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# Influence of Dielectric Constants on Complex Equilibria of Cu(II)-Salicylic Acid Complexes in Different Percentages of Methanol-Water Mixtures

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The interaction between Cu(II) and salicylic acid in different percentages of methanol-water mixtures at 0.1 M ionic strength has been studied pH-metrically at the temperature 29 ± 0.1°C. The data are used to study the values of proton-ligand and metal-ligand stability constants for 1 : 1 and 1 : 2 complexes. In the present investigation, the effect of dielectric constants on stability constants of complex equilibria is studied.

**Key Words: Influence, Dielectric constants, Cu(II), Complexes, Salicylic acid.**

## INTRODUCTION

Shelke *et al.*[1] have studied equilibrium constants of $UO_2$(II) and Cu(II) ions with dicarboxylic acid in dioxane-water mixtures. Metal-ligand stability constants of dicarboxylic acids (succinic acid, itaconic acid, adipic acid, etc.) with transition metal ions have been determined in aqueous medium by many workers[2]. Proton-ligand and metal-ligand stability constants of Th(IV) with some substituted pyrazolines have been investigated by Gudadhe *et al.*[3] Narwade *et al.*[4] have investigated the interaction of Fe(III) with substituted chalcones at 0.1 M ionic strength pH-metrically. The metal-ligand stability constants with 1,3-diketone substituted pyrazoles and pyrazolines have been studied by Sawalakhe *et al.*[5] spectrophotometrically. The interaction between Cu(II) chelates with 2-hydroxy aromatic ketones and alkalyl mono-amines is studied by Rabindranath[6]. Mandakmare *et al.*[7] have determined the stability constants of $UO_2$(II) complexes with some substituted coumarins by potentiometric and spectrophotometric techniques. Influence of dielectric constant on complex equlibria of Cu(II) *o*-amino-sulphonic acid complexes in different percentages of methanol-water mixtures have been studied by Sondawale *et al.*[8]

The study of the effect of dielectric constants of methanol-water media on Cu(II)-salicylic acid was still lacking. In view of analytical applications, it is of interest to know the physico-chemical properties of metal-ion complexes and the effect of dielectric constants on metal ion complexes of methanol-water mixtures. Therefore, the present work has been undertaken to make a systematic study of Cu(II) complexes with salicylic acid.

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## EXPERIMENTAL

All the chemicals such as sodium hydroxide, sodium perchlorate, perchloric acid, methanol, $Cu(NO_3)_2$ and salicylic acid were of AnalaR grade. Salicylic acid used was crystallized and its purity was checked before use. A solution of salicylic acid was prepared in aqueous medium by dissolving an approximate amount of it. The solution of $Cu(NO_3)_2$ was prepared in water and its concentration was checked by EDTA.

An Equiptronics model EQ-610 digital pH-meter was used in the present investigation for measuring the pH of the solution. It was calibrated by standard buffer solutions of pH 4.01, 7.00 and 9.12. By using Calvin-Bjerrum titration technique in an inert atmosphere, pH-metric titrations were carried out.

The experimental procedure involved pH-metric titrations of carbonate-free solutions of:

1. Free $HClO_4$ ($1.000 \times 10^{-2}$ M),
2. Free $HClO_4$ ($1.000 \times 10^{-2}$ M) + ligand ($20.000 \times 10^{-4}$ M), and
3. Free $HClO_4$ ($1.000 \times 10^{-2}$ M) + ligand ($20.000 \times 10^{-4}$ M) + metal ($4.00 \times 10^{-4}$ M against standard solution of sodium hydroxide (0.2 M) at temperature 29 ± 1°C.

The ionic strength of 0.1 M was maintained by adding an approximate amount of 0.1 M $NaClO_4$ solution. The same procedure was used for 10, 20, 30, 40, . . . % of methanol-water mixtures. pH values were corrected by the use of Van-Vilart and Haas equation[9].

## RESULTS AND DISCUSSION

### Proton-ligand formation constants

The deviation of (acid + ligand curves) started around pH 2.6 from the acid curve and increases continuously up to pH 10.5. The average number of proton associated with ligand ($\bar{n}_A$) was determined by the Irving-Rossotti's equation[10]. The formation curves were constructed by plotting values of $\bar{n}_A$ against pH of the system in all the percentage of methanol-water mixtures. The values $pK_{COOH}$ (dissociation constants) were estimated by noting the pH at which $\bar{n}_A = 0.5$ and accurate values were also determined by pointwise calculations. The $pK_{COOH}$ of salicylic acid in all the percentages of methanol-water are presented in Table-1. It could be seen from Table-1 that $pK_{COOH}$ values increased with increase in the percentage of methanol-water mixture.

TABLE-1

PROTON LIGAND STABILITY CONSTANTS OF SALICYLIC ACID IN DIFFERENT PERCENTAGES 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 | 0.010 | 4.80 |
| 20 | 70.10 | 0.0142 | 0.050 | 5.38 |
| 30 | 60.80 | 0.0164 | 0.160 | 6.30 |
| 40 | 60.20 | 0.0166 | 0.205 | 7.10 |
| 50 | 52.50 | 0.0190 | 0.435 | 7.95 |
| 60 | 50.20 | 0.0199 | 0.452 | 8.80 |
| 70 | 40.80 | 0.0245 | 0.490 | 9.55 |
| 80 | 40.10 | 0.0249 | 0.566 | 10.40 |

## The precision of experimentally determined pk values

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

The proton-ligand formation numbers ($\bar{n}_A$) at various pH values obtained from the two sets are presented in Table-2.

TABLE-2
COMPARISON OF $\Delta\bar{n}_A$ VALUES FOR TWO DIFFERENT SETS
IN 30% METHANOL-WATER MIXTURE

| pH | Set I $\bar{n}_A$ | Set II $\bar{n}_A$ | $\Delta\bar{n}_A$ | $\sigma = \left[\frac{\Sigma(\Delta\bar{n}_A)^2}{(n-1)}\right]^{1/2}$ |
|---|---|---|---|---|
| 2.4 | 0.7532 | 0.7535 | 0.0030 | |
| 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 | $\sigma = 0.0032$ |
| 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 | 0.0040 | |

The values of $\Delta\bar{n}_A$ at a particular pH are determined and standard deviation $\sigma$ of the values calculatated by using the expression

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

where n is the number of observations.

## Metal-ligand stability constants

The departure of (free acid + ligand + metal ion) curve from (free acid + ligand) curve was obtained around pH 3.5 in all the percentages of methanol-water media. This showed the commencement of complex formation before hydrolysis. The values of $\bar{n}$ (metal-ligand formation number) were calculated by using the 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 $\bar{n}$ *vs.* PL by half integral method as well as pointwise calculations in all the percentages of methanol-water mixtures (Table-3). It is observed from Table-3 that log $k_1$ and log $k_2$ values increase with increase in the percentage of methanol-water mixture.

This may be due to the effect of the bulk solvent which decreases formation constants but it increases metal-ligand stability constant.

TABLE-3
METAL-LIGAND STABILITY CONSTANTS (log k) OF Cu(II) COMPLEXES WITH SALICYLIC ACID IN DIFFERENT PERCENTAGES OF METHANOL-WATER MIXTURES pH-METRICALLY

| % of methanol-water mixture | Dielectric constant (D) | 1/D | Mole fraction | log $k_1$ | log k2 |
|---|---|---|---|---|---|
| 10 | 75.00 | 0.0133 | 0.010 | 2.90 | 1.15 |
| 20 | 70.10 | 0.0142 | 0.050 | 3.25 | 1.25 |
| 30 | 60.80 | 0.0164 | 0.160 | 3.60 | 1.40 |
| 40 | 60.20 | 0.0166 | 0.205 | 4.00 | 1.50 |
| 50 | 52.50 | 0.0190 | 0.435 | 4.40 | 1.65 |
| 60 | 50.20 | 0.0199 | 0.452 | 4.75 | 1.75 |
| 70 | 40.80 | 0.0245 | 0.490 | 5.10 | 1.90 |
| 80 | 40.10 | 0.0249 | 0.566 | 5.50 | 2.05 |

## The plots of pK/log k *vs.* 1/D (D = dielectric constant) and mole fractions

The plot between $pK_{COOH}$/log K *vs.* 1/D showed fairly good relationship at low percentage of methanol-water mixture and non-linear relationship for higher percentage of methanol-water mixture. The plots between $pK_{COOH}$/log K *vs.* mole fraction show a linear relationship (Figs. 1–6).

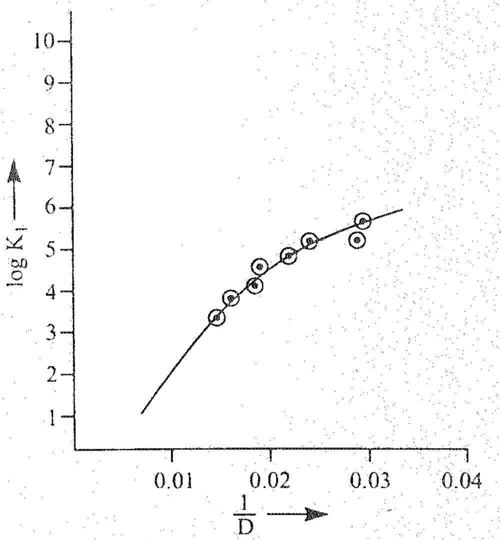

Fig. 1

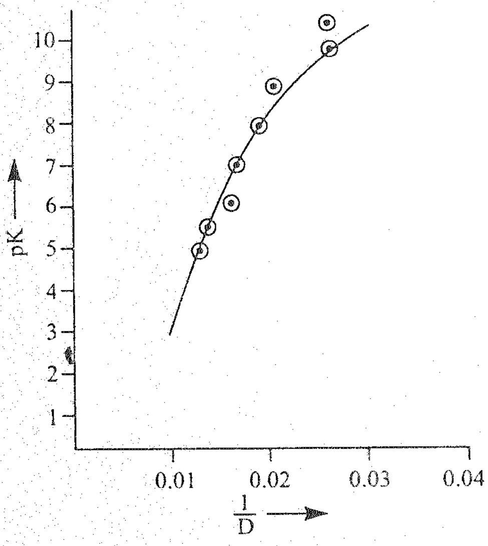

Fig. 2

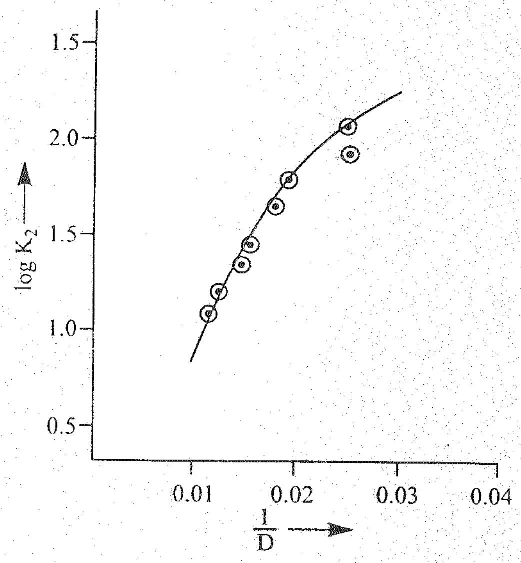

Fig. 3

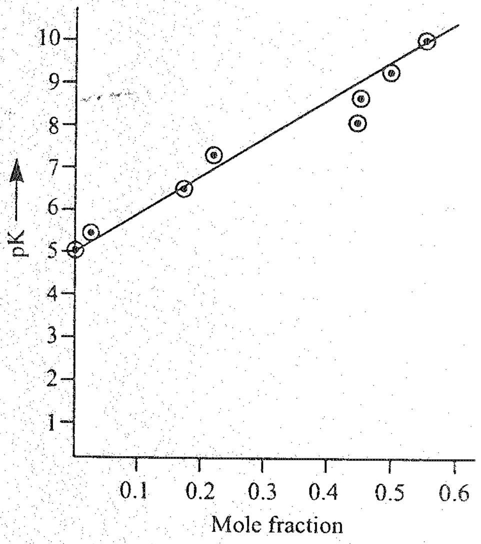

Fig. 4

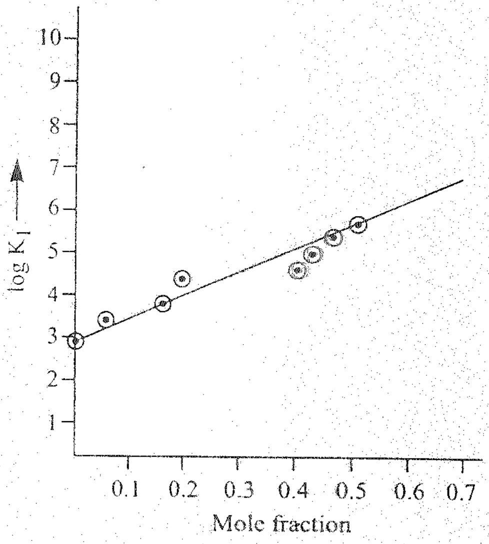

Fig. 5

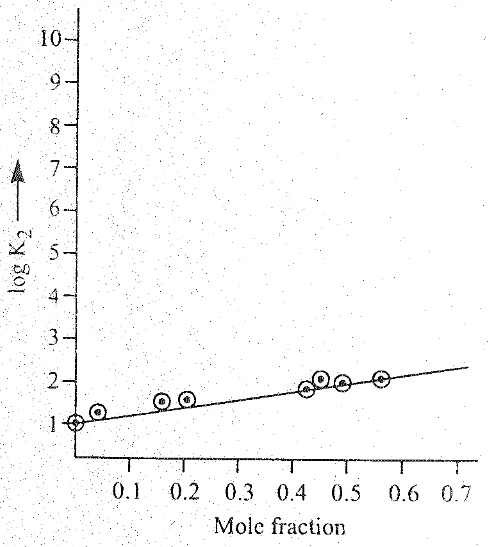

Fig. 6

Water is recognized as being a unique structural ligand in the sense of having three-diamensional ice-like framework. Franks and Ives[11] have shown the addition of first increment of other organic co-solvency to water. The dielectric constant of the 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.

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