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Studies in influence of ionic strength of medium on the complex equilibria of substituted hydoxy-1-3-propandiones with Cr(III) and La(III) metal ions pH metrically

Sumer D. Thakur, ***Devidas T. Mahajan, **Kamlesh P. Munot, *Rajesh D. Deshmukh, *Mangesh S. Tihile, Vijay H.Masand**

**R.D.I.K. & N.K.D. College, Badnera (Rly.), Amravati (M.S.), India*
*** S.P.M. College, Ghatanji, Dist. Yavatmal (M.S.), India*
****Vidya Bharti College Amaravati (M.S.) India*

ABSTRACT

The solution studies (the proton-ligand stability constant pK and metal-ligand stability constants log k) of binary (1 : 1) complexes of Cr(III) and La(III) with 1(2'-Hydroxy-5'-Bromophenyl)-3-(4'-chlorophenyl)-1,3-Propanedione [HB4CP] $[L_1]$ *and 1(2'-Hydroxy-5'-Bromophenyl), 3-(4'-Aminophenyl)-1,3-Propanedione [HB4AP]* $[L_2]$ *have been performed at 0.02 to 0.1 mol.dm*$^{-3}$ *ionic strength at* (29 ± 0.1)*°C in 70 % dioxane-water mixture pH-metrically. The pk and log k values are utilized to estimate the thermodynamic stability constants at zero ionic strength and to know the exact nature of complexation equilibria.*

Key words: - Ionic strength, Substituted hydroxy 1,3-propanedione, Dioxane-water.

INTRODUCTION

Substituted hydroxy-1,3-propanediones (β-doketones) are important as potential antimicrobial [1], antiviral [2], anti-inflammatory, antibacterial agents [3], Diketones are found to possess biological activity. In addition to fungicidal activity, diketones specially chlorodiketones are found to possess antihelminthic activities [4]. It is reported that the substituted diketones which are different in nature act as insecticides, bactericides, pharmaceuticals and fungicidal.

The lanthanide compounds have remarkable importance in every day life [5,6]. More explicitly in the previous decades their use in various organic technical processes led to a rapid growth especially in the field of complexes. In recent years the luminescence properties of rare earth metal complexes with different β-diketones have been widely studied due to their use in fabrication of polymer light emitting diodes to enable low cost, full colour, flat panel display. The effect of dielectric constants on pk and log k values is reported by many workers. [7-9].

The ionic strength is an electrical current produced by the ions of inert salt in solution which is one of the characteristics of liquid. The proton-ligand and metal-ligand stability constants are strongly affected by ionic strength of the medium. Sawalakhe et al[10] have investigated the stability constants of Cu(II) complexes with some substituted diketones at various ionic strength. Gudadhe et al [11] have investigated the stability constants of Cu(II) complexes with some substitutted propane-dione at various ionic strengths poteniomtrically. Agrawal et al [12] studied stability constants of Co(II), Sr(II), Pr(II) complexes with substituted azoles at various ionic strength. The influence of ionic strengths on complex equilibria of substituted pyrazoles with Sm(III) and Pr(III) studied by Naik et al [13]. The dissociation constants of L-2-amino-3-hydroxypropanic acid [14] have been determined at various ionic strengths. The stability constants of complexation of VO^{+}_{2} with glycine discussed the effect of ionic strengths on protonation and complexation [15]. The effect of ionic strength on N(trihydroxymethyl) glycine(Tricine) [16] with transition metal ion Co(II), Cu(II), Ni(II) and Zn(II) complexes have been studied. Speciation of binary complexes of Ca(II), Mg(II) and Zn(II) with L-glutamic acid in DMSO-water Mixtures has been studied [17].

In present work Cr(III) and La(III) metal ions complexes with HB4CP and HB4AP at various ionic strengths in 70 % dioxane-water mixture medium have been investigated by Calvin-Bjerrum pH metric technique at (29 ± 0.1) ^{0}C. The system has been studied at 0.02, 0.04, 0.06, 0.08 and 0.1 mol dm^{-3} ionic strength by varying the concentrations of sodium perchlorate.

MATERIALS AND METHODS

The ligands [HB4CP] L_1 and [HB4AP] L_2 were synthesised in the laboratory by knwon literature method. The purity of these compounds exceeds 99.5% and structures were confirmed by NMR, IR and melting points. The stock solutions of the ligands were prepared by dissolving required amount of ligands in a minimum volume of dioxane subsequently diluted to final volume. Metal ions solutions were prepared by dissolving metal nitrate (Sigma-Aldrich) and standardised by EDTA titration method as discussed in literature. Carbonate free sodium hydroxide solution was prepared by dissolving the Analar pellets in deionised water and solution was standardised [18]. The stock solution of percholric acid was prepared and used after standardization [19].

All measurements were carried out at (29 ± 0.1) ^{0}C. Systronic microprocessor based pH meter with magnetic stirrer used for pH measurements. The sensitivity of pH meter is 0.01 units. The instrument could read pH in the range 0.00 to 14.00 in the steps of 0.005. The pH meter was switched on half an hour before starting the titration for initial warm up of the instrument. It was calibrated before each titration with an aqueous standard buffer solution of pH 7.00 and 9.20 at

(29 ± 0.1) ^{0}C prepared from a 'Qualigens' buffer tablets. The hydrogen ion concentration was measured with combined glass electrode.
The experimental procedure involved the titrations of

i. Free acid $HClO_4$ (0.01 mol.dm^{-3})

ii. Free acid $HClO_4$ (0.01 mol.dm^{-3}) and ligand (20 x 10^{-4} mol.dm^{-3})

iii.Free acid $HClO_4$ (0.01 mole dm^{-3}) and ligand (20 x 10^{-4} mol.dm^{-3}) and metal ion (4 x 10^{-4} mol.dm^{-3}) against standard carbonate free sodium hydroxide (0.142 mol.dm^{-3}) solution using Calvin-Bjerrum and Calvin-Wilson pH titration techniques. The ionic strength of all the solutions were maintained constant by adding appropriate amount of $NaClO_4$ solution. All titrations were carried out in 70 % dioxane-water mixture and readings were recorded for each 0.1 ml addition. The curves of pH against volume of NaOH solution were plotted [20-22]. For calculation purpose, consider n = n and n_A=n_A.

RESULTS AND DISCUSSION

The extent of deviation may be the dissociation of -OH group. Substituted hydroxy-1, 3-propanedione may be considered as a monobasic acid having one replaceble H^+ ion from phenolic -OH group and can be represented as

— —

$$HL \rightleftharpoons H^+ + L^-$$

The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A+L) and acid + ligand + metal ion curve (A+L+M)] between volumes of NaOH against pH.

The proton-ligand formation number n_A were calculated by Irving and Rossotti expression (Table1)

$$n_A \quad = \quad \gamma - \frac{(E_0+N)\,(V_2-V_1)}{(V_0+V_1)\,T_L^0} \qquad .....(1)$$

where γ denotes the number of dissociable protons, N is the concentration of sodium hydroxide (0.142 mol.dm^{-3}), (V_2-V_1) is the measure of displacement of the ligand curve relative to acid curve, where V_2 and V_1 are the volume of alkali added to reach the same pH reading to get accurate values of (V_2-V_1): the titration curves were drawn on an enlarged scale: E^0 and T_L^0 are the resultant concentration of perchloric acid and concentration of ligand, respectively. V_0 is the initial volume of reaction mixture (50 cm^3). Proton-ligand stability constant pk values of ligands were calculated by alzebraic method point wise calculation and also, estimated from formation curves n_A Vs pH (hal integral method) by noting pH at which n_A = 0.5 [Bjerrum 1957].

Metal-ligand stability constants (log k) were determined by the half integral method by plotting n Vs pL. The experimental n values determined using expression

$$\bar{n} = \frac{(E_0+N)(V_3-V_2)}{(V_0 + V_2)\,T_m^0} \qquad .....(2)$$

Where N, E_0, V_o and V_2 have same significance as in equation (1), V_3 is the volume of NaOH added in the metal ion titration to attain the given pH reading and T^0_M (4×10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture.

The pk values of ligand and log K values of Cr(III) and La(III) metal ion complexes with [HB4CP] and [HB4AP] at various ionic strength were calculated by Irving and Rossotti's method are set out in (table 2 & 3). It could be observed that pk and log k values are found to decrease with increasing ionic strength that in accordance with Debye-Huckel theory. The pK / log K values were employed the calculate the thermodynamic constants with the help of Bronsted equation [23].

$$\text{Log } K = \log K^0 + A.\Delta z^2.\sqrt{\mu} \qquad ---3$$

and

$$pK = pK^0 - A.\Delta z^2.\sqrt{\mu} \qquad ---4$$

Where 'A' is the Debye-Huckel constant, $.\Delta z^2$ is difference in the square of the charges of product and reactant ions and K^0 formation constant at zero ionic strength.

The system has been studied at 0.02, 0.04, 0.06, 0.08 and 0.10 mol.dm^{-3} ionic strengths by varying the concentration of sodium perchlorate. In addition to sodium perchlorate, the titrating system contained ions from perchloric acid, metal nitrate and sodium hydroxide. The total ionic strength (μ) of the medium is calculated by following expression.

$$\mu = 1/2\, \Sigma\, CiZi^2 \qquad ---5$$

Where Ci and Zi are the concentration and valency of metal ions respectively.

The values of pK, log K_1, and log K_2 were plotted against $\sqrt{\mu}$, which gave straight lines. The magnitude of Δz^2 and slopes were calculated from graphs. (Table 3, 4) The data obtained of pK and log K could be used to know the mechanism of complexation equilibria. The expected and observed values for Δz^2 for the corresponding dissociation and association reaction equilibria are given (Table 4, 5). It is observed that slope values (observed) of pK and log K are less than the expected values. Those values do not give conclusive evidence regarding the magnitude of charge of reacting spacies except the information that these are oppositely charged. The discrepancy may be due to the limited applicability of Bronsted equation.

The plots of pK / log K Vs $[\sqrt{\mu}/(1+\sqrt{\mu})]$ and $[\sqrt{\mu}/(1+\sqrt{\mu}) - 0.3\sqrt{\mu}]$ are also plotted and are straight line and slope values were determined. It showed that modified Debye-Huckel equation also did not show much improvement in the slope values. This may be due to the fact that value for closest distance approach 'a' is fixed ($3.33\ A^0$). The discrepancy between observed and expected slope values was through of to be due to the concentration and not activity terms used in the equation of stability constants.

Table 1: Proton-ligand formation number (n_A) at (29 ± 0.1) ^{0}C and at ionic strength $\mu = 0.008$ mol.dm^{-3} in 70 %, dioxane-water mixture

Ligand	pH	V_1	V_2	(V_2-V_1)	n_A
HB4CP (L_1)	5.50	3.1312	3.2500	0.1187	0.8302
	5.75	3.1500	3.2625	0.1250	0.8213
	6.00	3.1562	3.2750	0.1250	0.8213
	6.25	3.1625	3.3000	0.1437	0.7945
	6.50	3.1625	3.3125	0.1500	0.7856
	6.75	3.1656	3.3375	0.1719	0.7546
	7.00	3.1718	3.3500	0.1782	0.7461
	7.25	3.1750	3.3750	0.2000	0.7142
	7.50	3.1812	3.4062	0.2250	0.6785
	7.75	3.1875	3.4500	0.2625	0.6230
	8.00	3.1968	3.5062	0.3094	0.5582
	8.25	3.2062	3.5500	0.3437	0.5089
	8.50	3.2125	3.6000	0.3875	0.4466
HB4AP (L_2)	6.75	3.1625	3.4375	0.275	0.6069
	7.00	3.1687	3.4500	0.2812	0.5980
	7.25	3.1750	3.4650	0.2937	0.5802
	7.50	3.1812	3.4812	0.3000	0.5712
	7.75	3.1875	3.5000	0.3125	0.5534
	8.00	3.2000	3.5125	0.3125	0.5535
	8.25	3.2125	3.5250	0.3125	0.5536
	8.50	3.2187	3.5375	0.3187	0.5449
	8.75	3.2312	3.5500	0.3188	0.5459
	9.00	3.2437	3.5680	0.3250	0.5361'
	9.25	3.2562	3.5812	0.3250	0.5361
	9.50	3.2687	3.6000	0.3313	0.5278
	9.75	3.2750	3.6250	0.3500	0.5008
	10.00	3.2875	3.6437	0.3562	0.4920
	10.25	3.3000	3.6625	0.3625	0.4832
	10.50	3.3125	3.6750	0.3625	0.4832

Thermodynamics stability constants (pK^0/log K^0):-

The thermodynamic stability constants (p K^0 & log K^0) are calculated at zero ionic strength from various plots [Table 6].

It can be seen from table 5 that the agreement of the thermodynamic constants (pK^0 & log K^0) obtained from various plots for a particular system are approximately same.

Table 2: Proton-ligand stability constant (pk) of ligands [L_1& L_2] at various ionic strengths (μ) in 70 % dioxane-water

Ligands	μ	$\sqrt{\mu}$	$\sqrt{\mu}/1+\sqrt{\mu}$	$\sqrt{\mu}/(1+\sqrt{\mu})-0.3\sqrt{\mu}$	pk
HB4CP [L_1]	0.10	0.3162	0.2402	0.1453	7.9300
	0.08	0.2828	0.2204	0.1355	8.3054
	0.06	0.2449	0.1967	0.1232	8.4300
	0.04	0.2000	0.1666	0.1066	9.3062
	0.02	0.1414	0.1239	0.8148	9.8600
HB4AP [L_2]	0.10	0.3162	0.2402	0.1453	9.0005
	0.08	0.2828	0.2204	0.1355	9.5708
	0.06	0.2449	0.1967	0.1232	9.6250
	0.04	0.2000	0.1666	0.1066	10.4500
	0.02	0.1414	0.1239	0.8148	11.1250

Table 3: Metal-ligand stability constant (log k) of various system at various ionic strengths (μ) in 70 % dioxane-water

System	μ	$\sqrt{\mu}$	$\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$	$\frac{\sqrt{\mu}}{(1+\sqrt{\mu})-0.3\sqrt{\mu}}$	log k_1	log k_2	log k_1 - log K_2
Cr(III)-HB4CP [L_1]	0.10	0.3162	0.2402	0.1453	6.0750	4.8250	1.2500
	0.08	0.2828	0.2204	0.1355	7.3125	5.7500	1.5625
	0.06	0.2449	0.1967	0.1232	7.7665	6.0750	1.6915
	0.04	0.2000	0.166	0.1066	8.7234	6.1729	2.5505
	0.02	0.1414	0.1239	0.8148	9.6428	6.8012	2.8416
La(III)-HB4CP [L_1]	0.10	0.3162	0.2402	0.1453	6.4877	5.9077	0.5800
	0.08	0.2828	0.2204	0.1355	7.3000	7.0400	0.2600
	0.06	0.2449	0.1967	0.1232	7.7300	7.1500	0.5800
	0.04	0.2000	0.166	0.1066	7.9620	7.6000	0.3620
	0.02	0.1414	0.1239	0.8148	8.8100	8.3200	0.4900
Cr(III)-HB4AP [L_2]	0.10	0.3162	0.2402	0.1453	7.1000	5.3375	1.7625
	0.08	0.2828	0.2204	0.1355	8.4750	7.3750	1.1000
	0.06	0.2449	0.1967	0.1232	8.6750	7.9250	0.7500
	0.04	0.2000	0.166	0.1066	10.3502	8.6173	1.7329
	0.02	0.1414	0.1239	0.8148	11.1100	9.4120	1.6980
La(III)-HB4AP [L_2]	0.10	0.3162	0.2402	0.1453	8.3875	7.1250	1.2625
	0.08	0.2828	0.2204	0.1355	8.7925	7.3500	1.4425
	0.06	0.2449	0.1967	0.1232	9.0123	7.8545	1.1578
	0.04	0.2000	0.166	0.1066	10.0732	8.0681	2.0051
	0.02	0.1414	0.1239	0.8148	10.8500	8.4750	2.3750

Table 4: Slopes and Δz^2 values from the plots of pk / log k Vs √μ

System	pk Vs $\sqrt{\mu}$		log K_1 Vs√μ		log K_2 Vs√μ	
	-Slope	Δz^2	-Slope	Δz^2	-Slope	Δz^2
HB4CP[L_1]	11.428	22.1274	---	----	----	----
HB4AP [L_2]	19.807	37.0610	---	----	----	----
Cr(III) HB4CP[L_1]	---	----	16.5957	-32.1559	7.6190	-14.7626
La(III) HB4CP[L_1]	---	----	12.6415	-24.44342	12.6315	-24.4749
Cr(III) HB4AP[L_2]	---	----	23.3333	-45.2108	15.7142	-30.4479
La(III) HB4AP[L_2]	---	----	14.5833	-28.2567	8.1250	-15.7430

Table 5: The different possible reactions and observed and expected values of Δz^2 for corresponding dissociation or association equilibria of various systems

System	Constant	Reaction Equilibria	Δz^2	
			Expected	observed
HB4CP[L_1]	pk	$HL \rightleftharpoons H^+ + L^-$	2.0	22.1274
HB4AP [L_2]	pk	$HL \rightleftharpoons H^+ + L^-$	2.0	37.0610
Cr(III) HB4CP[L_1]	log K_1	$L^- + Cr^{3+} \rightleftharpoons (CrL)^{2+}$	-6.0	-32.1559
	log K_2	$(CrL)^{2+} + L^- \rightleftharpoons (CrL_2)^+$	-4.0	-14.7626
La(III) HB4CP[L_1]	log K_1	$L^- + La^{3+} \rightleftharpoons (LaL)^{2+}$	-6.0	-24.4342
	log K_2	$(LaL)^{2+} + L^- \rightleftharpoons (LaL_2)+$	-4.0	-24.4749
Cr(III) HB4AP[L_2]	log K^1	$L^- + Cr^{3+} \rightleftharpoons (CrL)^{2+}$	-6.0	-45.2108
	log K_2	$(CrL)^{2+}L^- \rightleftharpoons (CrL_2)^+$	-4.0	-30.4479
La(III) HB4AP[L_2]	log K_1	$L^- + La^{3+} \rightleftharpoons (LaL)^{2+}$	-6.0	-28.2567
	log K_2	$(LaL)^{3+}L^- \rightleftharpoons (LaL_2)^+$	-4.0	-15.7430

Table 6: Thermodynamic dissociation constants at zero ionic strength (pK^0 and log K^0)

System	**Plot**	**(pK^0 and log K^0)**
HB4CP[L_1]	pk Vs $\sqrt{\mu}$	11.15
	pk Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)]	11.60
	pk Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)] -0.3 $\sqrt{\mu}$	11.10
HB4AP [L_2]	pk Vs $\sqrt{\mu}$	12.90
	pk Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)]	13.10
	pk Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)] -0.3 $\sqrt{\mu}$	12.50
Cr(III) HB4CP[L_1]	log k_1 Vs $\sqrt{\mu}$	11.95
	log k_1 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)]	12.40
	log k_1 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)] -0.3 $\sqrt{\mu}$	12.00
	log k_2 Vs $\sqrt{\mu}$	7.85
	log k_2 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)]	8.20
	log k_2 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)] -0.3 $\sqrt{\mu}$	7.80
La(III) HB4CP[L_1]	log k_1 Vs $\sqrt{\mu}$	10.60
	log k_1 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)]	10.95
	log k_1 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)] -0.3 $\sqrt{\mu}$	10.75
	log k_2 Vs $\sqrt{\mu}$	10.10
	log k_2 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)]	10.20
	log k_2 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)] -0.3 $\sqrt{\mu}$	10.35
Cr(III) HB4AP[L_2]	log k_1 Vs $\sqrt{\mu}$	14.15
	log k_1 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)]	14.50
	log k_1 Vs [$\sqrt{\mu}$ / (1 + $\sqrt{\mu}$)] -0.3 $\sqrt{\mu}$	14.20

	log k_2 Vs $\sqrt{\mu}$	11.60
	log k_2 Vs $[\sqrt{\mu} / (1 + \sqrt{\mu})]$	11.90
	log k_2 Vs $[\sqrt{\mu} / (1 + \sqrt{\mu})]$ -0.3 $\sqrt{\mu}$	11.62
La(III) HB4AP[L_2]	log k_1 Vs $\sqrt{\mu}$	12.40
	log k_1 Vs $[\sqrt{\mu} / (1 + \sqrt{\mu})]$	12.90
	log k_1 Vs $[\sqrt{\mu} / (1 + \sqrt{\mu})]$ -0.3 $\sqrt{\mu}$	12.30
	log k_2 Vs $\sqrt{\mu}$	9.62
	log k_2 Vs $[\sqrt{\mu} / (1 + \sqrt{\mu})]$	10.00
	log k_2 Vs $[\sqrt{\mu} / (1 + \sqrt{\mu})]$ -0.3 $\sqrt{\mu}$	9.70

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REFERENCES

[1] C. Caradonna, and M. L. Stein, *Pharmaco.Edu.Sci.*, **1960,** 1, 15, 675 .

[2] N.V.S. Stedger, Pat. 2555, 644 (Hoffman La Roche, Basle); *Chem. Abstr.*, **1951**, 45, 10289.

[3] T. Okud, T. Kirampra and K.A. A.ziker, *Proc. Giten Coll. Pharma.*, **1955,** 208.

[4] P.S. Bodkhe, "Synthesis of some new substituted 3-aroyl flavonoids, corresponding heterocycles and study of their biocidal effects". *Ph.D. Thesis*, Amravati University, Amravati, p. **2002**,183

[5] C.S. Reiners, *Chem. Uns. Zei.*, **2001,**2, 110

[6] R. Anwander, *Top Organometallic Chem.* Springer Verlag, Berlin, Hers-delberg, New York. **1999**

[7] V.D. Khanolkar, D.V. Jahagirdar and D.D. Khanolkar, *Ind. J. Chem.*, **1997**, 25, 220.

[8] P.J. Sondawale and M.L. Narwade, *Asian J. Chem.*, **1997**, 9(3), 479 .

[9] D. Gulwade, *"Studies in physical properties of some substituted Azoles and their chelates"*. Ph.D. Thesis Amravati University, Amravati **2005**.

[10] P.D. Sawalakhe, and M.L.Narwade, *Ph.D. Thesis*, Amravati University, Amravati **1994.**

[11] S. K. Gudadhe, V.S.Jamode and M.L. Narwade, M.L., *Acta Ciencia Indica*, **1985**, 9. C. 4, 234.

[12] P.B. Agrawal, A.S.Burghate, M. Idrees, and M.L.Narwade, *Oriental J.Chem.*, **2001**,17(1), 123 .

[13] A.B. Naik and M.L.Narwade, *Russian J. Co-ord Chem*; **2009,**Vol. 35, No. 12, pp 932-937 .

[14] A. Sharma, K.D.Gupta and K.K.Saxena, *J. Indian Council Chem.*, **2002**,vol.19,No. 2, P. 43.

[15] S.A. Khorrami, H. Bayat, S. Sharifi and M. Shafat, *J. Chem. Eng. Data*, **1996**,vol. 41, p. 1322

[16] O.M. El-Roudi and S.A. Abdel-Latif, *J. Chem. Eng. Data*, **2004** vol.49,p.1193.

[17] B. Ananda Kumar, S. Raju, K. Bharath Kumar Naik, B. B. V. Sailaja and G. Nageswara Rao, Der Pharma Chemica, 2011, 3 (5):155-167

[18] A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 4th ed; Longman; London **1978.**

[19] A.I. Vogel, *A Text Book of Quantitative Chemical Analysis*, 6th ed., Pearson **2003.**

[20] M. Calvin, and K.W. Wilson, *J. Am. Chem. Soc.* **1945**,vol. 67, p. 2003 .

[21] J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, Copenhagen : P. Hasse and Son **1941.**

[22] H. M. Irving and H.S. Rossotti, *J. Chem. Soc.*, **1954**, p. 2904 .

[23] E.S. Amis, *Solvent Effect on Relations ratos and mechanism, Academic Press*, **1966**, N.Y. 24.