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Equilibrium studies of ternary systems containing some selected transition metal ions, triazoles and aromatic carboxylic acids

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Abstract−Solution equilibria of the binary and ternary complex systems of the divalent transition metal ions Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+} with 1,2,4-triazole (TRZ), 3-mercapto-1,2,4-triazole (TRZSH), and 3-amino-1,2,4-triazole (TRZAM) and aromatic carboxylic acids (phthalic, anthranilic, salicylic, and 5-sulfosalicylic acid) have been studied pH-metrically at (25.0±0.1) ºC, and a constant ionic strength $I=1\times10^{-1}$ mol L^{-1} $NaNO_3$ in an aqueous medium. The potentiometric titration curves show that binary and ternary complexes of these ligands are formed in solution. The stability constants of the different binary and ternary complexes formed were calculated on the basis of computer analysis of the titration data. The relative stability of the different ternary complex species is expressed in terms of Δ log K values, log X and R. S.% parameters. The effect of temperature of the medium on both the proton-ligand equilibria for TRZAM and phthalic acid and their metal-ligand equilibria with Cu^{2+}, Ni^{2+}, and Co^{2+} has been studied along with the corresponding thermodynamic parameters. The complexation behavior of ternary complexes is ascertained using conductivity measurements. In addition, the formation of ternary complexes in solution has been confirmed by using UV-visible spectrophotometry.

Keywords: Triazoles, Equilibrium Studies, Stability Constants, Binary and Ternary Complexes, Aromatic Carboxylic Acids

INTRODUCTION

There has been considerable interest in the chemistry of metal complexes of triazole compounds due to their biological applications such as antifungal, antibacterial [1-3], anti-inflammatory, antimycobacterials [3,4], and anticonvulsant [5]. Triazole complexes are very important in the production of pharmaceutical drugs used to inhibit the growth of tumors and cancer in mammals [6-9]. The importance of the metal complexes of triazoles in biological systems is well-recognized in the literature [10]. Moreover, the bioactivities of such compounds have been correlated with their ability to form complexes with the metal ions in the biological system [11]. Therefore, understanding the interaction between triazoles and metal ions that commonly present in living systems usually yields important information about their biological activity.

Ternary complexes formed between metal ions and two different types of bioligands, namely heteroaromatic nitrogen bases and bioligands, may be considered as models for metal ion mediated biochemical interactions [12]. Among these compounds, copper (II) complexes of hetero cyclic amines are of great interest, since they exhibit numerous biological activities such as antitumor [13], anti-candida [14], antimycobacterial [15] activity, etc., in a number of biochemical processes, Cu^{++} is involved in mixed-ligand complex formation and ligand catalyzed complex formation reactions [16-18].

Extensive studies have been carried out on the synthesis and characterization of binary metal complexes of triazole compounds [19-23]. However, a number of studies were performed on binary systems of 1,2,4-triazole and its alkyl, mercapto, and amino derivatives with some metal ions in aqueous solutions by means of pH-metric titration and absorption spectra and have been revealed in the literature [24-27]. Studies of such ligands are relevant to medicine as they are linked with the problem of searching for compounds with potential properties as chelators for the removal of toxic metals from the body. Mixed ligand complexes are becoming increasingly more important in equilibrium chemistry. Using stability constants, the chemical behavior, coordination ability, coordination mode and the relation regarding the structure and stability of the complexes can be obtained, and are the basis of enzyme-mimicking investigations [28]. A survey of the literature has also revealed that little work, if any, has been done on ternary metal complexes containing triazole compounds [29,30].

Accordingly, continuing our published work on binary and ternary complexes [31-34], we report on complex formation between divalent transition metal ion, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+} and 1,2,4-triazole (TRZ), 3-mercapto-1,2,4-triazole (TRZSH), and 3-amino-1,2,4-triazole (TRZAM) and the biologically important aromatic carboxylic acids, phthalic, anthranilic, salicylic, and 5-sulfosalicylic in aqueous media at (25.0±0.1) ºC, and constant ionic strength I= 0.10 mol L^{-1} $NaNO_3$. The effect of temperature of the medium on both the proton-ligand equilibria for TRZAM and phthalic acid and their metal-ligand equilibria with Cu^{2+}, Ni^{2+}, and Co^{2+} has been studied along with the corresponding thermodynamic parameters. The complexation behavior of ternary complexes is ascertained using conductivity measurements for (Zn^{2+}+Salicylic acid+TRZ and Zn^{2+}+ 5-Sulfosalicylic acid+TRZ). In addition, the formation of ternary complexes in solution has been confirmed by UV-visible spectrophotometry for (Cu^{2+}+5-Sulfosalicylic acid+TRZ).

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EXPERIMENTAL SECTION

1. Materials

The triazole compounds, 1,2,4-triazole (TRZ), 3-mercapto-1,2,4-triazole (TRZSH), and 3-amino-1,2,4-triazole (TRZAM) were analytical-grade Fluka products; the purities of these compounds exceeded 99.4%, as verified by the Gran's method [35]. Aromatic carboxylic acids (phthalic, anthranilic, salicylic, and 5-sulfosalicylic) were from Merck PA. The metal salts were provided by BDH as nitrates or chlorides. Stock solutions of the metal salts were prepared in deionized water, and the metal ion concentrations were checked complexometrically by standard EDTA using suitable indicators [36]. Carbonate-free sodium hydroxide (titrant, prepared in 0.10 mol L^{-1} $NaNO_3$ solution) was standardized potentiometrically with KH phthalate (Merck AG). A nitric acid solution (≈0.04 mol L^{-1}) was prepared and used after standardization. Sodium hydroxide, nitric acid, and sodium nitrate were from Merck PA.

2. Potentiometric Measurements

2-1. Apparatus and Procedure

pH-measurements were performed using 702 titroprocessor equipped with a 665 dosimat (Switzerland) made by Metrohm. The electrodes were calibrated in both the acidic and alkaline regions by titrating 0.01 mol L^{-1} nitric acid with standard sodium hydroxide under the same experimental conditions. The concentration of free hydrogen ion, C_{H^+} at each point of the titration is related to the measured E of the cell by the Nernst equation:

$$E=E^{o}+Q\log E_{H^+} \quad (1)$$

where E^o is a constant that includes the standard potential of the glass electrode and Q is the slope of the glass electrode response. The value of E^o for the electrode was determined from a Gran plot derived from a separate titration of nitric acid with a standard NaOH solution under the same temperature and medium conditions as those for the test solution titration. The results so obtained were analyzed by the nonlinear least squares computer program (GLEE, glass electrode evaluation) [37] to refine E^o and the autoprotolysis constant of water, K_W. During these calculations K_W was refined until the best value for Q was obtained. The results obtained indicated the reversible Nernstian response of the glass electrode used. The investigated solutions were prepared (total volume 50 cm^3) and titrated potentiometrically against standard CO_2 free NaOH (0.10 mol L^{-1}) solution. A stream of nitrogen was passed throughout the course of the experiment to exclude the adverse effect of atmospheric carbon dioxide. For the determination of the binary systems (one ligand and M^{++}), solution containing ligand (triazoles or aromatic carboxylic acids) and M^{++} ion were titrated at 1 : 1-1 : 4 metal/ligand ratio and for ternary systems, the ratios used were 1 : 1 : 1 and 1 : 2 : 2. The concentration of ligand solutions in the titrated samples was always the same 1×10^{-3} mol L^{-1}. The 3-amino-1,2,4-triazole (TRZAM) was prepared in the protonated form. Titrations were performed up to pH≈11.

The stability constant values were calculated adopting the Irving and Rossotti technique [38,39]. Computations related to the estimation of stability constants were performed by regression analysis of titration curves using a computer program based on an unweighted linear least-squares fit. The stoichiometries and stability constants of complexes formed were determined by examining various possible composition models for the systems studied. The model selected was that which gave the best statistical fit. In addition, all of the pH-metric titrations were terminated when either the readings of the pH meter became unstable, showing a downward drift, or visual precipitation occurred. The concentration distribution diagrams were obtained with the program SPECIES [40] under the experimental conditions used.

Each of the investigated solutions was thermostated at the required temperature with accuracy of ±0.10 ºC, and the solutions were left to stand at this temperature for about 15 min before titration. Magnetic stirring was used during all titrations. About 100 to 140 experi-

Table 1. Summary of experimental parameters for the potentiometric measurements

System	Dissociation processes of ligands: triazoles (TRZ, TRZSH and TRZAM) and aromatic carboxylic acids (phthalic, Anthranilic, salicylic and 5-sulfosalicylic). Binary: phthalic/anthranilic/salicylic/5-sulfosalicylic acid, TRZ/TRZSH/TRZAM with Cu^{++}, Ni^{++}, Zn^{++} and Co^{++} in aqueous media. Ternary: phthalic/anthranilic/salicylic/5-sulfosalicylic acids, and TRZ/TRZSH/TRZAM with the same metal ions mentioned above in aqueous media.
Solution composition [Ligand]	Ligand concentration 1×10^{-3} mol dm^{-3}), metal/ligand ratios ranging from 1 : 1 to 1 : 4 for binary systems and 1 : 1 : 1 and 1 : 2 : 2 for ternary systems. Ionic strength: 0.10 mol dm^{-3} supporting electrolyte ($NaNO_3$).
Experimental method	pH-metric titration of 50 cm^3 samples up to pH≈11.
Instrument	SM 702 Metrohm automatic titrator with a combined pH glass electrode equipped with a 665 dosimat and a magnetic stirrer (Switzerland).
Calibration	By periodic titrations of HNO_3 solution (at the same temperature and ionic strength).
T (ºC)	(15-45) ºC
n_{tot}[a]	100-140
n_{tit}[b]	at lest four times
Method of calculation	Computer program based on unweighted linear least-square fit

[a]Number of titration points per titration

[b]Number of titrations per titration curve

mental data points were available for evaluation in each system. The titration was repeated at least four times for each titration curve. A summary of the experimental details for the potentiometric measurements is given in Table (1).

2-2. Conductometric Measurements

Conductometric titrations were followed with a HANNA conductivity meter HI-98304. The following mixture was titrated conductometrically against 0.10 mol L^{-1} NaOH solution: 1×10^{-2} mol dm^{-3} metal(II) ion (10 cm^3)+1×10^{-2} mol L^{-1} carboxylic acid (10 cm^3)+1×10^{-2} mol L^{-1} triazole compound (10 cm^3).

2-3. Spectrophotometric Measurements

The absorption spectra of freshly prepared solutions were recorded in the 300-1,100 nm range with a Shimadzu Corp. UV-Vis 1601 (PC)S spectrophotometer using matched quartz cells of 1.0 cm path length. The spectrophotometer and its accessories were controlled by software under Windows to provide advanced operational facilities.

RESULTS AND DISCUSSION

1. Proton-ligand Equilibria

The structural formulas of the investigated ligands are given in Chart 1. The protonation constants of triazoles and aromatic carboxylic acids have been redetermined at t=25 °C and I=0.10 mol L^{-1} $NaNo_3$ in an aqueous medium (Table 2). The obtained values are in good agreement with data found in the literature [41-43]. The 1,2,4-triazole (TRZ) and its 3-mercapto- (TRZSH) and 3-amino- (TRZAM) derivatives are considered to be protonated at low pH at the imidazolic nitrogen atom(N4), producing the protonated form, H_2L^+ [27,43,44]. Accordingly, such compounds are expected to have two ionization constants relevant to the following ionization steps:

$$H_2L^+ \rightleftharpoons HL+H^+ \quad (2)$$

$$HL \rightleftharpoons L^-+H^+ \quad (3)$$

The first ionization constant values for 1,2,4-triazole (TRZ) and 3-mercapto-1,2,4-triazole (TRZSH) are very low (<2.4) [43]; therefore, they could not be determined under the experimental conditions and were not used in the calculations. On the other hand, the aromatic carboxylic acids can generally be represented by H_2A, thus also having two dissociation constants. However, the first dissocia-

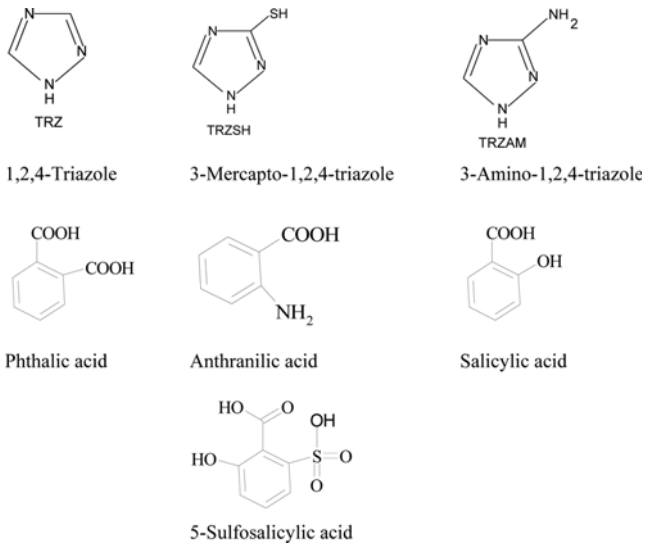

Chart 1.

Table 2. The dissociation constants of the ligands in aqueous media at 25.0±0.1 °C and I=0.1 mol L^{-1} $NaNO_3$

Ligand	pK_{a1}	pK_{a2}
TRZ	--	10.20±0.01
TRZSH	--	7.20±0.01
TRZAM	4.17±0.02	10.82±0.02
Phthalic acid	2.85±0.02	5.08±0.03
Anthranilic acid	2.10[c]	4.83±0.02
Salicylic acid	2.88±0.03	13.60[c]
5-Sulfosalicylic acid	2.48±0.04	11.60[c]

[c]Values were taken from reference [42]

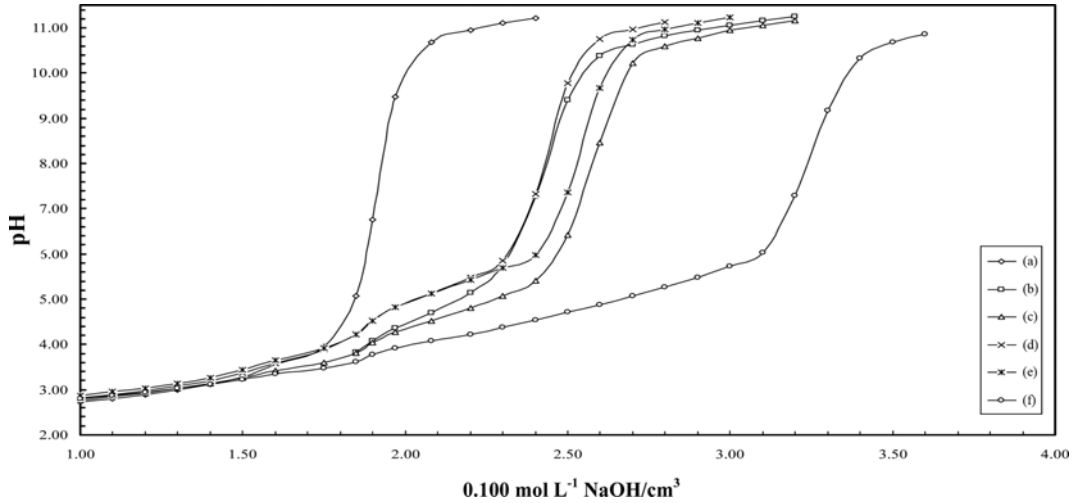

Fig. 1. Potentiometric pH titration curves for Cu^{++}-Anth-TRZAM system at 25 °C and I=1×10^{-1} mol L^{-1} $NaNO_3$ (a) 4×10^{-3} mol L^{-1} HNO_3 (b) solution a+1×10^{-3} mol dm^{-3} TRZAM; (c) solution b+5×10^{-4} mol L^{-1} Cu^{++}; (d) solution a+1×10^{-3} mol L^{-1} Anth; (e) solution d+5×10^{-4} mol L^{-1} Cu^{++}; (f) solution a+1×10^{-3} mol L^{-1} TRZAM+1×10^{-3} mol L^{-1} Anth+5×10^{-4} mol L^{-1} Cu^{++}.

tion constant of anthranilic acid could not be determined potentiometrically, because of the highly acidic nature of the associated proton [45]. The second dissociation constant values of salicylic acid and 5-sulfosalicylic acid are very high (pK_{a2}=13.60 and 11.60 for salicylic and 5-sulfo-salicylic acids, respectively) [45], and hence they could not be determined potentiometrically.

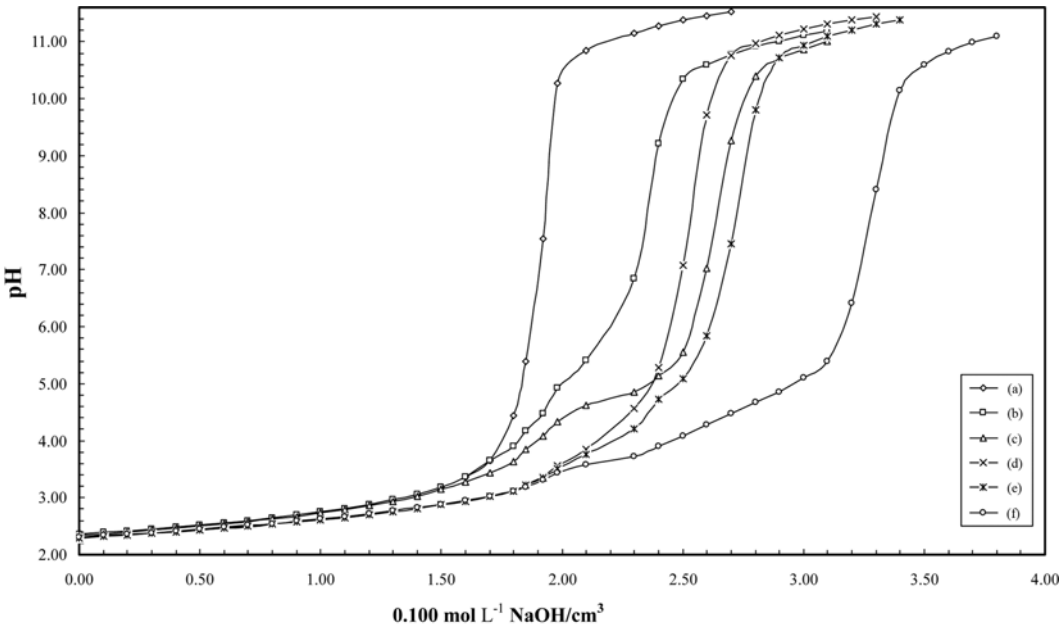

Fig. 2. Potentiometric pH titration curves for Cu^{++}-Sal-TRZAM system at 25 °C and I=0.10 mol L^{-1} $NaNO_3$ (a) 4×10^{-3} mol L^{-1} HNO_3 (b) solution a+1×10^{-3} mol L^{-1} TRZAM; (c) solution b+5×10^{-4} mol L^{-1} Cu^{++}; (d) solution a+1×10^{-3} mol L^{-1} Sal; (e) solution d+5×10^{-4} mol L^{-1} Cu^{++}; (f) solution a+1×10^{-3} mol L^{-1} TRZAM+1×10^{-3} mol L^{-1} Sal+5×10^{-4} mol L^{-1} Cu^{++}.

Table 3. Dissociation constant of TRZ, stability constants of 1 : 1 and 1 : 2 binary complexes at 25 °C and I=0.10 mol dm^{-3} ($NaNO_3$)

Cation	pKa_2 (this work)	pKa_2 [Ref.]	$\log K^{M}_{ML}$ (this work)	$\log K^{M}_{ML}$ [Ref.]	$\log K^{ML}_{ML_2}$	$\Delta \log K'$
H	10.20±0.03	9.95 [34]				
Cu^{II}			9.19±0.01	9.14 [43]	7.03±0.03	−2.16
Ni^{II}			7.01±0.03	6.93 [43]	4.56±0.02	−2.45
Co^{II}			6.18±0.01	6.10 [43]	4.14±0.01	−2.04
Zn^{II}			6.41±0.03		4.24±0.04	−2.17

Table 4. Dissociation constant of TRZSH, stability constants of 1 : 1 and 1 : 2 binary complexes at 25 °C and I=0.10 mol dm^{-3} ($NaNO_3$)

Cation	pKa_2 (this work)	pKa_2 [Ref.]	$\log K^{M}_{ML}$ (this work)	$\log K^{M}_{ML}$ [Ref.]	$\log K^{ML}_{ML_2}$	$\Delta \log K'$
H	7.20±0.01	7.10 [35]				
Cu^{II}			d	d		
Ni^{II}			3.58±0.02	3.60 [43]	2.35±0.03	−1.23
Co^{II}			3.09±0.02	3.02 [43]	2.27±0.02	−0.82
Zn^{II}			3.19±0.01		2.33±0.02	−0.86

d: could not be detected

Table 5. Dissociation constant of TRZAM, stability constants of 1 : 1 and 1 : 2 binary complexes at 25 °C and I=0.10 mol dm^{-3} ($NaNO_3$)

Cation	pKa_2 (this work)	pKa_2 [Ref.]	$\log K^{M}_{ML}$ (this work)	$\log K^{M}_{ML}$ [Ref.]	$\log K^{ML}_{ML_2}$	$\Delta \log K'$
H	10.82±0.01	10.72 [42]				
Cu^{II}			8.81±0.01	8.80 [43]	3.23±0.03	−5.58
Ni^{II}			6.06±0.03	6.14 [43]	d	
Co^{II}			5.48±0.01	5.54 [43]	d	
Zn^{II}			5.98±0.03		d	

d: could not be detected

2. Binary Complex Systems

Analysis of the binary complex curves for triazoles and the aromatic carboxylic acids (Fig. 1 and Fig. 2) indicates that the addition of the metal ion to the free ligand solution shifts the buffer region of the ligands to lower pH values. This shows that binary complex formation reaction proceeds by releasing protons from such ligands. The stability constants of the binary complexes of the considered ligands have been determined at t=25 °C and I=0.10 mol L^{-1} $NaNO_3$. The values obtained (Tables 3-9) are in good agreement with the literature data [41-43]. However, a survey of the literature revealed that no measurements have been done on Zn^{++} ions with the investigated triazoles. Also, the stability constants of the 1 : 2 binary complexes of the investigated triazoles were determined and there is no available literature data for comparison. The equilibria involved in the formation of the binary complexes may be represented as follows:

$$M + L \rightleftharpoons ML, \quad K_1 = \frac{[ML]}{[M][L]} \tag{4}$$

$$ML + L \rightleftharpoons ML_2, \quad K_2 = \frac{[ML_2]}{[ML][L]} \tag{5}$$

For the investigated triazoles, the pH value at which the binary complex begins to form decreases in the direction TRZSH>TRZ AM> TRZ, indicating a higher tendency of the triazole ligands toward binary complex formation in the same order. Except in the case of the binary complex [Cu^{++}+TRZSH], the different binary [M^{++}+triazoles] complex solutions do not give rise to a precipitate, indicating that hydrolysis reactions do not interfere in the formation of such complexes. On the other hand, an inflection was observed in the different binary [M^{++}+triazoles] titration curves at a pH value corresponding to the addition of 1 mol of base per 1 mol of triazole ligand. This behavior suggests that the triazole ligands bind to the metal ions as monovalent anions according to the following complexation equilibria:

$$M^{++} + H_2L^{+} \rightleftharpoons ML^{+} + 2H^{+} \tag{6}$$

$$M^{++} + HL \rightleftharpoons ML + H^{+} \tag{7}$$

for TRZAM (Eq. (6)) and TRZ or TRZSH (Eq. (7)), respectively. However, the binary [Cu^{++}+TRZSH] complex solution could not be studied as a result of the formation of a precipitate at low pH values (<2.5).

Examination of the stability constants of the binary complexes (Table 3-9) leads to the following remarks:

(a) The observed order of stability of binary systems with respect to the ligand aromatic carboxylic acids is salicylic>5-sulfosalicylic> phthalic>anthranilic, which is in accordance with the relative basicity of the carboxylate anion.

(b) The results obtained clearly indicate that, for a given metal ion, the stability of binary complex is influenced by changing the nature of the triazole ligand as follows: TRZ (pK_{a2}=10.2)>TRZAM (pK_{a2}=10.82)>TRZSH (pK_{a2}=7.16). Although TRZAM is a stronger base than TRZ, the binary complexes of TRZAM are less stable than those of TRZ. This behavior can likely be ascribed to the electrostatic repulsive interactions established during the formation of the binary complex of TRZAM{$M^{++}+H_2L^{+}=(ML)^{+}+2H^{+}$} compared to those in the formation of the binary complex of TRZ {$M^{++}+HL=(ML)^{+}+H^{+}$} [43].

(c) The stability constants of the different 1 : 2 metal-ligand complexes are lower than those of the corresponding 1 : 1 complex species, as expected from statistical consideration. The $K^{MA}_{MA_2} - \log K^{M}_{MA}$ values are negative as $K_1 > K_2$ (Tables 3-9). This is the normal trend for neutral ligands where the enthalpy is more favorable for a 1 : 1 species (exothermic) as compared to 1 : 2 species [46]. Also, the reduction in the values of stepwise constants is due to the fact that the entropy contribution to the free energy change becomes less favorable from one step to the next.

3. Ternary Complex Systems

The titration curves of all the mixed ligand complexes formed in solutions (Figs. 1 and 2) display an inflection at the titration point corresponding to the addition of a base concentration equivalent to 2 mol of aromatic carboxylic acid and 1 mol of triazole ligand. This clearly indicates that the aromatic carboxylic acids coordinate to the central metal ion as divalent bidentate anions (OO donors) and that triazoles bind to the metal ion as monodentate anions (N donors) through the pyrrolic nitrogen after deprotonation. The existence of a ternary complex is proved by comparison of the mixed ligand titration curve with the composite curve obtained by graphical addition of the secondary ligand (TRZAM) titration data to that of the metal-primary ligand (phthalic acid) titration curve. The Cu^{++}-phthalic acid-TRZAM system is taken as representative (Fig. 3). The mixed ligand 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, aromatic carboxylic acid interacts first with the metal ion forming a binary complex which is then followed by interaction of the triazole, i.e., the ternary complex formation could be considered in stepwise equilibria (Eqs. (8) and (9)).

$$M + A \rightleftharpoons MA, \quad K^{M}_{MA} = \frac{[MA]}{[M][A]} \tag{8}$$

$$MA + L \rightleftharpoons MAL, \quad K^{MA}_{MAL} = \frac{[MAL]}{[MA][L]} \tag{9}$$

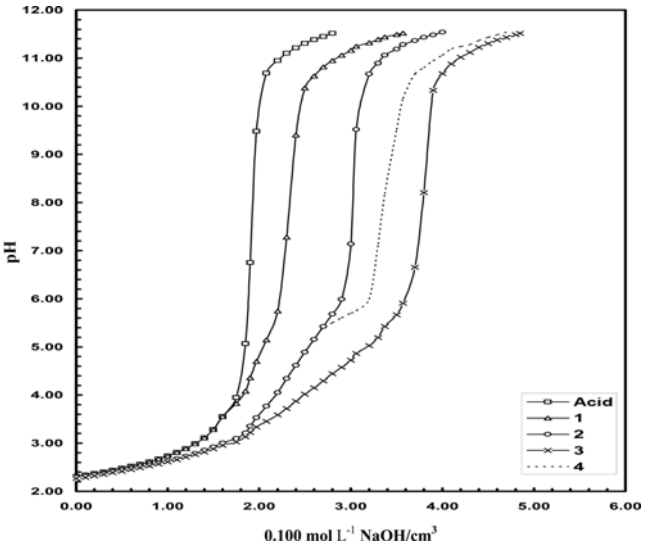

Fig. 3. Potentiometric pH-titration curves for Cu^{++}-Phth-TRZAM system at 25 °C and I=0.1 mol. L^{-1} $NaNO_3$, (1) TRZAM, (2) Cu^{++}-Phth, (3) Cu^{++}-Phth-TRZAM, (4) composite curve.

The overall stability constant β^{M}_{MAL} may be represented by Eq. (10)

$$M + A + L \rightleftharpoons MAL, \quad \beta^{MA}_{MAL} = \frac{[MAL]}{[M][A][L]} = K^{MA}_{MAL} \times K^{M}_{MA} \tag{10}$$

The β^{MA}_{MAL} constant express the stability of the mixed-ligand species; it doesn't represent directly the binding strength between L and M^{++} ions in the presence of A. This effect is much better reflected by the equilibrium constant, $LogK^{MA}_{MAL}$ calculated according to Eq. (11).

$$\log K^{MA}_{MAL} = \log \beta^{M}_{MAL} - \log K^{M}_{MA} \tag{11}$$

It shows how tightly L is bound to the simple MA complex. However, examining Fig. 1, ternary system involving M^{++}-anthranilic acid-TRZAM complex solutions (curve f) overlap with the titration curve of the binary Cu^{++}(TRZAM) (curve c) at low pH values, and a divergence of the ternary complex titration curve from that of the binary Cu^{++}(TRZAM) is observed at higher pH. This shows the coordination of the anthranilic acid to the Cu^{++}(TRZAM)-binary complex in a stepwise manner as represented by the following Eqs. (12) and (13):

$$Cu^{++} + TRZAM \rightleftharpoons Cu^{++}(TRZAM) \tag{12}$$

$$Cu^{++}(TRZAM) + \text{anthranilic acid} \rightleftharpoons M^{++}(TRZAM)(\text{anthranilic acid}) \tag{13}$$

Except for Cu^{++}+aromatic carboxylic acid+TRZSH systems, the mixed-ligand complexes are stable up to the pH values where the primary and secondary ligands are completely attached to the central divalent metal ion forming the ternary complexes, i.e., the hydrolysis reactions have no role in complex formation.

Based on the ternary complex stability constant values (Tables 6-9), the following conclusions could be drawn:

a) The observed order of stability of ternary systems with respect to the aromatic carboxylic acids is: phthalic>anthranilic>salicylic> 5-sulfosalicylic. The observed difference in stabilities of ternary complexes of anthranilic acid and salicylic acid can solely be attributed to the varying π-accepting properties of these ligands [47].

b) The higher stability of phthalic acid complex compared to salicylic acid may be explained as follows: since the carboxylate oxygen is not directly bound to the benzene ring, it therefore adjusts stereochemically more easily than the phenolate oxygen which is directly attached to the benzene ring [48]. 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. Thus

Table 6. Stability constants for Cu^{II} binary and ternary complexes in aqueous media at 25.0±0.1 °C and I=0.1 mol dm^{-3} $NaNO_3$

	$\log\beta^{M}_{MAL}$	$\log K^{MA}_{MAL}$	$\log K_1$			$\log K_2$		
			TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	3.48±0.03	2.52±0.03	9.26±0.01	-	10.78±0.02	12.74	-	14.26
Anthranilic acid	3.17±0.02	2.61±0.02	9.08±0.02	-	3.89±0.01	12.25	-	12.76
Salicylic acid	10.58±0.05	8.46±0.05	8.94±0.02	-	10.23±0.03	19.52	-	20.81
5-Sulfosalicylic acid	9.63±0.04	6.98±0.04	8.76±0.01	-	10.08±0.03	18.39	-	19.71

	ΔlogK			% R.S.			log X		
	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	0.07	-	1.97	0.76	-	22.36	8.97	-	15.81
Anthranilic acid	−0.11	-	0.72	−1.19	-	22.17	8.52	-	1.94
Salicylic acid	−0.25	-	1.42	−2.72	-	16.11	2.39	-	8.77
5-Sulfosalicylic acid	−0.43	-	1.27	−4.67	-	14.11	3.51	-	9.95

e: could not be determined because of precipitation

Table 7. Stability constants for Ni^{II} binary and ternary complexes in aqueous media at 25.0±0.1 °C and I=0.1 mol dm^{-3} $NaNO_3$

	$\log\beta^{M}_{MAL}$	$\log K^{MA}_{MAL}$	$\log K_1$			$\log K_2$		
			TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	3.27±0.05	1.92±0.05	8.95±0.01	4.15±0.03	10.57±0.01	12.22	7.42	13.84
Anthranilic acid	3.09±0.02	2.37±0.02	8.83±0.02	4.07±0.02	3.58±0.02	11.92	7.16	9.64
Salicylic acid	8.67±0.05	4.65±0.03	7.88±0.02	3.97±0.01	10.06±0.01	16.55	12.64	18.73
5-Sulfosalicylic acid	6.48±0.04	3.82±0.04	7.79±0.01	3.88±0.02	9.94±0.01	14.27	10.36	16.42

	ΔlogK			% R.S.			log X		
	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	1.94	0.54	4.31	27.67	14.95	71.12	11.42	4.03	-
Anthranilic acid	1.82	0.46	0.49	25.96	12.74	15.85	10.73	3.43	-
Salicylic acid	0.87	0.36	4.00	12.41	9.97	66.05	6.55	0.94	-
5-Sulfosalicylic acid	0.78	0.27	3.88	11.12	7.47	64.02	7.20	1.59	-

e: could not be determined because of precipitation

Table 8. Stability constants for Zn^{II} binary and ternary complexes in aqueous media at 25.0±0.1 °C and I=0.1 mol dm^{-3} $NaNO^3$

$\log\beta^{M}_{MAL}$		$\log K^{MA}_{MAL}$	$\log K_1$			$\log K_2$		
			TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	3.21±0.05	2.43±0.05	7.99±0.01	5.07±0.02	10.45±0.02	11.20	8.28	13.66
Anthranilic acid	3.05±0.02	2.28±0.02	7.89±0.02	4.95±0.02	3.52±0.02	10.94	8.00	9.50
Salicylic acid	8.29±0.03	4.21±0.03	7.78±0.02	4.92±0.01	10.04±0.01	16.07	13.21	18.33
5-Sulfosalicylic acid	6.38±0.04	3.62±0.04	7.43±0.01	4.76±0.01	9.88±0.02	13.81	11.14	16.26

	ΔlogK			% R.S.			log X		
	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	1.58	1.88	4.47	21.02	58.93	74.75	9.31	5.38	-
Anthranilic acid	1.54	1.76	0.47	18.13	55.17	15.40	9.26	5.29	-
Salicylic acid	1.38	1.73	4.06	17.42	54.23	67.89	7.11	3.30	-
5-Sulfosalicylic acid	1.02	1.57	3.90	13.62	49.21	65.52	7.00	3.57	-

e: could not be detected

Table 9. Stability constants for Co^{II} binary and ternary complexes in aqueous media at 25.0±0.1 °C and I=0.1 mol dm^{-3} $NaNO_3$

$\log\beta^{M}_{MAL}$		$\log K^{MA}_{MAL}$	$\log K_1$			$\log K_2$		
			TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	3.18±0.02	2.36±0.02	7.92±0.02	3.77±0.01	10.22±0.01	11.10	6.95	12.40
Anthranilic acid	2.91±0.02	2.12±0.02	7.86±0.01	3.64±0.02	3.42±0.02	10.77	6.55	9.60
Salicylic acid	7.33±0.03	3.78±0.03	7.73±0.02	3.58±0.01	9.78±0.01	15.06	10.91	17.11
5-Sulfosalicylic acid	6.25±0.04	3.47±0.04	7.36±0.02	3.40±0.01	9.70±0.01	13.61	9.65	15.95

	ΔlogK			% R.S.			log X		
	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM	TRZ	TRZSH	TRZAM
Phthalic acid	1.78	0.68	4.74	28.80	22.06	86.49	9.34	2.91	-
Anthranilic acid	1.68	0.55	0.51	27.18	17.79	17.52	9.46	2.90	-
Salicylic acid	1.59	0.49	4.30	25.72	15.85	78.46	7.54	1.11	-
5-Sulfosalicylic acid	1.18	0.31	4.22	19.10	10.56	77.01	7.11	1.06	-

e: could not be detected

the Δ log K should be higher when the ligand coordinates through the two carboxylate oxygens (phthalic acid) than when it is salicylic acid, which contains one carboxylate and one phenolate oxygen.

c) The relative stabilities of the ternary complexes of salicylic acid and 5-sulfosalicylic acid follow their relative basicities. It is well known that the increase in basicity of a ligand increases the stability of its metal complexes. This is reflected in an increase of the σ-donor character of the conjugate bases in the same order.

d) Salicylic acid behaves as a monodentate ligand [49] owing to the high dissociation constant of the hydroxyl group (pK_{a2}=13.6). The lower stability of complexes involving 5-sulfosalicylic acid may be ascribed to the presence of the electron-withdrawing sulfonic group.

e) The stabilities of the ternary complexes of the same metal ion follow the sequence TRZAM>TRZ>TRZSH. This behavior can be explained in the basis of the effective basicity decreases on going from TRZAM to TRZSH.

f) The complex stability of the ternary systems with respect to the metal ion present follows the order: Zn^{++}<Cu^{++}>Ni^{++}>Co^{++}. The order of stability in the case of transition metal ions is that which is expected on the basis of their position in the Irving-William's series.

Estimation of the concentration distribution of various complex species in solution provides a useful picture of metal ion binding in biological systems. A species distribution diagram obtained for Cu^{++} +Anthranilic acid+TRZAM, shows the formation of [MA] starts

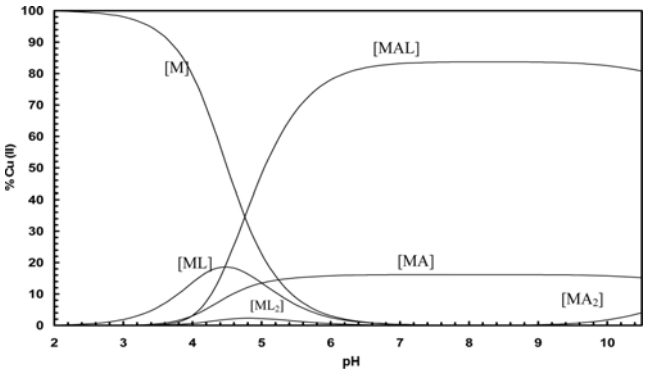

Fig. 4. Representative concentration distribution curves as a function of pH calculated for Cu^{++}-Anthr-TRZAM system in the ratio 1 : 2 : 2 at 25 °C, I=0.10 mol L^{-1} $NaNO_3$ and C_{ligand}=1×10^{-3} mol L^{-1}.

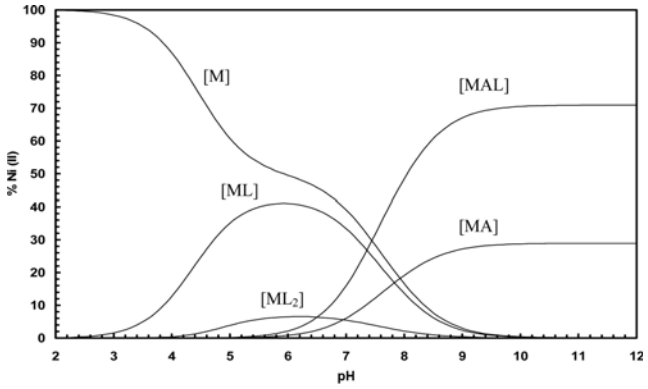

Fig. 5. Representative concentration distribution curves as a function of pH calculated for Ni^{++}-Anthr-TRZAM system in the ratio 1 : 2 : 2 at 25 °C, I=0.10 mol L^{-1} $NaNO_3$ and C_{ligand}=1× 10^{-3} mol L^{-1}.

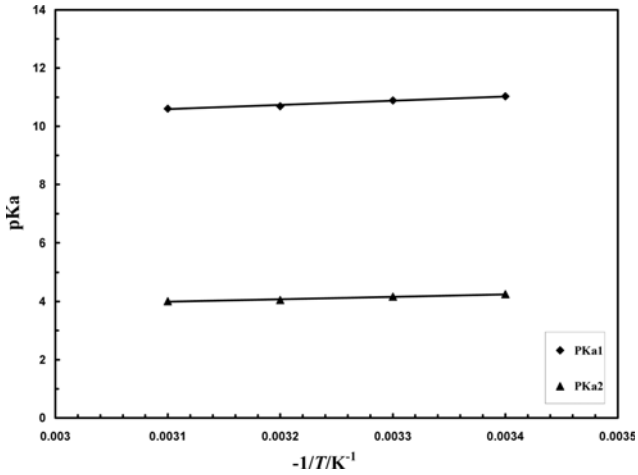

Fig. 6. Plot of pKa of TRZAM *vs* –1/T at I=0.10 mol L^{-1} $NaNO_3$.

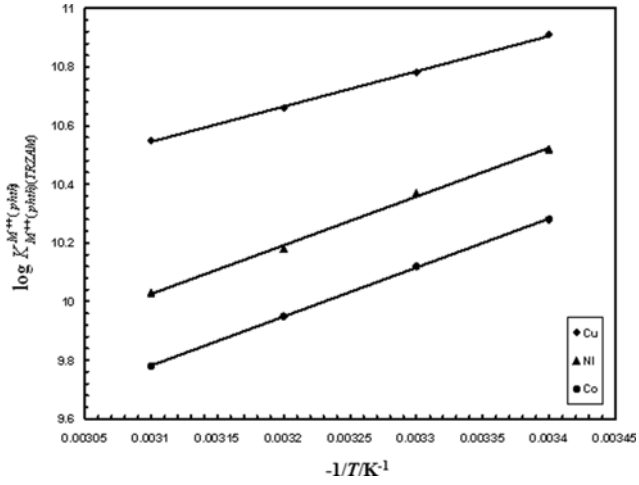

Fig. 7. Plot of $\log K^{M^{++}(phth)}_{M^{++}(phth)(TRZAM)}$ *vs* –1/T at I=0.10 mol L^{-1} $NaNO_3$.

at pH 3.8, reaches a maximum concentration (15.87% total Cu^{++}) at pH 6.1 and decreases when [MAL] becomes predominant as shown in Fig. 4. For Ni^{++}+Anthranilic acid+TRZAM, system; Fig. 5 shows the formation of [MA] starts at pH 5.9, reaches a maximum concentration (28.46% total Ni^{++}) at pH 9.6 and decreases when [MAL] becomes predominant.

The relative stability of the ternary complexes compared to that of the corresponding binary complexes, can be quantitatively expressed in different ways. A review of those methods [50] has shown that for a variety of reasons, the most suitable comparison is in terms of ΔlogK. Tables (6-9) demonstrate the difference in stabilities of binary and ternary complexes in terms of ΔlogK, as defined by Eq. (14)

$$\Delta\log K = \log K^{MA}_{MAL} - \log K^{M}_{ML} \quad (14)$$

In general, positive ΔlogK values for the ternary systems investigated indicated favored formation of the MAL ternary complexes over the corresponding binary ones. The positive value of ΔlogK obtained for the different ternary complexes containing TRZAM can be attributed to the high electrostatic repulsive forces in the binary complex formation between TRZAM and the aquated metal ion $\{M^{++}+H_2L^+ \rightleftharpoons (MA)^-+2H^+\}$. Such forces are low during mixed-ligand complex formation $\{MA+H_2L^+ \rightleftharpoons MAL^-+2H^+\}$. The negative ΔlogK values for some ternary systems may be attributed to the higher stability of binary complexes than those corresponding to the ternary complexes, i.e., the association of TRZ or TRZSH with the aquated metal ion is more favored than that with the binary complex MA. This behavior is likely due to the smaller number of coordination sites available for bonding on the binary MA complex than on the aquated M^{++} complex. The values of log X (the constant due to the equilibrium $[MA_2]+[ML_2] \rightleftharpoons 2[MAL]$ [51] (Tables 6-9). The values of log X are higher than that expected on a statistical basis (0.60) [52, 53]. This means that the formation of mixed complexes is favored in these systems. Another parameter, percent relative stabilization (% R.S.) to quantify the stability of a ternary complex may be defined as:

$$\%\text{R.S.} = [(\log K^{MA}_{MAL} - \log K^{M}_{ML})/\log K^{M}_{ML}] \times 100 \quad (15)$$

The values obtained agree with the ΔlogK values as shown in Tables (6-9).

The effect of temperature of the medium on the dissociation of TRZAM and phthalic acid ligands and the stability of their 1 : 1 binary and 1 : 1 : 1 ternary complexes with Cu^{++}, Co^{++} and Ni^{++} metal ions was also investigated at I=0.10 mol L^{-1} ($NaNO_3$). The values of the protonation and binary (1 : 1) equilibrium constants for TRZAM and phthalic acid were found to be linearly dependent on the inverse of temperature, indicating negligible change in heat capacity for each of these protonation and complexation reactions [54]. The pK_a values of TRZAM and $\log K^{M^{++}(phth)}_{M^{++}(phth)(TRZAM)}$ *vs* –1/T at I=0.10 mol L^{-1} ($NaNO_3$) are plotted for different temperatures (Figs. 6 and 7). The equilibrium constants have been evaluated at the different temperatures [(15, 25, 35, and 45) °C], along with the thermodynamic quantities and the values obtained are cited in Table 10. The values of ΔH^o for the ionization of the ligands were found to be positive, indicating the endothermic nature of the deprotonation process (Table 11). The positive values of the standard free energy change ΔG^o for the dissociation processes of the ligands denote these processes are not spontaneous. Also, the negative values of ΔS^o are pointing to increased ordering due to association. The values of the formation constants of the complexes formed decrease with temperature, indicating that the complex formation reactions are exothermic (Le Chat-

Table 10. The dissociation constants of TRZAM and phthalic acid ligands, and stability constants of their binary and ternary complexes with Cu^{++}, Ni^{++} and Co^{++} at 1 : 1 and 1 : 1 : 1 molar ratios in aqueous media and I=0.10 mol L^{-1} $NaNO_3$ at different temperatures

Ligand or complex	Cation	pK's or log K			
		t/°C=15	25	35	45
TRZAM	H	11.42±0.02	10.82±0.02	10.69±0.02	10.61±0.03
	H	4.37±0.02	4.17±0.02	4.05±0.02	4.01±0.03
(1 : 1) Binary complex	Cu^{++}	9.08±0.02	8.81±0.01	8.66±0.02	8.43±0.01
of TRZAM	Ni^{++}	6.46±0.01	6.06±0.01	5.82±0.01	5.50±0.02
	Co^{++}	5.79±0.02	5.48±0.01	5.16±0.03	4.82±0.01
Phthalic acid	H	5.24±0.01	5.08±0.03	5.01±0.02	4.95±0.03
	H	3.03±0.01	2.85±0.03	2.72±0.02	2.65±0.03
(1 : 1) Binary complex	Cu^{++}	3.63±0.01	3.48±0.03	3.36±0.01	3.29±0.03
of phthalic acid	Ni^{++}	3.32±0.03	3.27±0.05	3.15±0.01	3.09±0.02
	Co^{++}	3.29±0.02	3.18±0.02	3.08±0.04	2.99±0.01
(1 : 1 : 1) Ternary complexes	Cu^{++}	10.91±0.02	10.78±0.02	10.66±0.01	10.55±0.04
involving M++-TRZAM-	Ni^{++}	10.82±0.02	10.57±0.01	10.37±0.01	10.18±0.02
Phthalic acid	Co^{++}	10.38±0.04	10.22±0.01	9.95±0.02	9.78±0.02

Table 11. The thermodynamic quantities associated with the dis- sociation of TRZAM and phthalic acid ligands, and their interaction with Cu^{++}, Ni^{++} and Co^{++} at 1 : 1 and 1 : 1 : 1 molar ratios in aqueous media at 25.0±0.1 °C and I=0.10 mol L^{-1} $NaNO_3$

Ligand or complex	Cation	ΔH^o kJ·mol^{-1}	ΔG^o kJ·mol^{-1}	ΔS^o J·mol^{-1}K^{-1}
TRZAM	H	27.95	62.14	−116.03
	H	16.08	23.79	−26.61
(1 : 1) Binary complex	Cu^{++}	−71.71	−52.44	36.85
of TRZAM	Ni^{++}	−49.46	−35.51	85.38
	Co^{++}	−44.69	−31.30	99.33
Phthalic acid	H	17.96	29.70	−35.71
	H	14.30	16.26	−25.18
(1 : 1) Binary complex	Cu^{++}	−18.63	−21.39	2.89
of phthalic acid	Ni^{++}	−16.42	−18.66	8.09
	Co^{++}	−15.18	−15.80	10.99
(1 : 1 : 1) Ternary complexes	Cu^{++}	−32.84	−61.31	87.55
involving M|-TRZAM-	Ni^{++}	−31.60	−58.91	99.94
Phthalic acid	Co^{++}	−30.30	−52.21	134.74

elier's principle). The values of enthalpy changes ΔH^o for the binary and ternary systems investigated are negative. The complex formation process is spontaneous in nature, as characterized by the negative ΔG^o values. The values of ΔS^o substantiate the suggestion that the different binary and ternary complexes are formed due to coordination of the ligand anion to the metal cation. Furthermore, the positive values of ΔS^o suggest also a desolvation of the ligands, resulting in weak solvent-ligand interactions, to the advantage of the metal ion-ligand interaction [55].

4. Conductometric Measurements

Conductometric titrations have been investigated to indicate the complexation behavior of the ternary system studied in solution. The conductometric titration curve for the ternary complex of Zn^{++}, salicylic acid and TRZ is displaced in Fig. 8. The titration curve shows an initial decrease and an inflection at a=2 (a=moles of base added per mole of ligand) due to the neutralization of H^+ ions resulting from the formation of the Zn^{++}+salicylic acid binary complex. Between 2<a<3, the slight increase of conductance is due to the formation of the ternary complex and is associated with the release of one proton from the secondary ligand (TRZ). Beyond a=3, the conductance increases more uniformly due to the presence of excess base (NaOH). The conductometric titration curve for Zn^{++}+5-sulfosalicylic acid +TRZ is displaced in Fig. 9. The titration curve shows an initial decrease and an inflection at a=3 due to the neutralization of H^+ ions resulting from the 5-sulfosalicylic acid binary complex. Between 3<a<4, the slight increase of conductance is due to the formation of the ternary complex and is associated with the release of one proton from TRZ. Beyond a=4, the conductance increases more uniformly due to the presence of excess NaOH.

5. Spectrophotometric Measurements

The UV-visible absorption spectra of the Cu^{++}+5-sulfo-salicylic acid+TRZ systems (Fig. 10) are investigated at pH=3.0. The spectrum of aquated Cu^{++} ion (1.10^{-2} mol L^{-1}) shows an absorption band at about 807 nm, being attributed to the $2T_2g \leftarrow 2Eg$ [56] transition. The spectral band of the binary solution containing TRZ (1.10^{-2} mol L^{-1}) and Cu^{++} (1 : 1 molar ratio) shows a new band at 791 nm

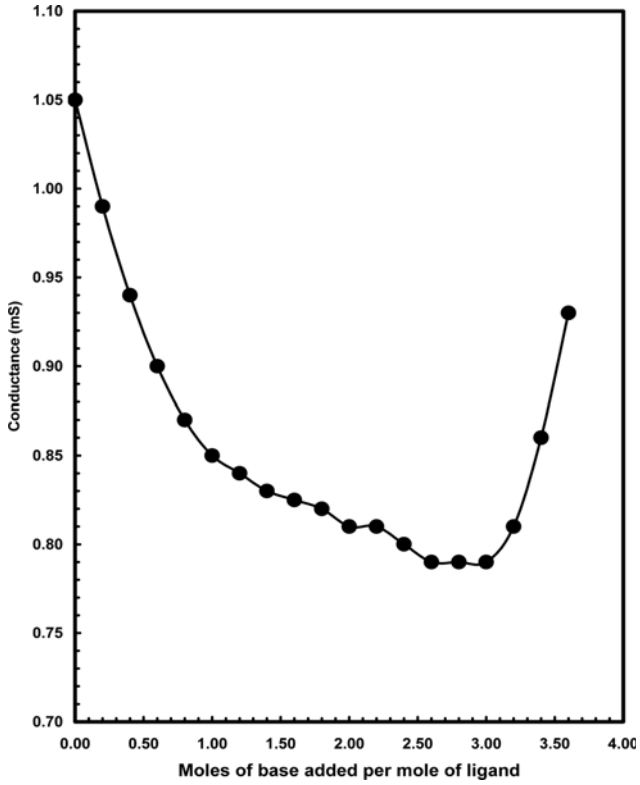

Fig. 8. Conductometric titration curve for Zn^{++}-Sal-TRZ system.

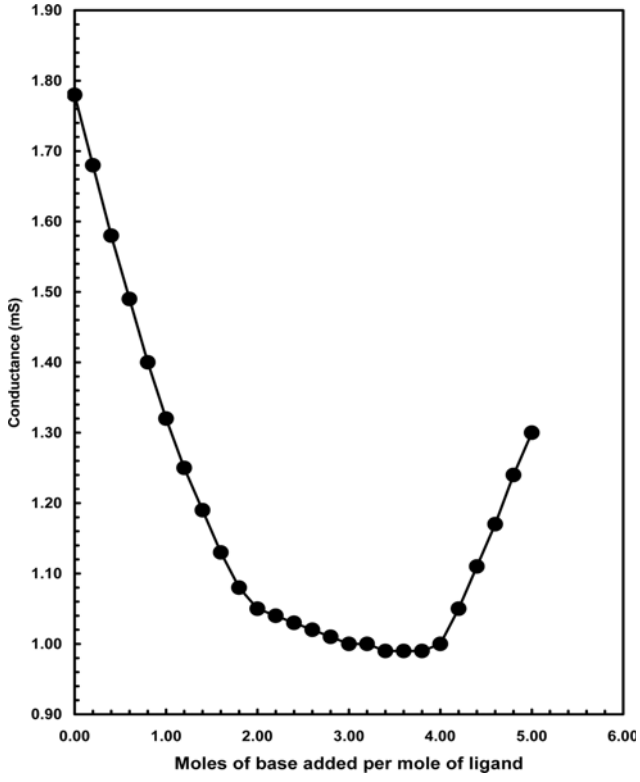

Fig. 9. Conductometric titration curve for Zn^{++}-5-Sulfosalicylic-TRZ system.

due to the formation of a binary complex. However, the solution containing 5-sulfosalicylic acid (1.10^{-2} mol L^{-1}), TRZ and Cu^{++} ion

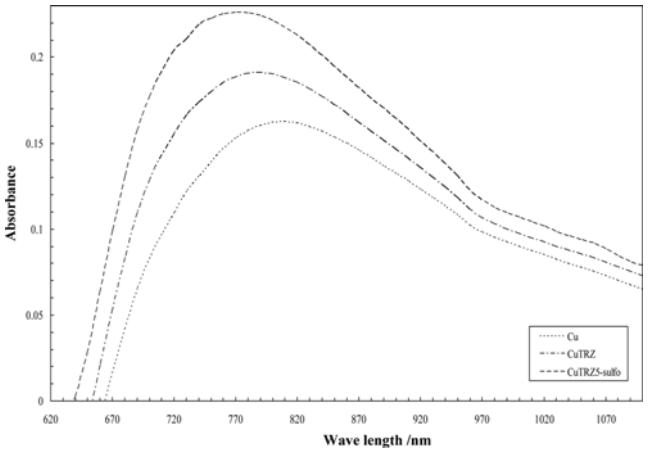

Fig. 10. Visible absorbance spectra for the Cu^{++}+TRZ-5-Sulfosalicylic-system.

(1 : 1 : 1 molar ratio) shows a different band at 772 nm due to the formation of the ternary complex.

CONCLUSION

This study offers intensive investigation and mechanistic details associated with formation of binary and ternary complexes formed in solution. The ternary complexes are formed in a stepwise process; the values of the equilibrium constants were discussed. The relative stability of the different ternary complex species formed is expressed in terms of ΔlogK values, log X and % R.S. parameters. The distribution of binary and ternary complexes in solution was evaluated. The effect of temperature of the medium on both the proton-ligand equilibria for TRZAM and phthalic acid and their metal-ligand equilibria with Cu^{++}, Ni^{++}, and Co^{++} has been studied along with the corresponding thermodynamic parameters.

The potentiometric technique was used as a validating method of the speciation model calculated on the basis of using a computer program based on unweighted linear least-squares fit to obtain reliable formation constant values.

The complexation behavior of ternary complexes is ascertained using conductivity measurements. Finally, the formation of ternary complexes in solution has been confirmed by UV-visible spectrophotometry. The ligand, the binary and ternary complexes may have interesting biological activity. This would require specially designed research conducted by specialized biologists.

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