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Effect of dielectric constants of methanol- water and acetone-water mixtures on proton-ligand and metal-ligand stability constants of Cu(II)-salicylic acid complex

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ABSTRACT

The interaction between Cu(II) and salicylic acid has shown 1:1 and 1:2 complex formation. The complex formation has been investigated pH metrically in different percentage of methanol-water and acetone-water mixture at temperature (29°C + 0.1°C). The method Bjerrem and Kelvin as modified by Irving and rossotti has been used in the present work. It shows that proton – ligand and metal – ligand stability constant increased with increasing the percentages of methanol – water and acetone – water.

Key words: Dielectric constants, protons ligand, stability constants.

INTRODUCTION

A survey of literature reveals that metal – ligand stability constants of amino acid, adipic acid, itaconic acid and sulphonic acid derivatives with metal ions have been studied by many workers[1]. The narwade *et al.,*[2] have investigated the stability constant of lanthanides ions with some substituted sulphonic acid spectrophotometrically. The proton - ligand stability constants of o-hydroxy acetophenonoxime and its substituted derivatives have been reported Ingle and Khanolkar[3]. Narsade etal[4] have investigated the interaction between Fe(III) and substituted Chalcones at 0.1M ionic strength potentiometrically. The interaction between Cu (II) chelates and 2-hydroxy aromatic ketones and alkyl mono-amines is studied by Rabindranth[5]. The metal – ligand stability constants with 1, 3-diketone and substituted pyrazoles and pyraxolines have been studied by Sawalakhe *et al.,*[6] spectrophotometrically. Narwade *et al.,*[7] have investigated the interaction of Fe (III) with substituted chalcones at 0.1M ionic strength pH metrically. Shelke etal[8] have studied equilibrium constants of UO_2(II) and Cu (II) ions with dicarboxylic acid in dioxane-water mixtures.

In a view of analytical application, it is worthwhile to know the physico-chemical properties of metal ion complexes and the effect of dielectric constants of methanol-water and acetone-water mixtures on stability constants. Therefore the present work is undertaken to make a systematic study of Cu(II) complexes with salyclic acid pH metrically.

EXPERIMENTAL

Chemicals

All the chemicals such as sodium hydroxide, sodium perchlorate, perchloric acid, methanol, acetone, Copper nitrate, salicylic acid were of analar grade.

Chelating Agent

Salicylic acid ligand used was crystallized and its purity was checked before use. The solution of ligand (Chelating agent) was prepared in aqueous medium by dissolving an approximate amount of it.

Metal ion

The solution of Copper nitrate (BDH) was prepared in water and its concentration was checked by EDTA.

pH-meter

pH meter EQUIP-TRONICS Model EQ-610 Digital pH METER was used in the present investigation for measuring the pH of solution. It was calibrated by standard buffer solution pH 4.04, 7.0 and 9.12.

Calvin-Bjerrum Titration

pH metric titrations were carried out by using Calvin-Bjerrum titration technique in an innert atmosphere by bubbling oxygen-free nitrogen gas through an assembly containing electrodes in order to keep away CO_2.

Experimental procedure involved pH metric titrations in different percentages of methanol-water and acetone-water mixtures (10%, 20%, 30% .....) of carbonate free solution of;

(1) Free $HClO_4$ (1.00×10^{-2} M)
(2) Free $HClO_4$ (1.00×10^{-2} M) + Ligand (20.000×10^{-4} M) and
(3) Free $HClO_4$ (1.00×10^{-4} M) + Ligand (20.000×10^{-4} M) + metal (4.000×10^{-4} M) against standard solution of sodium hydroxide (0.2 M) at temperature 29°C.

Ionic strength of 0.1 M was maintained by adding an approximate amount of 0.1M $NaClO_4$ solution. Same procedure was used for (10, 20, 30, 40 .... %) of acetone –water mixtures. pH values were corrected by use of Van-Vitart and Hass equation[9].

RESULTS AND DISCUSSION

The plots of pH Vs. volume of NaOH showed that, the deviation of (acid + ligand) curves started around pH 2.6 for all the percentage of methanol-water and acetone-water mixtures and continued up to pH 10.6. The average number of proton associated with the ligand (n_A) were determined by Irving-Ropssotti's equation[10]. The formation curves were constructed by plotting the values of n_A against pH of the system in all the percentages of methanol-water and acetone-water mixtures. The pK_{COOH} values (Dissociation constant) of (-COOH) were estimated by noting the pH at which nA=0.5 accurate values were also determined by a point wise calculations. The pK_{COOH} of salicylic acid in all the percentage of methanol – water and acetone – water were presented in table – 1 and 2 respectively.

It is observed from Table 1 and 2 that, pK values increased with increasing the percentage of methanol-water and acetone-water mixtures. It could also be seen that the pK values in methanol-water mixture are grater than the pK values of acetone-water mixtures.

Table 1: Proton – ligand stability constants of salicylic acid indifferent % of methanol-water mixtures of 0.1 M ionic strength

% of Methanol-water mixture	Dielectric Constant (D)	1/D	Mole Fraction	pK_{COOH}
10	75.00	0.0133	0.01	4.8
20	70.10	0.142	0.05	5.38
30	60.80	0.0164	0.160	6.3
40	60.20	0.0166	0.205	7.1
50	52.50	0.019	0.435	7.95
60	50.20	0.0199	0.452	8.8
70	40.80	0.0245	0.49	9.55
80	40.10	0.0249	0.566	10.4

The precision-of experimentally determined pK values

The precession of experimental pK values are examined by determining the pK values of the ligand, from two sets pH metric titrations. All the experimental conditions except the concentration of the ligand and sodium hydroxide were kept identical for two sets.

Table 2: Proton - ligand stability constants of salicylic acid indifferent % of acetone-water mixtures of 0.1 M ionic strength

% of Methanol-water mixture	Dielectric Constant (D)	1/D	Mole Fraction	pK_{COOH}
0	78.00	0.0128	--	3.8
10	73.00	0.0136	0.0360	4.1
20	67.00	0.0149	0.0790	4.4
30	61.00	0.0163	0.1290	4.7
40	55.00	0.0181	0.1850	4.95
50	48.00	0.0208	0.2630	5.25

Table 3: Determination of standard deviation (σ) in 30% methanol-water mixtures

pH	Set In_A	Set IIn_A	Δn_A	$\sigma=\left[\frac{\Sigma(\Delta\bar{n}_A)^2}{(n-1)}\right]^{1/2}$
2.4	0.7532	0.7535	0.003	σ= 0.0032
2.6	0.6918	0.6925	0.0017	
2.8	0.6513	0.6615	0.0002	
3.0	0.6005	0.6009	0.0003	
3.2	1.5905	0.5906	0.0001	
3.4	0.5342	0.5413	0.0071	
3.6	0.5165	0.5008	0.0157	
3.8	0.5005	0.4900	0.0105	
4.0	0.3942	0.3900	0.0042	
4.2	0.1225	0.1265	0.0040	
4.4	0.0910	0.0950	0.004	

Table 4: Determination of standard deviation (σ) in 10% acetone-water mixtures

pH	Set In_A	Set IIn_A	Δn_A	$\sigma=\left[\frac{\Sigma(\Delta\bar{n}_A)^2}{(n-1)}\right]^{1/2}$
4.9	0.8352	0.8311	0.0041	σ= 0.03783
5.0	0.7572	0.7552	0.0020	
5.1	0.5631	0.5531	0.0100	
5.2	0.4667	0.4652	0.0015	
5.3	0.3207	0.4117	-0.0910	
5.4	0.2251	0.2160	0.0091	
5.5	0.1266	0.1290	-0.0024	

The proton – ligand formation no. (n_A) at various pH values obtained from two sets are presented in table -3 and 4.

The values of $\hat{n}_A$ at a particular pH are determined and standard deviation σ of the values calculated by using expression

$$\sigma=\left[\frac{\Sigma(\Delta\bar{n}_A)^2}{(n-1)}\right]^{1/2}$$

where n is number of observations.

Metal-ligand stability constants

The departure of (free acid + ligand + metal ion) curve from (free acid + ligand) curves were obtained around pH 3.75 in all the % of methanol-water and acetone-water mixtures. This showed the commencement of complex formation between ligand and metal ion before the hydrolysis. The values of n (metal=ligand formation number) were calculated by using Irving-Rossotti's Expression[10]. The values of log k_1 (metal-ligand stability constant for 1:1 complex) and log k_2 (metal-ligand stability constant for 1:2 complex) were obtained from the plots of n Vs. PL by half integral method as well by point-wise calculations in all the percentages of methanol-water and acetone-water mixtures and these are given in table 5 and 6. It is observed from these tables that log k_1 and log k_2 values increased with increasing the percentages of methanol-water and acetone-water mixtures. This may be due to the fact of the effect of organic bulky solvent which decreases the formation constant but increases log k_1/log k_2 values.

Table 5: Metal - ligand stability constants (log k) of Cu(II) complexes with salicylic acid in different percentage of methanol-water mixtures pH metrically

% of Methanol-water mixture	Dielectric Constant (D)	1/D	Mole Fraction	log k_1	log k_2
10	75.00	0.0133	0.01	2.9	1.154
20	70.10	0.0142	0.05	3.25	1.25
30	60.80	0.0164	0.160	3.6	1.4
40	60.20	0.0166	0.205	4.0	1.5
50	52.50	0.0190	0.435	4.4	1.65
60	50.20	0.0199	0.452	4.75	1.75
70	40.80	0.0245	0.49	5.1	1.9
80	40.10	0.0249	0.566	5.5	2.05

Table 6: Metal - ligand stability constants (log k) of Cu(II) complexes with salicylic acid in different percentage of acetone-water mixtures pH metrically

% of Methanol-water mixture	Dielectric Constant (D)	1/D	Mole Fraction	log k_1	log k_2
0	78.00	0.0128	--	2.52	1.01
10	73.00	0.0136	0.036	2.65	1.12
20	67.00	0.0149	0.079	2.80	1.25
30	61.00	0.0163	0.129	2.95	1.35
40	55.00	0.0181	0.185	3.05	1.45
50	48.00	0.208	0.263	3.20	1.55

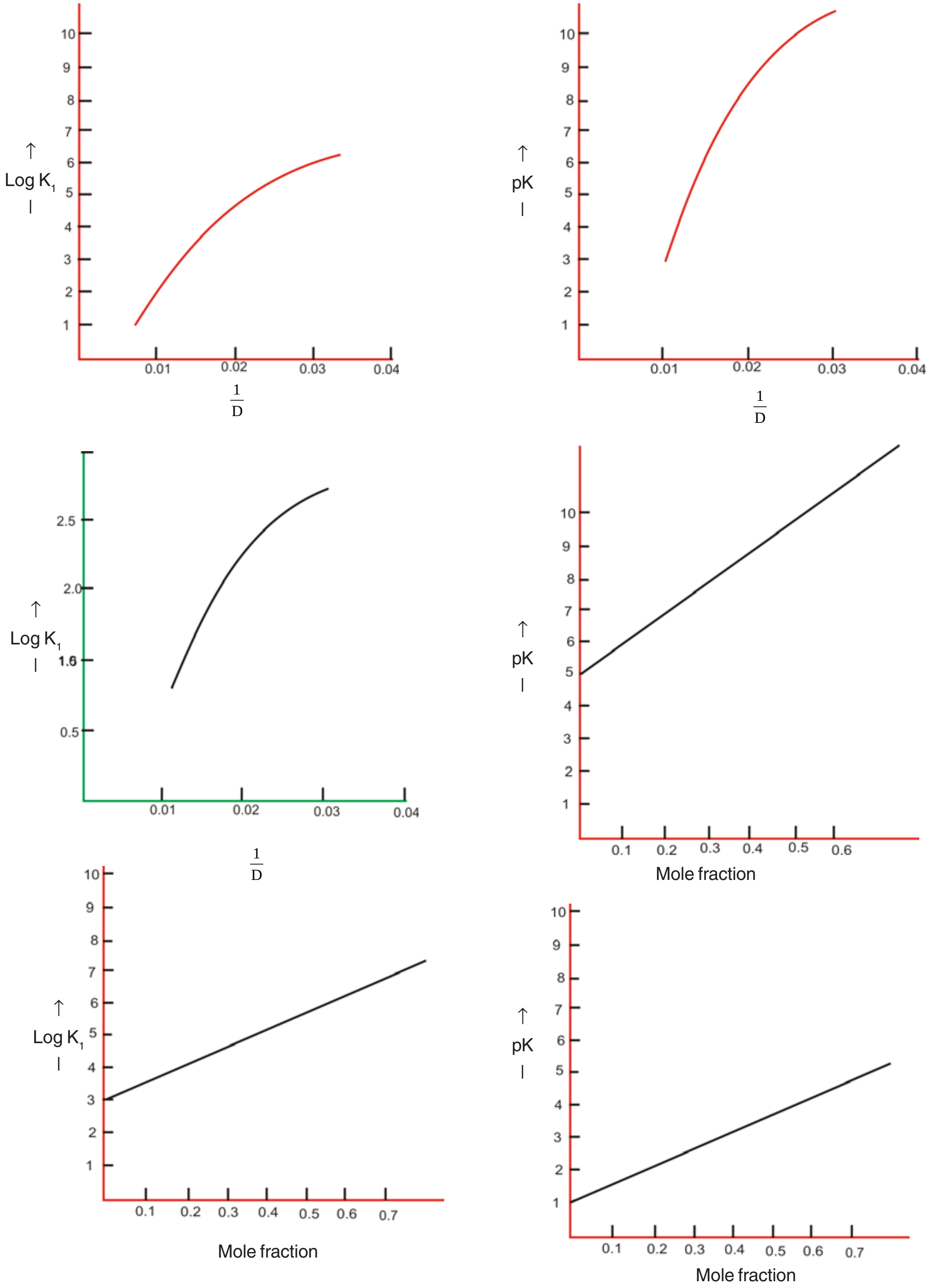

Fig. 1-6: The Plots of pK/Log k Vs. 1/D and mole fractions for methanol-water mixtrue

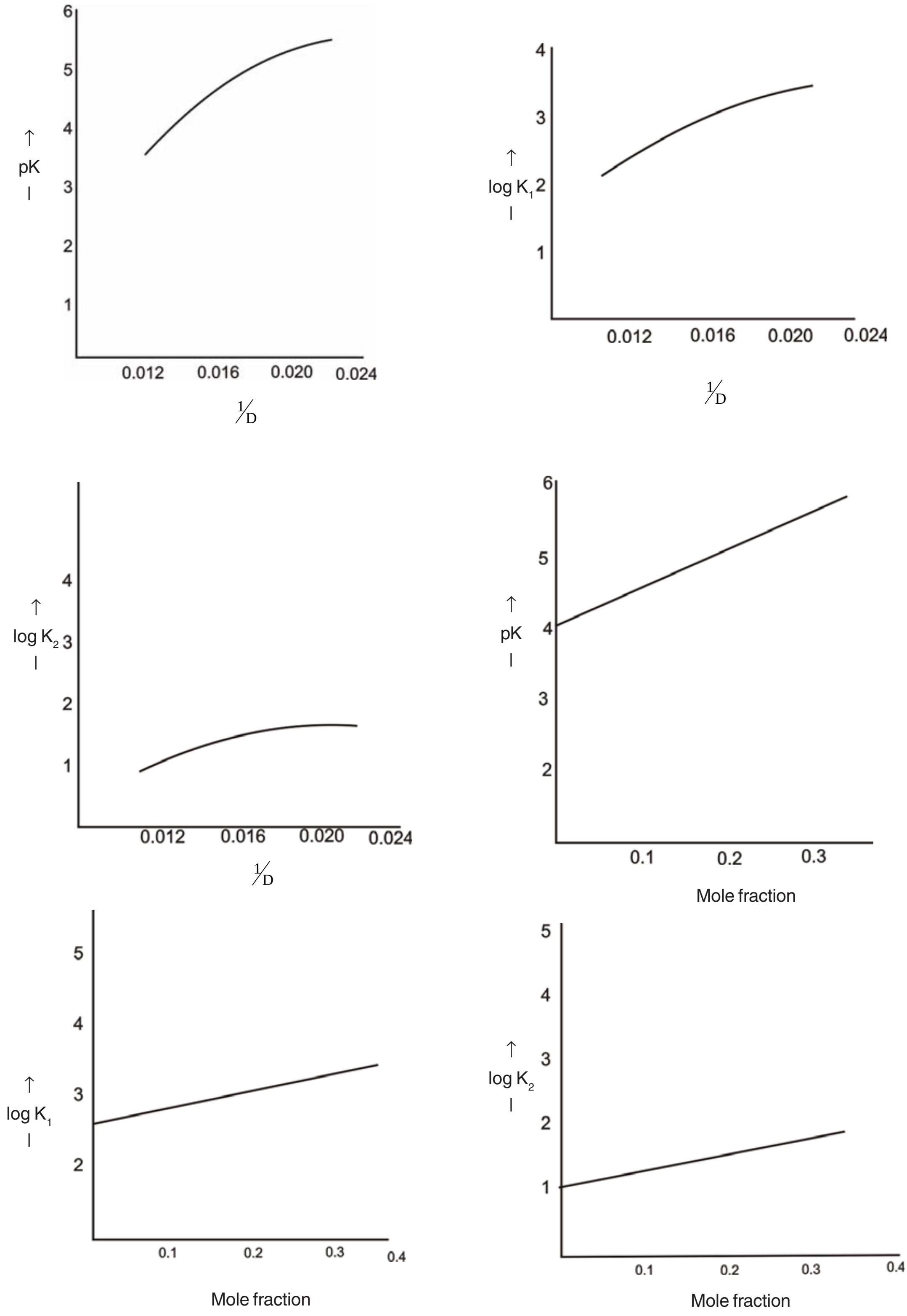

Fig. 7-12: The Plots of pK/Log k Vs. 1/D and mole fractions for acetone-water mixtrue

The values of log k_1 and log k_2 in different percentages of methanol-water mixtures are grater than the values log k_1 and log k_2 for different percentages of acetone-water mixtures.

The data obtained from our present investigation are found to be in good agreement with the values obtained by Yasuda[11] and Jahagirdar[12].

The Plots of pK/Log k Vs. 1/D (D-Dielectric Constant) and Mole Fractions Fig.(1-12)

The plot between pK / log K Vs. 1/D showed fairly linear relationship at low % of methanol-water and acetone mixture (Fig. 1 – 12). But at high percentages of methanol-water and acetone-water mixtures it showed non-linear relationship. The plots between pK /log K Vs. mole fraction of different percentages of methanol-water and acetone-water fairly linear relationship. Narwade etal[13] have studied the same relationship by diketone complexes with transition metal-ion. The work of Harned Owen[14] has shown an approximate linear relationship for pK values of acetic acid in different percentages of dioxane-water mixtures. Mandakmare etal[15] have studied the same phenomenon for substituted coumarins in different percentages of dioxane – water, DMF – water and THF – water mixtures.

Water is recognised in the solution field as being unique structural ligand in the sense of having three dimensional ice-like frame work.

Franks and Ives[16] have shown the addition of first increment of other organic co-solvency to water. The dielectric constant of medium is not solely responsible for the extent of dissociation; there is at least an additional factor of chemical role of the solvent in most cases. Yasuda[17] has expressed the dissociation constant of some weak acids as a function of dielectric constants of the bulk solvent. Ohtaki[18] showed the solvent effect on dissociation of Ammonium and Pyridinium ions.

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REFERENCES

1. Martell A.E.: "*Stability constants of metal ion complexes".* Special publication Nos. 17 and 25 Chemical Society London, (1960) and (1971).
2. B.G. Khobragade and M. L. Narwade, *J. Indian Chem. Soc.,* **61:**870 (1971).
3. D.B. Ingle and D.D. Khanolkar, *India J. Chem.,* **14A:** 596 (1976).
4. M. L. Narwade, M. M. Chincholkar, *J. Indian Chem. Soc.,* **62:** 194 (1985).
5. Rabindranath and Bhatnagar R.P., *J. Ind. Chem. Soc.,* **LXIII:** 463 (1986).
6. Sawalakhe P. D. and Narwade M. L., *J. India Chem. Soc.,* **71:** 49 (1994).
7. Narwade M. L., Chincholkar M. M. and Sathe S. U., *J. Ind. Chem. Soc.,* **62:** 194 (1985).
8. D. N. Shelke and D.V. Jahagirdar, *J. Inorg. Nucl. Chem.,* **14:** 925 (1979).
9. Van-Vitart L. G. and Hass C. G., *J. Am. Chem. Soc.,* **75:** 541 (1953).
10. Irving H. M. and Rossotti H. S., *J. Chem. Soc.,* **54:** 3397 (1953).
11. Yasuda M., *Bull Chem. Soc. Japan,* **32:** 429 (1959).
12. Narwade M. L., and Jahagirdar D.V., *J. Ind. Chem. Soc.,* 627 (1973).
13. P. D. Sawalakhe and M. L. Narawade, *J. Ind. Chem., Soc.,* **71:** 49 (1994).
14. H. S. Harned and B.B. Owen, *The Physical Chemistry of Electrolyte Solution,* Ed. Rainbold. New York, p. 547 (1950).
15. Mandakmare A. U. and Narwade M. L., *J. Ind. Chem. Soc.* (in press).
16. Frank F. and Ives D.S. G., Quart, Rev. **20:**1 (1966).
17. M. Yasuda, Bull, *Chem. Soc.,* **42:** 573 (1969).
18. H. Ohtaki, *Bull, Chem., Soc. (Japan),* **32:** 429 (1954).