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Role Of Dielectric Environment Over The Stability And Molar Absorptivity Of 1:1Fe(III)-5-Sulphosalicylicylate Complex In Mixed Solvent At RTP.

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Abstract: Spectrophotometric method have been employed for the study of 1:1Fe(III)-5-Sulphosalicylicylate Complex in the mixed solvent of different percentage of methanol-water mixed solvent (Methanol-water mixture - 5%, 10%, 15%, 20% and 25%) at RTP (298.15K). The stability constant and molar absorptivity coefficients of the Ligand to Metal charge transfer complex (LMCT) formed by Fe(III) and 5-Sulphosalicylate ion (5-SSA) were determined, simultaneously using a novel graphical computational method developed in our Electrochemical sensor laboratory. The changing trends in these parameters are correlated with the various molecular and intermolecular factors affecting it such as hydrogen bonding, charge transfer interaction, dipole-dipole interaction, Di electricity and Van der Waals interaction etc.

Keywords: 1:1Fe(III)-5-Sulphosalicylate complex, stability constant, molar absorptivity coefficients, molecular and intermolecular factors, mixed solvent system, Novel Graphical Computational method.

Introduction

As for as metal ligand interaction and process of complexation is concerned, metal-ligand Equilibria is the study of phenomena through which metal ion undergoes formation of complex with different species. Fe(III) forms charge-transfer complexes (CT Complexes) with several inorganic and organic ligands in aqueous as well as mixed solvent systems. The metal ligand equilibrium studies have been undertaken by a number of workers for charge-transfer complexes using spectrophotometric as well as ultrasonic techniques[1-5]. Inspite of these, some other techniques have also been used but given limited results.

Charge-transfer complexes (CT- Complexes) are formed in case of molecular association[3] as well as metal ligand complexation. Many scholars have undertaken, systematic studies of electrolytic solutions and determined ultrasonic parameters of electrolytic solutions, ultimately for the determination of stability of resulting complex[6-11]. Some of these were carried out in pure and binary liquids (Mixed solvent)[12-19].

Studies on bivalent metal complexes of organic liquids have been undertaken in different mixed solvents at different temperatures[4,20]. In present work, we have undertaken a systematic study of Fe(III)-5-SSA system using spectrophotometric methods (A novel graphical computational method), in methanol-water binary solvent mixture, at 298.15K.

Theory:-

Spectrophotometric measurements:-

For a simple complexation process, let us consider the formation of 1:1 charge-transfer complexes as fallows –

$$M \quad + \quad L \quad \leftrightarrow \quad ML \qquad \ldots\ldots \qquad (1)$$

The stability constant is expressed by-

$$K = \frac{[ML]}{[M][L]} \qquad \ldots\ldots \qquad (2)$$

As for as development of different methods are concerned, a number of graphical methods have been developed for the determination of stability constant[21-25]. However all these methods give approximate values, as to derive the linear equation in which one or the other parameters have been neglected[26].

Therefore, it was necessary to develop a method which does not neglect any parameter. The method is outlined bellow-

From the equation (2), it fallows-

$$K = \frac{[ML]}{(M^o - [ML])(L^o - [ML])} \qquad \ldots\ldots\ldots\ldots \qquad (3)$$

Where M^0 and L^0 are the analytical concentration of metal ion and ligand respectively. Charges are omitted for the simplification. If metal ion, ligand and complex absorb light in the region of study, the absorbance per unit path can be expressed as fallows

$$A = (M^o - [M\,L])\,\varepsilon_m + [M\,L]\,\varepsilon_{ml} + (L^o - [M\,L])\,\varepsilon_l \qquad \ldots\ldots\ldots \qquad (4)$$

Where ε_m ,ε_{ml} and ε_l are the molar absorptivity of the species M,ML and L respectively.

The equation (3) can be rearranged as-

$$[ML]^2 - (M^o + L^o + 1/K)\,ML + M^oL^o = 0 \qquad \ldots\ldots\ldots \qquad (5)$$

From which it follows

$$[ML] = [M^o\ L^o]/[M^o+L^o+1/K]\ \ +[M^o\ L^o]^2/[M^o+L^o+1/K\ ]^3\ \ +\qquad \ldots\ldots \qquad (6)$$

If A is the absorbance of the solution under study then for 1 cm path length one can write

$$A=\mathcal{E}\ [ML] \qquad \ldots\ldots \qquad (7)$$

If the higher terms in the equation (6) can be omitted then[23]–

$$A = \mathcal{E}\ M^o\ L^o\ /\ [M^o + L^o+1\ /\ K] \qquad \ldots\ldots \qquad (8)$$

This on rearrangement converted to-

$$M^o\ L^o\ /\ A = M^o + L^o/\ \mathcal{E}\ \ +1\ /\ \mathcal{E}\ K \qquad \ldots\ldots. \qquad (9)$$

If $M^o\ L^o/\ A$ is plotted against $(M^o +L^o)$ a straight line with slop $1/\mathcal{E}$ and intercept $1\ /\ \mathcal{E}\ K$ would obtain.

However if we do not neglect the higher terms then we get the equation-

$$\frac{M^oL^o}{A} \quad + \quad \frac{A}{\varepsilon^2} \quad = \quad \frac{1}{\varepsilon}(M^0+L^0) \quad + \quad \frac{1}{\varepsilon K} \qquad \ldots\ldots.. \qquad (10)$$

In above equation the value of $\mathcal{E}$ is not known and hence a trial value of $\mathcal{E}$ can be taken and the left hand side is plotted against (M^0+L^0) to get a straight line. From the slope of this straight line a new value of $\mathcal{E}$ will be obtained, which could be refined by successive approximations gradually. The process of iteration to be continued, till two trial value and calculated value not resulting same.

Results and Discussion:

The 1:1 complex formed by Fe(III) with Sulphosalicylate shows strong absorption in the visible range of the spectra with λ_{max}at 490 nm.This value remain same even when the proportion of the binary solvent mixture is varied. This is because of the fact that there is formation of only one type of complex in the solution even by variation of the concentration of ligand.

The high values of molar absorptivity (Table-1) reveal that the spectral band is due to the formation of ligand to metal charge-transfer complex. The stability constant values calculated by spectrophotometric method developed in our electrochemical sensor laboratory. The changing trend of stability constant by changing the proportions of solvent mixture is shown in (Table-1).

We know that with the increase in the concentration of Methanol in the solvent mixture, the polarity of the solvent decreases, which in turn decreases the extent of hydrogen bonding and dielectric constant of the medium. This increases the probability of the formation of the complex, that’s why it increases the extent of complexation (Fig-1).

Experimental:

Materials and methods:-

Ferric Chloride (BDH), sodium salicylate (E.Merck) and methanol (E.Merck) all were of AR grade and used as such without any further purification. For the preparation of methanol-water mixed solvent (5%, 10%, 15% 20% and 25%, v/v) and other solutions triply distilled water was used. All samples were prepared in 25 mL and 50 mL measuring flasks with tied mouth ends. Absorbances of the complex solution were measured by 1cm path length DIGITAL UV VISIBLE double beam spectrophotometer (SYSTRONICS) at λ_{max} 490 nm. For spectroscopic measurements, the set of five solutions were prepared in which the concentration of Fe(III) ion was kept higher so that only 1:1 complex is formed. In these solutions the concentration of 5-Sulphosalicylate ion was kept constant where as the concentration of Fe(III) was varied.

For weighing the different materials a digital balance was used with an accuracy of ± 0.0001%. During experimentation the binary solvent mixture was prepared before two hours for maintaining the equilibrium between components. All standard solutions of components as well as complex were prepared freshly for to prevent hydrolysis and deformation.

Conclusion:-

As far as the present experiment is consider, A Novel Graphical computational method (Developed in our Electrochemical Sensor laboratory) was used for Spectrophotometric study for Fe(III)-5-SSA complex. The impact of dielectric environment over stability of this CT complex, the observation was almost in the linear fashion (Table-1, Fig-1) which is clearly indicating that as the percentage of non-aqueous component in the mixed solvent increases which gradually increases the stability of the complex and the same observation in the change in Gibbs free energy and molar absorptivity recognized. A possible considerable reason that, as the non-aqueous content of the mixed solvent increases, the dielectric power of the media gradually deceases because the polarity of the solvent mixture decreases, accordingly which favorers more stabilization of the CT complex in comparison to pure media(Table-1). The stabilization of this Chelate Complex is very high than simple non chelate complex such as Fe(III)-thiocynate CT Complex etc.

References

1. K.D. Umaley, P.G. Rohankar and A.S. Aswer, *J.Pure Appl.Ultrason*., 2007,**29** ,104.

2. S. Xavier Jesu Raja, V.Kannappan and R. Jaya Santhi, *Phys. Chem. Liq*.,2003, **14**, 133.

3. M.S. Refat, S.M. Aqeeland I.K. Grabtchev, *Can. J. Anal. Sci. Spect*.,2004, **49**, 4.

4. P.B. Raghuwansi, A.G. Doshi andD.T. Tayade, *J.Pure appl. Ultrason*., 2009, **29**, 99.

5.V.Ulagendran,R.Kumar,S.Jayakumarand V.Kannappan, *J.Mol.Liq*.,2009, **148**,67.

6. M.M. EL-Bahay,M.C. EL-Messal and A.D. Ellal, *J.Pure Appl.Ultrason*.,1999, **21**,103.

7.S.V. Soitkar andS.N. Jojoo*Acoustic Lett*., 1984, **7**,191.

8. S. Kalyanasundaram and Saraswati.,*Ind. J.Pure Appl. Phy*.,1993, **31**,936.

9. V. Arumugam et al, *J.Pure Appl.Ultrason*.,1999, **21**, 38.

10.Mohd. Idrees and Mohd.Sidique, *Ind.J.Chem*., 2003, **42**, A.

11. S.B. Jahagirdar,*Ind. J. Pure Appl.Phy*.,1996, **34**, 425.

12.M.G. Sheshagiri Rao, *Ind.J.Pure Appl.Phys*.,1971, **9,**169.

13.R.P.Varma and Surendrakumar, *Ind.J.PureAppl.Phy*., 2000, **38**, 96.

14.U.N. Das and M.R. Patnaik, Ind.*J.Appl.Phys*.,1997, **35**, 87.

15. S.K. Upadhyay, *Ind.J.Pure Appl.Phys*.,2000, **39**, 537.

16.A. Anwer Ali and A. K. Nain, *Ind.J.Pure Appl.Phys*., 1999, 14.

17.N.G. Belsare, V.P. Akhare and V.S. Deongaokar, *Acoustic Lett*.,1999, **14,** 37.

18. P.B. Agrawal and M.L. Narwade, *A. cine.Ind*.,2002, **38**, 163.

19.A.V. Satyavathi,K. Sundarma, B. Sanjeeva Rao, *J.Pure Appl.Ultrason*.,2008, **30**, 57.

20.C.C. Deshmukh, A.G. Doshi and C.M. Desmukh, *J.PureAppl.Ultrason*., 2003, **25**, 105.

21.H.S. Frnk and R.L. Oswalt. *J.Am.Chem.Soc*. 1947**, 69**, 1321.

22. H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc*., 1949, **71**, 2703.

23. H. McConnel and N. Devidson, *J.Am. Chem. Soc*., 1950, **72**, 3165.

24. R.W. Ramette, *J. Chem. Ed*.,1963, **40**, 71.

25. P.R. Hammond, *J.Chem. Soc*.,1964, 479.

26. S. Srivastava, S.S. Sanjay and M.C. Chattopadhyaya.*J. Inst. chemists (India).*, 2010, **82**, Part 6.

27.O. Nomoto, *J. Phys. Soc. Japan.*,1958, **13**, 1528.

28. S. Prabakar,K. Rajagopal, *J. Pure Appl. Ultrason.*, 2005, **27**, 41.

29. D. Geetha and C.Rakkhppan, *J.Mol.Liq.*,2005,**121**, 102.

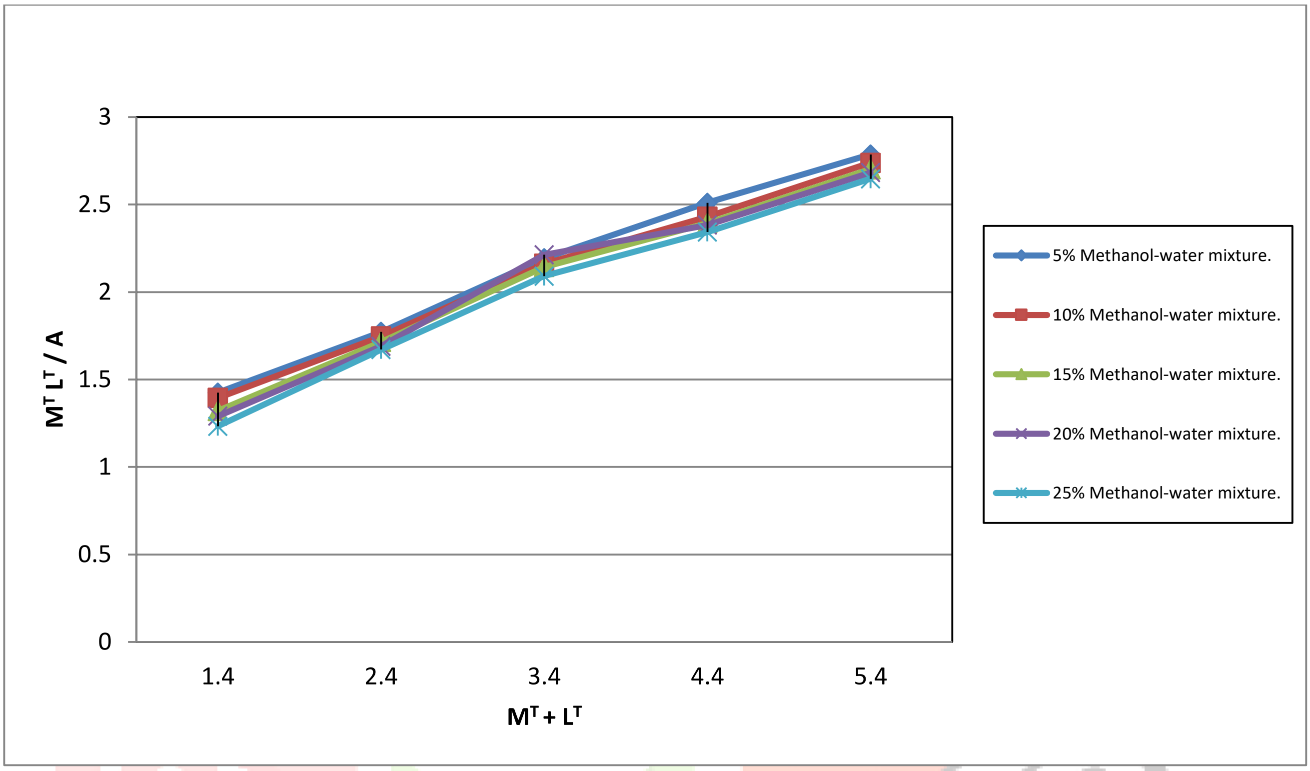

Fig. 1. A graph between $M^T L^T$ / A versus $M^T + L^T$ for Fe(III)-5-SSA System in different proportions of methanol-water mixture.

Table-1: Comparative analysis (In acidic medium) of stability constant, log K, molar absorptivity, Change in Gibb’s free energy for Fe(III)-5-SSA CT complex and variation in these parameters with change in the methanolic proportions in mixed solvents at RTP.

Methanol-Water as solvent mixture.	Medium (pH range 2.0– 3.0)	λ_{max} (nm)	Stability constant (K)	Log K	ΔG^0 **($KJmol^{-1}$)** $x10^{-4}$	ε x 10^{-3}
0%	Acidic Medium	490	138	2.1398	-1.21	3.95
5%		490	476	2.6776	-1.50	3.99
10%		490	493	2.6928	-1.52	4.19
15%		490	512	2.7092	-1.54	4.45
20%		490	630	2.7993	-1.59	4.73
25%		490	812	2.9095	-1.65	4.98