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Research Article

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Influence of dielectric constants of medium on the complex equilibria of substituted hydroxy-1,3-propandiones with Cr(III) metal ions pH metrically

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ABSTRACT

The stability constants of 1-(2'-Hydroxy-5'-Bromophenyl)-3-(4'Chlorophenyl)-1,3-Propanedione [HB4CP] (L) with Cr(III) metal ion in different percentage of Dioxane-water, DMF-water and DMSO-water mixtures having varying dielectric constants have been determined pH metrically. The ionic strength (μ = 0.1 mol.dm^{-3}) was maintained constant. The stability constants (log k) of binary (1:1) systems found to increase with increase in percentage of Dioxane, DMF and DMSO. The studies of effect of dielectric constants of medium on the stability constants of (HB4CP) and Cr(III) metal ion have also been studied.

Key words :- Dielectric constant, Hydroxy-1,3-Propanedione, stability constants.

INTRODUCTION

Substituted hydroxy-1,3-propanediones (β-diketones) 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 insecticidals, bactericidals, pharmaceuticals and fungicidals.

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 dielectric constant is one of the characteristics of liquid. The proton-ligand and metal-ligand stability constants are strongly affected by the dielectric constant of the medium because of the fact that at least one of the constituents is charged and other is either changed or has a dipole. Variations in the relative strengths of acids and bases with changing solvents should be a function of the charge, the radius of the ion and the dielectric constants of the medium. It has been reported that an acid in solvents of similar dielectric constants exhibits different strengths e.g. dissociation of substituted benzoic acids in aliphatic alcohols and aqueous dioxane with identical dielectric constants, is different.

The determination of pK and log K values in various percentages of dioxane-water and other organic solvent-water mixtures have been made by a number of workers [7-12]. Reddy et al [13] have studied the effect of dielectric constant on the stability of Co(II) and Ni(II) with 2-mercaptoethyl benzimidazole, glycine, ethylene diamine and

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salicylic acid in various proportions of ethyl-water mixtures at 30 ^{0}C and μa = 0.1 M ($NaClO_4$), Influence of dielectric constants on stability constants of Cu(II) complexes with substituted isoxazoline have been studied by Patil et al [14]. Speciation of binary complexes of Ca(II), Mg(II) and Zn(II) with L-glutamic acid in DMSOwater Mixtures has been studied [15].Recently Thakur et al[16,17] have studied in influence of ionic strength of medium on the complexequilibria of substituted hydoxy-1-3-propandiones with Cr(III) andLa(III) metal ions and Metal-ligand stability constants of Th(III), Sm(III), Nd(III) and Pr(III) metalion complexes with 2-mercapto-4-substituted phenyl-6-substituted phenyl pyrimidines at 0.1 M ionic strength pH metrically . Nageswara Rao et al[18,19] have studied influence of dielectric constant on Protonation Equilibria of LMethionine in aqueous solutions of propylene glycol and acetonitrile & on Complex Equilibria of L- dopa Complexes of Toxic Metal ions. Narwade et al[20] have investigated the Metal-ligand Stability Constants of Cu(II) Complexes and Measurement of Viscosity, Refractivity Index with some substituted Pyrazoles and Diketones at 0.1M Strength. Shivaraj et al [21] have studied formation constants and thermodynamic parameters of bivalentmetal ion complexes with 3-amino-5-ethyl isoxazole Schiff basesand N, N; N, O and O, O donor ligands in solution

The present paper describe the complexation of Cr(III) metal ion with 1-(2'-Hydroxy-5'-Bromophenyl)-3-(4'Chlorophenyl)-1,3-Propanedione [HB4CP] (L) at 0.1 mole.dm^{-3} ionic strength in various percentages of Dioxane, DMF and DMSO in water mixtures by Calvin-Bjerrum pH metric technique at (29 ± 0.1)^{0}C. It also deals with the study of the effect of dielectric constants of medium on proton-ligand and metal-ligand stability constants of Cr(III) with [HB4CP] (L).

EXPERIMENTAL SECTION

The ligands [HB4CP] L was synthesized in the laboratory by known 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 ligand was prepared by dissolving required amount of ligand in a minimum volume of dioxane subsequently diluted to final volume. Metal ion solution was prepared by dissolving metal nitrate (Sigma - Aldrich) and standardized 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 standardized . The stock solution of percholric acid was prepared and used after standardization .

Measurements :-

All measurements were carried out at (29 ± 0.1) ^{0}C. Systronic microprocessor based pH meter with magnetic stirrer and combined glass and calomel electrode assembly 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.

Procedure :-

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 60, 70, 75 and 80 percentages of Dioxane, DMF and DMSO-water mixtures and reading were recorded for each 0.1 ml addition. The curves of pH against volume of NaOH solution were plotted [22-24].

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 replaceable 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 volume of NaOH against pH.

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

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

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 Ligand were calculated by algebraic 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

$$n = \frac{(E_0+N)(V_3-V_2)}{(V_0+V_2)\,T_m{}^0} \qquad .....(1)$$

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 x 10^{-4} mol dm^{-3}) is the concentration of metal ion in reaction mixture.

The thermodynamic dissociation constants (proton-ligand stability constants) pK for the different systems are listed in table 1. These values were calculated by using an appropriate co-relation made to glass electrode for converting the 'B' values (pH meter readings) into pH values by the method of Van-Vitert and Fernedius [25]. The pH meter reading B was converted into hydrogen ion concentration using the equation.

$$-\log H = B \log 1/r + \log U^0{}_H$$

It could be seen from table 1 that pK values increases with increase in percentage of Dioxane, DMF and DMSO in mixtures. The variations in the values with the dielectric constants were investigated from the plots of pK versus 1/D and pK versus mole fraction of organic solvent.

Effect of Dielectric Constants:-

The proton-ligand (pK) and metal-ligand stability constants (log K) are strongly affected by the dielectric constants of the medium because of the fact that at least one of the constituents is charged and other is either charged or has a dipole moment.

The plots of pK, log K versus 1/D shows non-linear relationship in our present investigations. The linear relationship between pK versus 1/D holds good only for low percentages of organic solvents. But at a higher percentage, there is a non-linear ship which is an agreement with the observation of Aditya et al [26]. Ikhe [27] have also investigated the similar type of study of different complex equilibria. The plot of pK, log K versus mole fraction exhibits linear relationship for various percentage of organic solvent. The slope values vary from 9.0 to 12.0. The observed slope value from the plot of pK versus mole fraction for HB4CP (L) is 8.2532. The slope value is smaller than that of acetic acid and propionic acid. This may be due to the fact that acetic acid and propionic acids are neutral molecules while the ligand used in present investigation is charged ions, when H$^+$ ion is displaced from -OH group.

Jahagirdar and Khanolkar (10) have investigated the effect of dielectric constants on pK and log K values of Cu (II)-3, 5-dibromosalicylic acid. Sondawale et al [11] have investigated the effect of dielectric constants of methanol-water mixtures on stability constants of Cu (II) amino acid peptide complexes. Khobragade [28]has investigated the effect of dielectric constants of non proteic solvent and protetic solvent (ethanol) on dissociation and association of Cu (II) Glycyl-Glycine. Gulwade [29] has reported the effect of dielectric constant of Co (II) and Sm(II) with 2-(5-mercapto- [1-2-3]-oxadiazol-2-yl)-phenol in DMF-water mixture. Naik et al [30] have investigated influence of dielectric constants on complex equiliria between substituted pyrazolines and lanthanides metal ions in dioxane-water mixture.

The thermodynamic stability constants (log K) of Cr(III)-HB4CP (L) complexes in different percentage of dioxane-water, DMF-water and DMSO-water mixtures are determined and tabulated in table 2. It could be seen from table 2 that log K values increased with the increase in percentage of organic solvents and that would be due to the effect of bulky organic solvents.

The difference between log K_1 and log K_2 :-

The difference between log K_1 and K_2 values is calculated for representative system and is presented in table 3. It is observed from table 3 that difference between log K_1 and log K_2 continuously decreases with the increase in percentages of Dioxane, DMF and DMSO. This means that either log K_1 is relatively decreasing or log K_2 relatively increasing as a dielectric constant is increased. The increased dielectric constant would decrease the electrostatic forces of attraction between metal ion and negatively charged ligand to form 1:1 complex. The formation of 1:2 complexes on the other hand is due to the reaction between similarly charged ions.

Table 1 Proton-ligand stability constants (pK) of HB4CP (L) in different % of organic solvent-water mixture at 0.1 mol.dm^{-3} ionic strength

% of Dioxane	Dielectric Constant(D)	1/ D	Mole Fraction	pK
60	25.85	0.03868	0.2408	7.9825
70	17.69	0.05652	0.3308	8.8750
75	14.40	0.06944	0.3881	9.3062
80	10.90	0.09174	0.4582	9.8500

% of DMF	Dielectric Constant(D)	1/ D	Mole Fraction	pK
60	22.02	0.0454	0.2605	9.080
70	25.69	0.0389	0.3539	9.175
75	27.76	0.0360	0.4134	9.760
80	29.61	0.0337	0.4843	9.820

% of DMSO	Dielectric Constant(D)	1/ D	Mole Fraction	pK
60	72.10	0.0138	0.2756	8.5647
70	71.08	0.0140	0.3718	8.6575
75	70.40	0.0142	0.4322	8.8500
80	69.80	0.0143	0.5037	8.9921

Table 2 Metal-ligand stability constants (log K) of Cr(III) HB4CP (L) in different % of organic solvent-water mixture at 0.1 mol.dm^{-3} ionic strength

% of Dioxane	Dielectric Constant(D)	1/ D	Mole Fraction	log K_1	log K_2	logK_1-log K_2
60	25.85	0.03868	0.2408	7.0000	4.2510	2.749
70	17.69	0.05652	0.3308	7.6750	5.0240	2.651
75	14.40	0.06944	0.3881	8.7234	6.1729	2.550
80	10.90	0.09174	0.4582	9.6250	7.2750	2.350

% of Dioxane	**Dielectric Constant(D)**	1/ D	**Mole Fraction**	**log K_1**	**log K_2**	**logK_1-log K_2**
60	22.02	0.0454	0.2605	7.5375	5.5495	1.9880
70	25.69	0.0389	0.3539	7.6880	5.7380	1.9500
75	27.76	0.0360	0.4134	8.3125	6.7279	1.7846
80	29.61	0.0337	0.4843	9.1861	7.5620	1.6241

% of Dioxane	**Dielectric Constant(D)**	1/ D	**Mole Fraction**	**log K_1**	**log K_2**	**logK_1-log K_2**
60	72.10	0.0138	0.2756	6.3875	4.1750	2.2125
70	71.08	0.0140	0.3718	6.5757	4.9625	1.6132
75	70.40	0.0142	0.4322	6.5968	5.1764	1.4204
80	69.80	0.0143	0.5037	7.5625	6.2875	1.2750

Table 3 System : Cr(III) - HB4CP (L)

% of Dioxane-Water	**log K_1-logK_2**	**% of DMF-Water**	**log K_1 - log K_2**	**%of DMSO-Water**	**logK_1-log K_2**
60	2.749	60	1.988	60	2.212
70	2.661	70	1.950	70	1.613
75	2.550	75	1.784	75	1.420
80	2.350	80	1.624	80	1.275

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