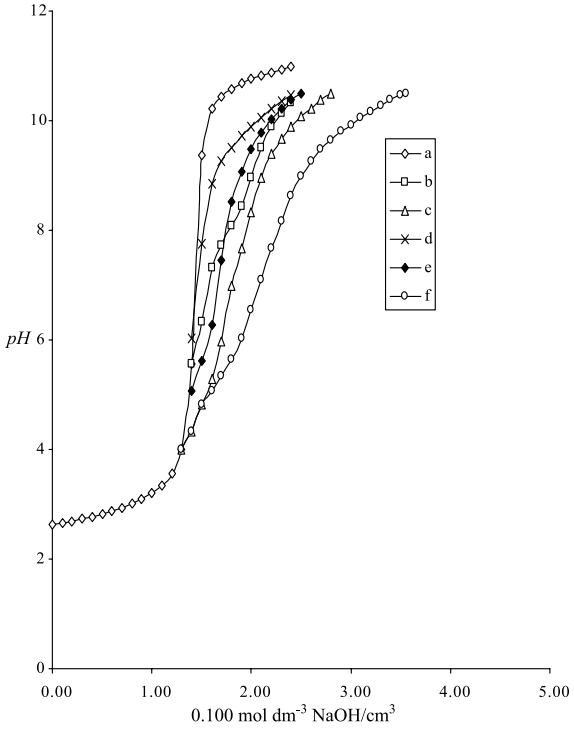


Fig. 1. Potentiometric titration curves for the Ni^{II}-tricine-α-alanine system at 25°C and $I = 0.1\,\text{mol}\,\text{dm}^{-3}$ $NaNO_3$

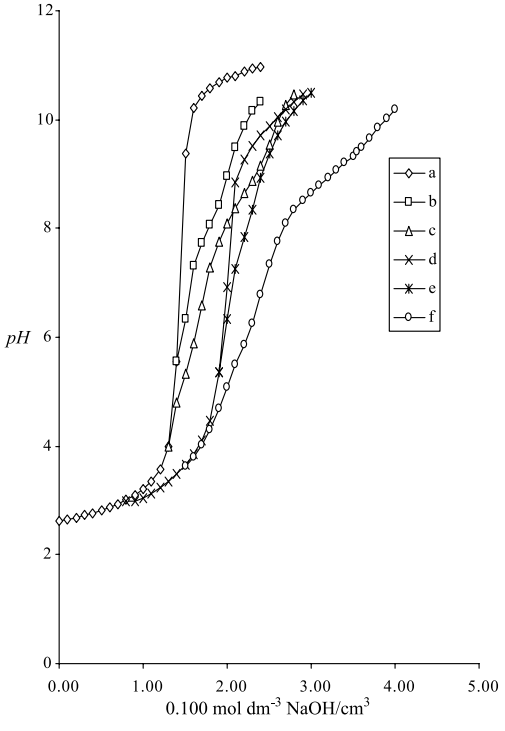
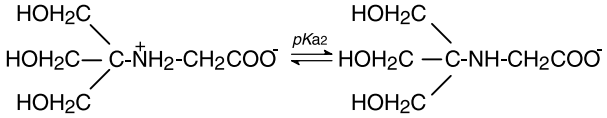


Fig. 2. Potentiometric titration curves for the Ce^{III}-tricine-aspartic acid system at 25°C and $I = 0.1\,\text{mol}\,\text{dm}^{-3}$ $NaNO_3$



Scheme 1

solutions. Therefore, these values are not used in calculations, since the *pH*-metric data are measured in the range $3 \leq pH \leq 10.5$.

Analysis of the complexed ligands curves (c) and (e), as shown in Figs. 1 and 2, 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 complexation reaction proceeds by releasing of protons from such ligands. Generally, it is observed that the binary metal complexes of tricine and monocarboxylic amino acids begin to form in the *pH* range of 3.2–5.5 and 3.6–6.8, respectively. With respect to the titration curves of the binary metal complexes involving aspartic acid, one may deduce that these complexes begin to form in the *pH* range 2.8–3.0.

The complexes are quite stable up to high *pH* values. 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 stability constants of 1:1 and 1:2 binary complexes of tricine with the metal ions selected have been determined at 25°C and $I = 0.1\ \mathrm{mol\,dm^{-3}}$ $NaNO_3$. The values obtained are more or less in good agreement with the literature data [11, 12]. However, our stability constant for the Ce^{III}-tricine 1:2 complex is lower than that determined recently [11] by 1.24 units. The disagreement found may be ascribed to the different methods, temperature, and ionic strength used for determination.

In our study, tricine (*A*) is considered as a primary ligand and monocarboxylic amino acids (*L*) as secondary ligands, since *MA* species are formed at lower *pH* values than for *ML* species. The observed lowering of the 1:1:1 ternary complex titration curve (f) in comparison to binary *MA* and *ML* titration curves (c) and (e), indicates the formation of ternary complexes in solution as shown in Fig. 1.

The existence of a ternary complex is also ascertained by comparison of the ternary complex titration curve with the composite curve, obtained by graphical addition of the monocarboxylic amino acid titration data to that of the 1:1 metal–tricine titration curve. The ternary system was found to deviate considerably from the resultant composite curve indicating the formation of a ternary complex. Therefore, it is assumed that in the presence of both ligands tricine is ligated to the metal ion, then followed by ligation of the monocarboxylic amino acid; that is, the ternary complex formation could be considered in stepwise complexation equilibria (Eqs. (1) and (2):

$$M + \text{tricine} \rightleftharpoons M(\text{tricine}) \tag{1}$$

$$M(\text{tricine}) + L \rightleftharpoons M(\text{tricine})(L) \tag{2}$$

$$K^{M(\text{tricine})}_{M(\text{tricine})(L)} = \frac{[M(\text{tricine})(L)]}{[M(\text{tricine})][L]} \tag{3}$$

where $L =$ monocarboxylic amino acid.

It is observed, from the titration curves representing metal – tricine – aspartic acid system, that the complexation equilibria are as follows:

$$M + \text{aspartic acid} \rightleftharpoons M(\text{aspartic acid}) \tag{4}$$

$$M(\text{aspartic acid}) + \text{tricine} \rightleftharpoons M(\text{aspartic acid})(\text{tricine}) \tag{5}$$

$$K^{M(\text{aspartic acid})}_{M(\text{aspartic acid})(\text{tricine})} = \frac{[M(\text{aspartic acid})(\text{tricine})]}{[M(\text{aspartic acid})](\text{tricine})]} \tag{6}$$

In Fig. 2 a representative set of potentiometric titration curves for the ternary complex of Ce^{III} with aspartic acid and tricine is displayed. The behavior reveals that in the presence of the two ligands, α,β-dicarboxylic aspartate interacts first with the metal ion forming a highly stable binary complex, and then interacts with tricine, forming a ternary complex.

Examination of the stability constant values of the same metal ion ternary complexes (Table 1) reveals the following remarks:

(a) A comparison of the stability constants of the metal – tricine – amino acid ternary systems indicates higher stabilities of the ternary complexes containing the α,β-dicarboxylic amino acid (aspartic acid). This behavior can be mainly attributed to the fact that the dicarboxylic amino acid is much more prone to complex formation than the monocarboxylic amino acids (glycine, α-alanine, proline, serine, or asparagine). This is due to the effective high basicity of the dicarboxylic amino acid as well as its tendency to act as ONO tridentate.

(b) Stability of ternary complexes involving glycine are higher than those containing α-alanine. This behavior does not follow the basicities as expected, probably because the pKa values of the amino acids are so similar. It is suggested that the steric hindrance, caused by the presence of a methyl group on the carbon bearing the amino group (α-alanine), is responsible for the lower stability of its ternary complexes.

(c) The complex stability of the same metal ion ternary complexes containing proline and serine follows the order: proline $>$ serine. This behavior can be explained in terms of the effective basicity of the free conjugate base of these monocarboxylic amino acids, *i.e.* their affinity to act as σ-donor. Accordingly, the observed high stability of proline ternary complex on comparison to that of the corresponding one containing serine, can be ascribed to the high basicity of its free conjugate base ($pK\text{a}_2 = 10.41$ and 9.05 for proline and serine, respectively). This reflects itself to the fact that proline behaves as a better σ-donor than serine. It is worth mentioning that ternary complexes of proline or serine with Mn^{II} metal ion could not be detected potentiometrically under our experimental conditions; hence, the stability constants of their ternary complexes could not be determined.

Table 1. Stability constants of 1:1:1 ternary complexes of tricine with α-amino acids and $\Delta \log K$ values at 25°C, $I = 0.10\,\text{mol}\,\text{dm}^{-3}$ $NaNO_3$

Cation	$\log K^{MA}_{MAL}$ / α-Amino acids					
	Glycine	α-Alanine	Proline	Serine	Asparagine	Aspartic acid
Co^{II}	5.66 ± 0.03	4.58 ± 0.05	4.74 ± 0.03	4.57 ± 0.02	4.48 ± 0.08	6.31 ± 0.03
Ni^{II}	7.58 ± 0.05	6.60 ± 0.03	7.21 ± 0.05	6.37 ± 0.02	6.05 ± 0.05	7.59 ± 0.04
Cu^{II}	9.14 ± 0.04	7.96 ± 0.04	8.62 ± 0.02	7.68 ± 0.07	7.53 ± 0.05	9.24 ± 0.03
Zn^{II}	6.91 ± 0.07	6.72 ± 0.05	6.72 ± 0.04	5.93 ± 0.03	5.28 ± 0.02	7.02 ± 0.06
Cd^{II}	4.76 ± 0.04	4.69 ± 0.03	4.71 ± 0.06	4.63 ± 0.03	4.48 ± 0.09	5.49 ± 0.07
Mn^{II}	4.52 ± 0.08	4.41 ± 0.06	–	–	3.79 ± 0.03	5.23 ± 0.03
Pb^{II}	7.95 ± 0.06	6.85 ± 0.05	7.42 ± 0.03	6.53 ± 0.08	6.81 ± 0.02	7.82 ± 0.02
Th^{IV}	9.55 ± 0.06	9.19 ± 0.04	9.41 ± 0.06	8.86 ± 0.03	8.63 ± 0.03	10.38 ± 0.04
UO_2^{II}	8.47 ± 0.02	8.09 ± 0.03	8.31 ± 0.05	7.77 ± 0.02	7.19 ± 0.05	9.02 ± 0.08
Ce^{III}	6.02 ± 0.04	5.88 ± 0.06	5.97 ± 0.02	5.69 ± 0.05	4.62 ± 0.04	7.14 ± 0.03

Cation	$\Delta \log K$ / α-Amino acids					
	Glycine	α-Alanine	Proline	Serine	Asparagine	Aspartic acid
Co^{II}	0.44	0.35	0.43	0.31	0.45	1.71
Ni^{II}	1.39	1.12	0.39	0.99	0.69	1.45
Cu^{II}	1.25	0.32	0.36	0.66	0.62	1.57
Zn^{II}	1.40	1.35	0.40	1.12	0.81	1.66
Cd^{II}	−0.17	0.25	−0.05	0.22	0.24	0.91
Mn^{II}	0.56	0.57	–	–	0.27	1.72
Pb^{II}	1.74	0.97	1.29	0.50	1.19	1.66
Th^{IV}	0.33	0.18	0.26	0.18	0.12	2.68
UO_2^{II}	0.20	0.07	0.13	0.09	0.15	2.28
Ce^{III}	1.25	1.20	1.27	1.19	1.01	1.66

(d) The observed low stability of the ternary complexes containing asparagine can be mainly attributed to the low basicity of asparagine free conjugate base ($pKa_2 = 8.82$).

The relative stability of the ternary and binary complexes can be quantitatively expressed in a number of different ways. It has been argued that a comparison can best be made in terms of $\Delta \log K$ values [19]. Table 1 demonstrates the difference in stabilities of the binary and ternary complexes in terms of $\Delta \log K$, as defined by Eq. (7)

$$\begin{aligned} \Delta \log K &= \log K^{M(\text{tricine})}_{M(\text{tricine})(L)} - \log K^{M}_{M(L)} \\ &= \log K^{M(\text{aspartic acid})}_{M(\text{aspartic acid})(\text{tricine})} - \log K^{M}_{M(\text{tricine})} \end{aligned} \tag{7}$$

where $L =$ monocarboxylic amino acid.

The second form of Eq. (7) is used in the case of metal – aspartic acid – tricine ternary systems, where aspartic acid acts as a primary ligand and tricine as a secondary ligand, as mentioned previously in this work.

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

The ionic strength of solutions is a measure of total electrolyte concentration and is defined according to Ref. [20] by: $I = 1/2\ \Sigma\ C_i\ Z_i^2$ where Z_i is the charge on each individual ion, and C_i is the concentration of the ion i. The ionic strength of the medium is related to the activity coefficients of the ions in solution by the following relation: $-\log f_i = 0.51\ Z_i^2 \sqrt{I}/(1 + 0.33\,\alpha_i\ \sqrt{I})$ where f_i is the activity coefficient for ion i, the numbers 0.51 and 0.33 are constants for water at 25°C, and the former includes the $-3/2$ power of both the dielectric constant of the solvent and the absolute temperature; α_i is the ion size parameter, which is the effective diameter of the hydrated ion. Therefore, an increase in ionic strength will decreases the activity coefficient and, consequently, the activity of the ions. The tendency for dissociation of the ligands and, consequently, the complexation process decreases as reflected by the decreasing of the dissociation constants of the ligands and the stability constants of metal complexes. This is in full agreement with the *Debye–Hückel* equation [21].

The ternary system M^{II}-tricine-α-alanine (where $M^{II} = Co^{II}$, Ni^{II}, and Cu^{II}) was chosen for studying the effect of ionic strength on dissociation of the ligands as

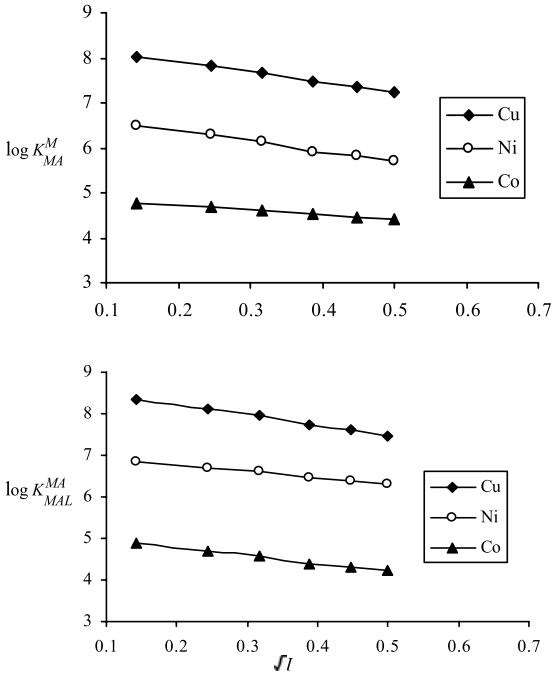


Fig. 3. Plot of $\log K^M_{MA}$ and $\log K^{MA}_{MAL}$ *vs.* $\sqrt{I}$ at 25°C

Table 2. Dissociation constants of tricine and α-alanine and stability constants of their 1:1 binary and 1:1:1 ternary complexes at 25°C and different ionic strengths

Ionic strength I ($NaNO_3$)	pKa_2		$\log K^M_{MA}$		
	Tricine	α-Alanine	Co^{II}	Ni^{II}	Cu^{II}
0.25	7.80 ± 0.03	9.42 ± 0.02	4.40 ± 0.02	5.71 ± 0.03	7.25 ± 0.04
0.20	7.88 ± 0.02	9.48 ± 0.03	4.46 ± 0.04	5.81 ± 0.05	7.34 ± 0.03
0.15	7.94 ± 0.05	9.54 ± 0.03	4.51 ± 0.03	5.92 ± 0.02	7.46 ± 0.07
0.10	8.06 ± 0.05	9.68 ± 0.05	4.60 ± 0.04	6.14 ± 0.07	7.67 ± 0.06
0.06	8.14 ± 0.06	9.74 ± 0.02	4.68 ± 0.06	6.28 ± 0.03	7.82 ± 0.02
0.02	8.26 ± 0.06	9.88 ± 0.04	4.78 ± 0.05	6.48 ± 0.04	8.02 ± 0.03
0.00	8.44 ± 0.02	10.06 ± 0.03	4.93 ± 0.02	6.76 ± 0.07	8.32 ± 0.05

Ionic strength I ($NaNO_3$)	$\log K^M_{ML}$			$\log K^{MA}_{MAL}$		
	Co^{II}	Ni^{II}	Cu^{II}	Co^{II}	Ni^{II}	Cu^{II}
0.25	4.34 ± 0.02	4.98 ± 0.05	7.18 ± 0.03	4.22 ± 0.06	6.32 ± 0.03	7.48 ± 0.04
0.20	4.41 ± 0.03	5.12 ± 0.03	7.28 ± 0.04	4.31 ± 0.02	6.38 ± 0.05	7.60 ± 0.03
0.15	4.49 ± 0.05	5.26 ± 0.06	7.40 ± 0.04	4.40 ± 0.04	6.46 ± 0.03	7.73 ± 0.05
0.10	4.63 ± 0.02	5.48 ± 0.04	7.64 ± 0.03	4.58 ± 0.05	6.60 ± 0.03	7.96 ± 0.04
0.06	4.74 ± 0.04	5.72 ± 0.02	7.78 ± 0.07	4.70 ± 0.03	6.70 ± 0.03	8.12 ± 0.02
0.02	4.91 ± 0.02	5.98 ± 0.03	7.98 ± 0.02	4.88 ± 0.06	6.83 ± 0.06	8.36 ± 0.03
0.00	5.08 ± 0.03	6.36 ± 0.04	8.30 ± 0.05	5.06 ± 0.02	7.05 ± 0.04	8.72 ± 0.02

well as the stability of 1:1 binary and 1:1:1 ternary complexes. The plot of $\log K^M_{MA}$ and $\log K^{MA}_{MAL}$ *vs.* $\sqrt{I}$ is linear as shown in Fig. 3. The thermodynamic equilibrium constants (at $I = 0.0$) were determined by applying linear regression analysis. The results obtained are reported in Table 2.

The thermodynamic quantities associated with (a) the dissociation of the ligands chosen (tricine and α-alanine), (b) the formation of 1:1 binary complexes, and (c) the formation of 1:1:1 ternary complexes in the ternary system M^{II}-tricine-α-alanine (where $M^{II} = Co^{II}$, Ni^{II} and Cu^{II}) were also studied at the constant ionic strength $I = 0.10\,\text{mol}\,\text{dm}^{-3}$ $NaNO_3$. The equilibrium constants have been evaluated at 25, 35, 45, and 55°C along with the different thermodynamic parameters. The values obtained are given in Table 3.

The enthalpy changes for the dissociation of the ligands are positive (endothermic). The positive values of ΔG° for the dissociation processes of the ligands denote that such processes are not spontaneous. In addition, the negative values of entropy changes pointing to increased ordering due to association.

The values of $\log K^M_{MA}$, $\log K^M_{ML}$, and $\log K^{MA}_{MAL}$, at different temperatures (Table 3), show 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 [21]. A plot of $\log K^M_{MA}$, and $\log K^{MA}_{MAL}$ *vs.* $-1/T$ gives a straight line (Fig. 4).

Table 3. Thermodynamic quantities associated with the dissociation of the ligands studied, the interaction of metal ion with the ligands at 1:1 molar ratio, and the interaction of metal ion with the ligands at a 1:1:1 molar ratio, $I = 0.10\,\mathrm{mol\,dm^{-3}}$ $NaNO_3$

Ligand or complex	Cation	pKa_2 or $\log K$			
		$t/°C = 25$	35	45	55
tricine	H	8.06 ± 0.02	7.94 ± 0.04	7.84 ± 0.02	7.72 ± 0.03
α-alanine	H	9.68 ± 0.04	9.52 ± 0.03	9.38 ± 0.02	9.22 ± 0.02
(1:1) binary complex of tricine	Co^{II}	4.60 ± 0.02	4.50 ± 0.06	4.41 ± 0.03	4.32 ± 0.05
	Ni^{II}	6.14 ± 0.03	6.01 ± 0.03	5.89 ± 0.04	5.76 ± 0.06
	Cu^{II}	7.67 ± 0.05	7.47 ± 0.04	7.29 ± 0.03	7.11 ± 0.06
(1:1) binary complex of α-alanine	Co^{II}	4.63 ± 0.05	4.51 ± 0.02	4.40 ± 0.06	4.30 ± 0.03
	Ni^{II}	5.48 ± 0.02	5.31 ± 0.02	5.17 ± 0.03	5.04 ± 0.02
	Cu^{II}	7.64 ± 0.04	7.46 ± 0.04	7.30 ± 0.02	7.13 ± 0.04
(1:1:1) ternary complex	Co^{II}	4.58 ± 0.06	4.46 ± 0.05	4.36 ± 0.04	4.25 ± 0.04
	Ni^{II}	6.60 ± 0.06	6.45 ± 0.02	6.21 ± 0.04	6.07 ± 0.02
	Cu^{II}	7.96 ± 0.03	7.68 ± 0.04	7.44 ± 0.06	7.18 ± 0.03
Ligand or complex	Cation	$\Delta H°$ $kJ \cdot mol^{-1}$	$\Delta G°$ $kJ \cdot mol^{-1}$	$\Delta S°$ $J \cdot mol^{-1} \cdot K^{-1}$	
tricine	H	21.07	46.00	−144.79	
α-alanine	H	28.73	55.25	−172.37	
(1:1) binary complex of tricine	Co^{II}	−17.24	−26.25	80.05	
	Ni^{II}	−24.90	−35.04	106.87	
	Cu^{II}	−34.47	−43.77	130.81	
(1:1) binary complex of α-alanine	Co^{II}	−19.15	−26.42	79.29	
	Ni^{II}	−25.85	−31.28	92.31	
	Cu^{II}	−30.64	−43.60	132.15	
(1:1:1) ternary complex	Co^{II}	−21.07	−26.14	78.33	
	Ni^{II}	−26.81	−37.67	112.33	
	Cu^{II}	−47.88	−45.43	128.51	

It is of interest to note that the $\Delta H°$ values for the ternary systems studied are more negative as compared to those of the corresponding binary ones, and ensure that despite the steric hindrance due to the primary ligand, tricine, the bond is stronger in the ternary complex formation [22]. Also, the relatively high negative values of $\Delta H°$ for ternary complexes may be due to less competition faced by a secondary ligand at this step from a water molecule [22]. However, the complexation process is spontaneous in nature, as characterized by the negative $\Delta G°$ values. The $\Delta S°$ values obtained substantiate the suggestion that the different binary and ternary complexes are formed due to the coordination of the ligand anion to the metal cation. Moreover, the positive values of $\Delta S°$ suggests also a desolvation of the ligands, resulting in weak solvent–ligand interactions, to the advantage of the metal ion–ligand interaction [23]. It was found that magnitude of the $\Delta H°$, $\Delta G°$, and $\Delta S°$ values for all the complexes investigated, in terms of the nature of the

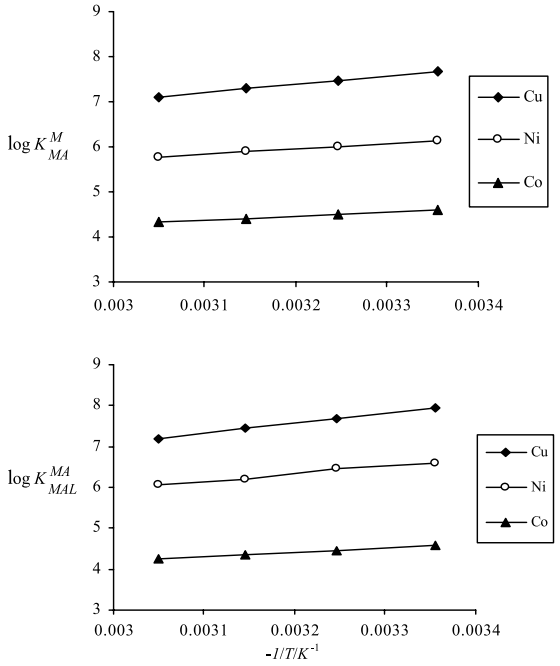


Fig. 4. Plot of $\log K^{M}_{MA}$ and $\log K^{MA}_{MAL}$ *vs.* $-1/T$ at $I = 0.10\,\mathrm{mol\,dm^{-3}}$ $NaNO_3$

metal ion, increases in the order $Cu^{II} > Ni^{II} > Co^{II}$, which follows the *Irving–Williams* order [24]. This behavior is consistent with results obtained for the values of the stability constants of the complexes studied, as confirmed recently by *Khan* et al. [25].

Experimental

Materials and Solutions

N-[Tris(hydroxymethyl)methyl]glycine (tricine) of analytical reagent grade (Sigma) was used without further purification. Chromatographically pure amino acids were A.R. grade, BDH products. The metal salts were provided also by BDH as nitrates or chlorides. All solutions were prepared in bidistilled water. A stock solution of tricine was prepared by dissolving an accurate amount by mass in the appropriate volume of bidistilled water. The metal ion solutions were standardized by *EDTA* using suitable indicators [26]. Carbonate-free sodium hydroxide solution was prepared by dissolving the Analar pellets in bidistilled water, and the solution was standardized potentiometrically with potassium hydrogen phthalate (Merck AG). Nitric acid, sodium hydroxide, and sodium nitrate were from Merck p.a.

Apparatus and Procedure

The *pH* titrations were performed using a Metrohm 702 titroprocessor equipped with a 665 dosimat (Switzerland). The titroprocessor and electrode were calibrated with standard buffer solutions; based on the scale of the U.S. National Bureau of Standards [27]. The *pH*-metric titrations were carried out at the desired temperature in a purified nitrogen atmosphere.

The following solutions were prepared (total volume 50 cm^3) and titrated potentiometrically against standard carbonate-free NaOH (0.10 mol dm^{-3}) solution:

(a) HNO_3 (0.003 mol dm^{-3}) + $NaNO_3$ (0.10 mol dm^{-3})
(b) solution a + 0.001 mol dm^{-3} tricine
(c) solution b + 0.0004 mol dm^{-3} metal ion
(d) solution a + 0.001 mol dm^{-3} amino acid
(e) solution d + 0.0004 mol dm^{-3} metal ion
(f) solution a + 0.001 mol dm^{-3} metal ion + 0.001 mol dm^{-3} tricine + 0.001 mol dm^{-3} amino acid

Each of the above solutions was thermostated at the required temperature with an accuracy of $\pm 0.1°C$, where the solutions were left to stand for about 15 min before titration. Magnetic stirrer was used during all titrations. Multiple titrations were carried out for each system. All calculations were performed using a computer program based on unweighted linear least-squares fits.

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