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Potentiometric Studies of Some 1-(4-Substituted)-1,3,5-Triazino-3-Methyl Thiocarbamide Complexes of Co^{2+}, Ni^{2+} and Cu^{2+}

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The interactions of Co(II), Ni(II) and Cu(II) with 1-(4-hydroxy)-1,3,5-triazino-3-methyl thiocarbamide and 1-(4-hydroxy-6-methyl)-1,3,5-triazino-3-methyl thiocarbamide have been investigated potentiometrically in 70% dioxane-water mixture at constant ionic strength. Bjerrum's potentiometric titration method as adopted by Calvin and Wilson is applied in the present work. Proton ligand and metal-ligand stability constants have been determined by Irving-Rossotti's expression at (27 ± 0.1°C). The pK values are determined by half integral method and by pointwise calculations. The chelation properties can be related to the metal ion. The relative stabilities of the complexes of the bivalent metal ions have been verified.

Key Words: Potentiometric, 1-(4-Substituted)-1,3,5-triazino-3-methyl thiocarbamide, Complexes, Co^{2+}, Ni^{2+} and Cu^{2+}

INTRODUCTION

Triazine and its derivatives are one of the important classes of heterocyclic compounds. In view of analytical applications of 1-(4-substituted)-1,3,5-triazino-3-methyl thiocarbamides, it is of interest to know the physico-chemical properties, such as proton-ligand stability constants, the chelation properties and the relative stability of complexes of bivalent metal ions. By employing potentiometric method, Khadikar and coworkers[1] studied very few metal-complexes. Recently Narwade *et al.*[2] have studied the stability constants of Fe(III) complexes at various ionic strengths. Martell *et al.*[3] investigated metal chelates with Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(I). Jamode *et al.*[4] have studied the physical properties of Th(IV) complexes. It therefore appears sufficiently interesting to investigate the physico-chemical properties of 1-(4-hydroxy)-1,3,5-triazino-3-methyl thiocarbamide (ligand 1) and 1-(4-hydroxy-6-methyl)-1,3,5-triazino-3-methyl thiocarbamides (ligand 2) under suitable conditions. In the present work the interactions of Co(II), Ni(II) and Cu(II), with 1-(4-hydroxy)-1,3,5-triazino-3-methyl thiocarbamide (L_1) and 1-(4-hydroxy-6-methyl)-1,3,5-triazino-3-methyl thiocarbamide (L_2) have been investiganted potentiometrically in 70% dioxane-water mixture at 0.1 M ionic strength.

EXPERIMENTAL

All the chemicals such as sodium hydroxide, sodium perchlorate, perchloric acid and metal nitrates were of AnalaR grade. Metal salts were dissolved in perchloric acid and their concentrations were estimated by standard procedure[5].

The chelating agents 1-(4-hydroxy)-1,3,5-triazino-3-methyl thiocarbamide and 1-(4-hydroxy-6-methyl)-1,3,5-triazino-3-methyl thiocarbamide were synthesised in the laboratory as described[6].

pH measurements were carried out with ELICO-LI 10 pH-meter (accuracy ± 0.05) using glass and calomel electrodes at (27 ± 0.1°C). The values (pH meter reading in 70% dioxane-water mixture) were converted to (H^+) values by applying the correlation proposed by Van-Viter and Hass[7].

Calvin-Bjerrum titration: The experimental procedure involved potentiometric titrations of carbonate-free solution of (i) free $HClO_4$ (1.00×10^{-2} M) (ii) free $HClO_4$ (1.00×10^{-2} M) and ligand (20.00×10^{-4} M) and (iii) free $HClO_4$ (1.00×10^{-2} M), metal ion solution (4.00×10^{-4} M) against standard solution of sodium hydroxide (0.10 M). The ionic strength of each solution was maintained constant by adding a calculated amount of 1 M $NaClO_4$ solution. The titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen gas through an assembly containing the electrodes in order to drive out CO_2.

RESULTS AND DISCUSSION

Proton-ligand stability constant: L_1 and L_2 used in the present investigation have only one dissociable H^+ ion from —OH group and can, therefore, be represented as HL. The increase of dissociation from pH 10.5 to 11.75 showed the complete dissociation of —OH group; the proton-ligand formation number ($\bar{n}A$) was calculated by Irving-Rossotti equation[8] and presented in Tables 1 and 2. It is seen from these tables that the values of $\bar{n}A$ decreased with increase in pH values. This is due to increase in dissociation of —OH group. pK values are initially calculated from the formation curves ($\bar{n}A$ *vs.* pH). The value of pH at nA equals 0.5, corresponding to the value of pK (for only one dissociable —OH group). The accurate values of pK are determined by pointwise calculations, which are summarized in Table-3. The values of pK calculated for all the systems by pointwise calculation method are in good agreement with the values obtained by half integral method. The pK value of L_2 is greater than pK value of L_1 and this may be due to the presence of electron releasing group —CH_3, that decreases the dissociation of —OH group and increases the pK value in metal-ligand stability constants. The formation of chelates between Co(II), Ni(II) and Cu(II), metal ions and L_1 and L_2 were indicated by significant departure starting at pH 6.25 of metal complex titration curves. In calculating the metal-ligand formation number ($\bar{n}$) and P_L, the concentrations were corrected for change in volume by the addition of alkali during titration. The values of $\bar{n}$ corresponding to pH values are utilised to construct the formation curves. The formation curves between the values of $\bar{n}$ and of P_L are used to calculate the first metal-ligand stability constant (log K_1) and the second metal-ligand stability constant (log K_2). The values of log K_1 and log K_2 are calculated from the formation curves by the known values of P_L at which $\bar{n}$ is 0.5 and 1.5 respectively (half integral method). The most accurate values estimated by pointwise calculation are presented in Table-4.

TABLE-1
POTENTIOMETRIC DATA OF THE PROTON-LIGAND FORMATION NUMBER ($\bar{n}A$)
AT VARIOUS pH VALUES WITH L_1

T_0L = Total concentration of ligand

V = Volume of NaOH required for titration of $HClO_4$

V_1 = Volume of NaOH required for titration of $HClO_4$ + ligand

$V_2 = (V + V_1)$

pH	V_1	V_2	V	$\bar{n}A$
$T_0L = 20.00 \times 10^{-4}$ M Cu(II)				
8.00	3.40	3.58	0.18	0.8116
8.20	3.45	3.62	0.17	0.8223
8.40	3.50	3.75	0.25	0.7388
8.60	3.58	3.80	0.22	0.7705
8.80	3.60	3.88	0.28	0.7080
9.00	3.60	4.05	0.45	0.5307
9.20	3.60	4.20	0.60	0.3745
9.40	3.62	4.44	0.82	0.1452
$T_0L = 20.012 \times 10^{-4}$ M Ni(II)				
8.00	3.48	3.58	0.10	0.8955
8.20	3.50	3.65	0.15	0.8433
8.40	3.54	3.70	0.16	0.8330
8.60	3.56	3.80	0.24	0.7496
8.80	3.58	3.90	0.32	0.6662
9.00	3.60	4.02	0.42	0.5620
9.20	3.60	4.20	0.60	0.3743
9.40	3.62	4.40	0.78	0.1869
$T_0L = 20.018 \times 10^{-4}$ M Co(II)				
8.00	3.40	3.56	0.16	0.8326
8.20	3.42	3.62	0.20	0.7908
8.40	3.44	3.70	0.20	0.7281
8.60	3.50	3.78	0.28	0.7075
8.80	3.55	3.85	0.30	0.6869
9.00	3.58	4.88	0.30	0.6871
9.20	3.60	4.20	0.60	0.3743
9.40	3.62	4.40	0.78	0.1869

TABLE-2
POTENTIOMETRIC DATA OF THE PROTON-LIGAND FORMATION NUMBER ($\bar{n}A$) AT VARIOUS pH VALUES WITH L_2

pH	V_1	V_2	V	$\bar{n}A$
$L_0L = 20.00 \times 10^{-4}$ M (concetration of ligand) Cu(II)				
8.00	3.35	3.50	0.15	0.8429
8.20	3.40	3.60	0.20	0.7907
8.40	3.45	3.68	0.23	0.7595
8.60	3.50	3.78	0.28	0.7075
8.80	3.55	3.90	0.35	0.6347
9.00	3.58	4.00	0.42	0.5619
9.20	3.60	4.20	0.60	0.4743
9.40	3.62	4.50	0.88	0.0826
$T^0L = 20.012 \times 10^{-4}$ M Ni(II)				
8.00	3.40	3.55	0.15	0.8430
8.20	3.42	3.60	0.18	0.8117
8.40	3.44	3.65	0.21	0.7804
8.60	3.50	3.78	0.28	0.7075
8.80	3.58	3.90	0.32	0.6662
9.00	3.60	4.00	0.40	0.5829
9.20	3.60	4.20	0.60	0.3743
9.40	3.62	4.35	0.73	0.2390
$T^0L = 20.012 \times 10^{-4}$ M Co(II)				
8.00	3.48	3.55	0.07	0.9264
8.20	3.55	3.60	0.05	0.9478
8.40	3.55	3.65	0.20	0.7913
8.60	3.58	3.78	0.20	0.7906
8.80	3.60	3.85	0.25	0.7393
9.00	3.60	4.00	0.40	0.5829
9.20	3.60	4.20	0.60	0.3743
9.40	3.62	4.45	0.83	0.1348

TABLE-3
PROTON-LIGAND STABILITY CONSTANTS

System	Half integral constant pK	Pointwise calculations
L_1	9.05	9.10 ± 0.05
L_2	9.10	9.15 ± 0.05

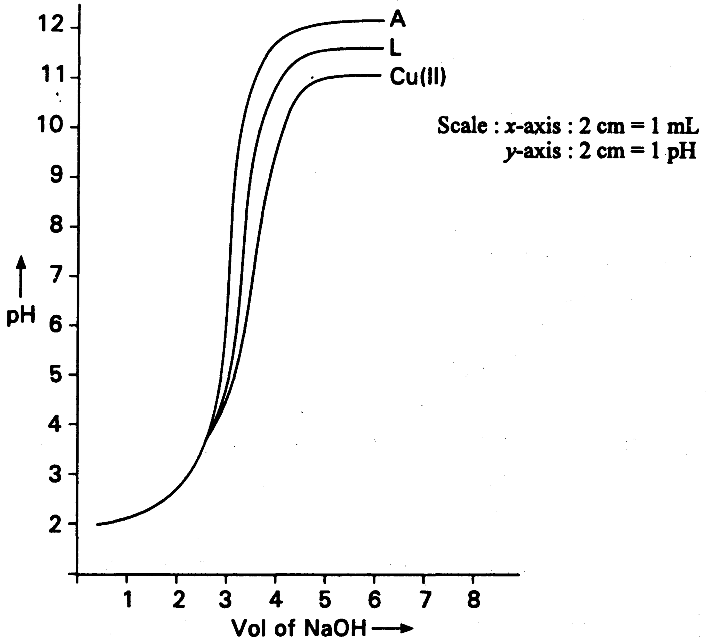

Fig. 1. Plot between volume of NaOH *vs.* pH (System: Cu-L_1 complex)

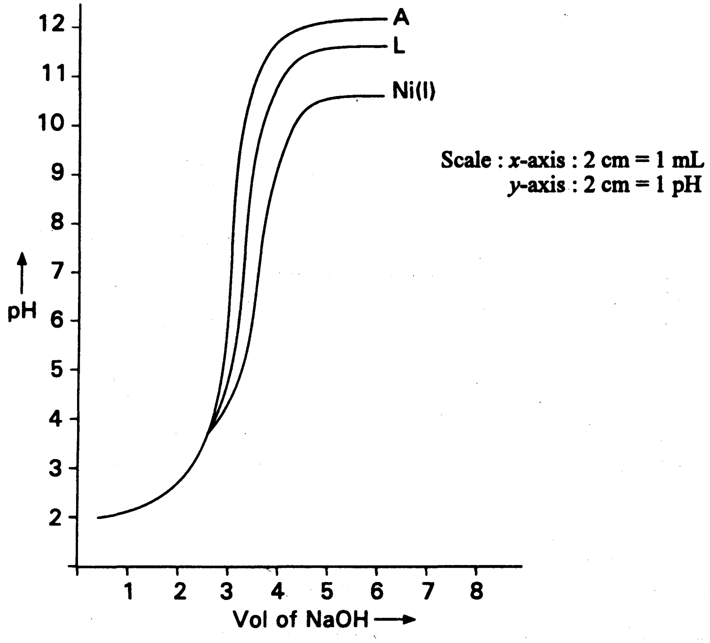

Fig. 2. Plot between volume of NaOH *vs.* pH (System: Co-L_1 complex)

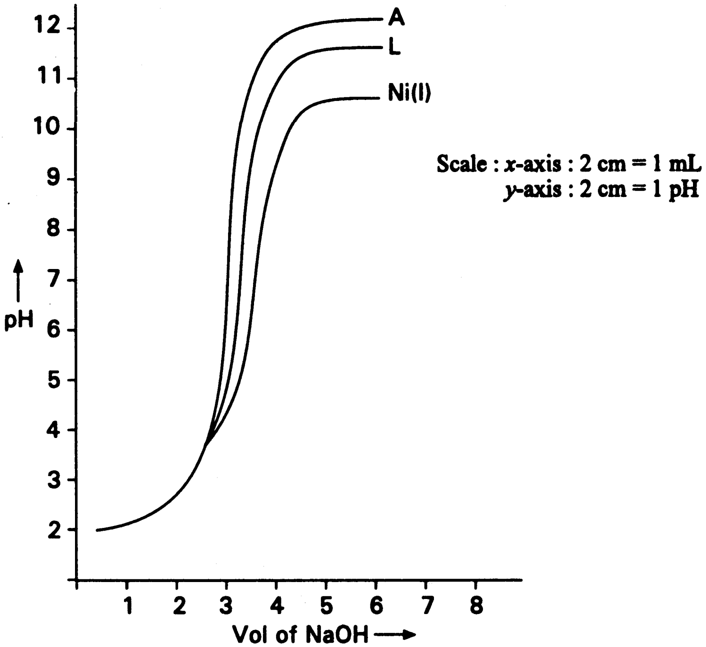

Fig. 3. Plot between volume of NaOH *vs.* pH (System: Ni-L_1 complex)

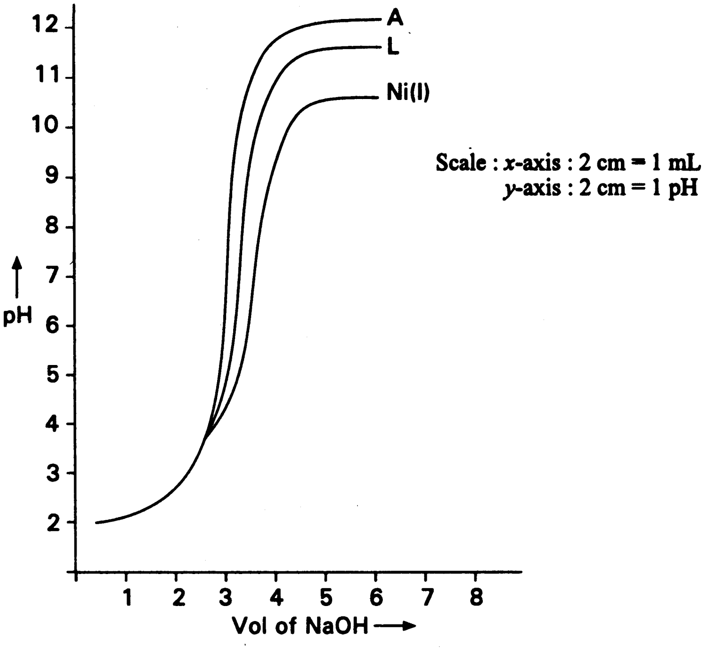

Fig. 4. Plot between volume of NaOH *vs.* pH (System: Cu-L_2 complex)

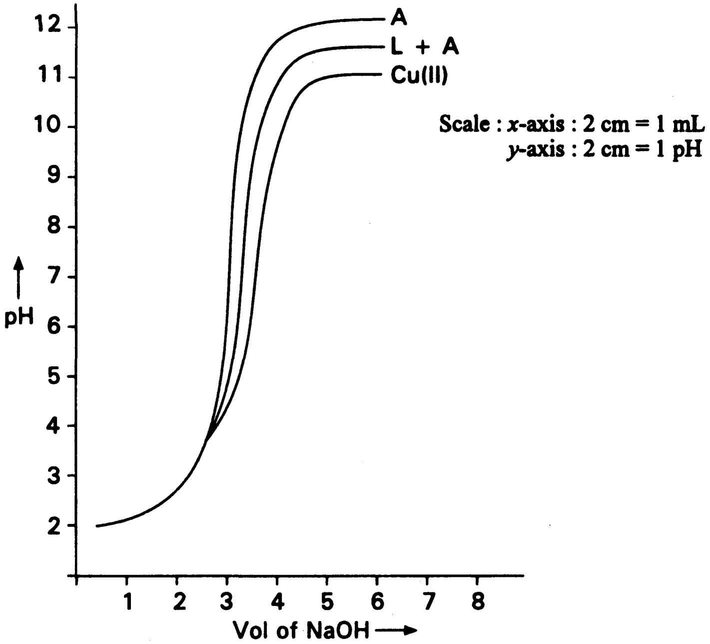

Fig. 5. Plot between volume of NaOH *vs*. pH (System: Co-L_2 complex)

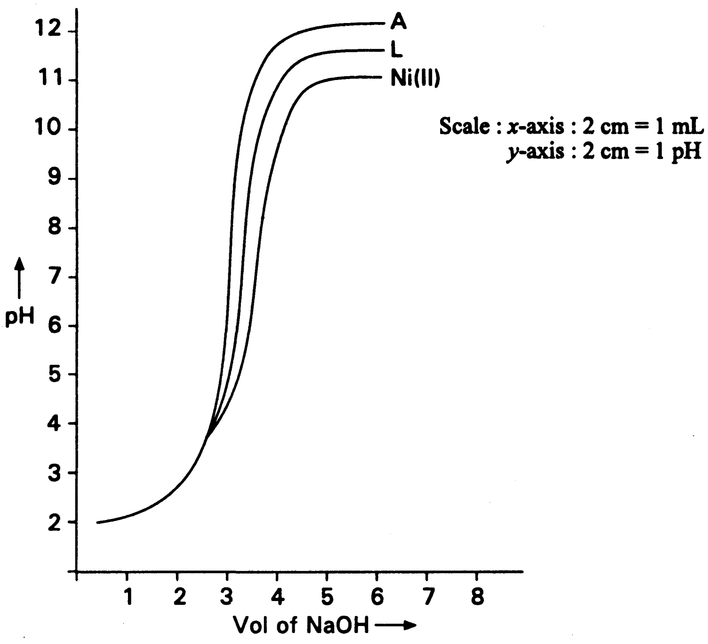

Fig. 6. Plot between volume of NaOH *vs*. pH (System: Ni-L_2 complex)

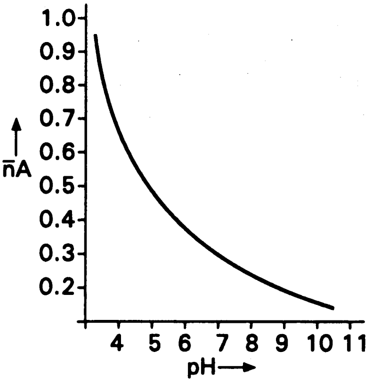

Fig. 7. Plot between pH vs. n̄A for L_1

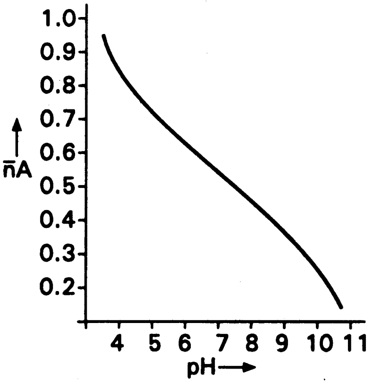

Fig. 8. Plot between pH vs. n̄A for L_2

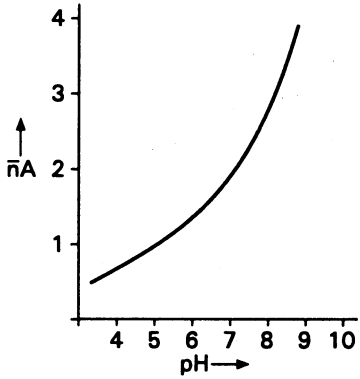

Fig. 9. Plot between pH vs. n̄ for L_1

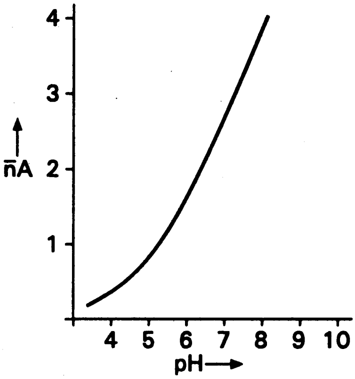

Fig. 10. Plot between pH vs. n̄ for L_2

TABLE-4
METAL-LIGAND STABILITY CONSTANTS

System	log K_1	log K_2
Cu(II) + L_1	4.7096	4.2155
Co(II) + L_1	4.9146	4.3237
Ni(II) + L_1	4.8946	4.6038
Cu(II) + L_2	5.0946	4.7538
Co(II) + L_2	4.9440	4.2837
Ni(II) + L_2	4.8746	4.6038

Difference between log K_1 and log K_2 values are studied for Cu(II) system and represented in Table-5. It shows that the ratio log K_1/log K_2 is possible. Separation factors between first and second formation constants are well within the expected range and the absence of high values implies that there is little steric hindrance to addition of second ligand molecule.

TABLE-5

DIFFERENCE BETWEEN log K_1 AND log K_2 FOR Cu(II)-COMPLEXES

System	log K_1	log K_2	log K_1 – log K_2	log K_1/log K_2
Cu(II)-L_1	4.7096	4.2155	0.4941	1.1172
Cu(II)-L_2	5.0946	4.7538	0.3408	1.0716

Relation between log K and pK: The linear relationship between log K and pK has been found out by some workers[9]. In the present investigation the relationship log k = apK + b is examined for Cu(II), Co(II) and Ni(II) complexes with ligands L_1 and L_2. It was found that all the points fall on the straight line on the plot of log K *vs.* pK. Jones *et al.*[9] suggested that since Cu(II) and Ni(II) act as electron donors and Co(II) acts as electron acceptor for a series of closely related ligands, the chelation properties can be related to the metal ion. In our present investigation the order of relative stability of complexes of bivalent metal ions (log K_2) was found to be Co > Ni > Cu.

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