Asian Journal of Chemistry Vol. 9, No. 2 (1997), 224–233

Effect of Dielectric Constants of Ethanol-Water and Acetone-Water Mixtures on Proton-Ligand and Metal-Ligand Stability Constants of Cu(II)-*o*-Aminobenzene Sulphonic Acid Complexes

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The interaction between Cu(II) and *o*-aminobenzene sulphonic acid has shown 1 : 1 and 1 : 2 complex formation. The complex formation has been investigated potentiometrically in different percentage of ethanol-water and acetone-water mixtures at (27 ± 0.1°C). The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used in the the present work. It showed that proton-ligand and metal-ligand stability constants increased with increasing the percentage of ethanol-water and acetone-water mixtures.

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 proton-liquand stability constants of *o*-hydroxy-acetophenoneoxime and its substituted derivatives have been reported by Ingle and Khanolkar[2]. Metal-chelates of hydrazo-dimedone dyes are studied by Atef *et al.*[3] Narwade *et al.*[4] have investigated the stability constants of lanthanide ions with some substituted sulphonic acids spectrophotometrically.

Shelke *et al.*[5] have studied equilibrium constants of UO_2(II) and Cu(II) ions with dicarboxylic acids in dioxane-water mixtures. Narwade *et al.*[6] have investigated the interaction between Fe(III) and substituted chalcones at 0.1 M ionic strength potentiometrically. Raghuwanshi *et al.*[7] have shown 1 : 1 and 1 : 2 complex formation of Cu(II), Co(II) and Ni(II) with some substituted chalcones and isoxazolines potentiometrically. The interaction between Cu(II) chelates and 2-hydroxy aromatic ketones and alkyl mono-amines is studied by Rabindranath[8]. Mandakamare *et al.*[9] have determined stability constants of UO_2(II) complexes with some substituted coumarins by potentiometric technique. Raghuwanshi *et al.*[10] have studied the conditional stability constants of Cu(II) complexes with substituted chalcones and isoxazolines spectrophotometrically.

In a view of analytical applications, it is worthwhile to know the physico-

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chemical properties of metal ion complexes and effect of dielectric constants of ethanol-water and acetone water mixtures on stability constants. Therefore, the present work is undertaken to make a systematic study of Cu(II) complexes with *o*-aminobenzene sulphonic acid potentiometrically.

EXPERIMENTAL

Standard solutions of 0.2 M NaOH, 1.0 M KNO_3 and 0.1 M HNO_3 were prepared by using analytical grade reagents. The aqueous solution of copper nitrate (BDH) was prepared in double distilled water and its concentration was checked by EDTA. *o*-Aminobenzene sulphonic acid used was crystallised and its purity was checked before use. The solution of chelating agent (ligand) was prepared in aqueous medium by dissolving an appropriate amount of it.

pH meter ELICO LI-12 T was used in the present investigation for measuring the pH of solution. It was calibrated by standard buffer solution of pH 4.01, 7.00 and 9.15 time to time.

Calvin-Bjerrum titrations: Potentiometric titrations are carried out by using Calvin-Bjerrum titration technique in an atomosphere by bubbling oxygen-free nitrogen gas through an assembly containing electrodes in order to keep away CO_2.

Experimental procedure involves potentiometric titration in different percentage of acetone-water and ethanol-water mixtures (10%, 20%, 30%, . . .) of carbonate-free solutions (4×10^{-4} M) of:

(i) nitric Acid (10^{-2} M),
(ii) nitric acid (10^{-2} M) + ligand (20.0001×10^{-4} M), and
(iii) nitric acid (10^{-2} M) + ligand (20.0001×10^{-4} M) + metal ion solution (4×10^{-4} M)

against standard solution of NaOH. The temperature of solution was maintained at (27 ± 0.1°C) and ionic strength of solution was maintained 0.1 M constant by adding an appropriate amount of 1 M KNO_3 solution. pH values were corrected by use of Van-Vitart and Hass equation[11].

RESULTS AND DISCUSSION

Proton-ligand dissociation constants: The proton is liberated from the protonated ($—NH_3^+$) group of *o*-aminobenzene sulphonic acid.

Existence of proton-ligand equilibria corresponds to dissociation of proton from the ligand.

$$HL \rightleftarrows H^+ + L^- \qquad (1)$$

The plots of pH *vs.* volume of NaOH showed that the deviation of (acid + ligand) curves from acid curves started around pH 4.5 for all percentages of acetone-water and ethanol-water mixtures and continued up to pH 11.0. The deviation is due to the dissociation of ($—NH_3^+$) group.

Average number of protons associated with the ligand ($\bar{n}_A$) were determined by Irving and Rossotti's equation[12]. The formation curves were constructed by plotting the values of $\bar{n}_A$ against pH of solution in all the percentages of acetone-water and ethanol-water mixtures. The pk values (dissociation constants) of (—NH_3^+) were estimated by noting the pH at which $\bar{n}_A = 0.5$ and accurate values were determined by pointwise calculations. The pk values of *o*-aminobenzenesulphonic acid in acetone-water and ethanol-water mixtures are presented in Tables 1 and 2.

It is observed from Tables 1 and 2 that pk values increased with increasing the percentage of acetone-water and ethanol-water mixture. It could be also seen that pk values in acetone-water mixtures are greater than pk values of ethanol-water mixture. Ethanol is more polar than acetone. Polar-polar slovent (ethanol-water) is weaker interaction and hence that results to increase the dissociation and decrease the pk values.

TABLE-1

PROTON-LIGAND STABILITY CONSTANTS (pk) OF *o*-AMINOBENZENE SULPHONIC ACID IN DIFFERENT PERCENTAGES OF ACETONE-WATER MIXTURES

% Acetone	Dielectric constant D	1/D	Mole fraction	pk
0	78.0	0.0128	—	3.25
10	73.0	0.0136	0.0360	3.30
20	67.0	0.0149	0.0790	4.15
30	61.0	0.0163	0.1290	4.81
40	55.0	0.0181	0.1850	4.99
50	48.0	0.0250	0.2630	5.21

TABLE-2

PROTON LIGAND STABILITY CONSTANTS (pk) OF *o*-AMINOBENZENE SULPHONIC ACID IN DIFFERENT PERCENTAGE OF ETHANOL-WATER MIXTURES

% Ethanol	Dieletric constant D	1/D	Mole fraction	pk
0	78.0	0.0128	—	3.15
10	75.0	0.0133	0.0070	3.30
20	69.0	0.0144	0.0150	3.58
30	63.5	0.0157	0.1000	3.91
40	57.5	0.0173	0.1800	4.25
50	52.0	0.0192	0.2650	4.55

The precision of experimentally determined pk values

The precision of the experimental pk values are examined by determining the pk values of the ligand from two sets of potentiometric titration. All the experimental conditions except the cencentration of 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 two sets are presented in Tables 3 and 4.

The values of $\Delta\bar{n}_A$ at various pH are determined and standard daviation (δ) of the values is calculated by using the expression:

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

when n' is number of observations.

TABLE-3
DETERMINATION OF STANDARD DEVIATION (δ) IN 10% ACETONE-WATER MIXTURE

pH	Set I $\bar{n}_A$	Set II $\bar{n}_A$	Δ $\bar{n}_A$	$\delta = \left[\frac{\Sigma[\Delta\bar{n}_A]^2}{n'-1}\right]^{1/2}$
4.9	0.8352	0.8311	0.0041	$\delta = 0.03783$
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	

TABLE-4
DETERMINATION OF STANDARD DEVIATION (δ) IN 10% ETHANOL-WATER MIXTURE

pH	Set I $\bar{n}_A$	Set II $\bar{n}_A$	Δ $\bar{n}_A$	$\delta = \left[\frac{\Sigma[\Delta\bar{n}_A]^2}{n'-1}\right]^{1/2}$
3.1	0.7925	0.7825	0.0100	$\delta = 0.012215$
3.2	0.7132	0.7232	–0.0100	
3.3	0.5000	0.4985	0.0015	
3.4	0.4135	0.4250	–0.0115	
3.5	0.3500	0.3666	–0.0166	
3.6	0.3100	0.3000	0.0100	
3.7	0.2115	0.3125	–0.1010	
3.8	0.2000	0.2115	–0.0115	
4.0	0.1001	0.1105	–0.0104	

Metal-ligand stability constants

The deviation of (acid + ligand + metal ion) curves from (acid + ligand) curves was obtained around pH 3.0 and then it increased continuously for all the percentages of acetone-water and ethanol-water mixtures. This indicated the commencement of complex formation between ligand and metal ion before the hydrolysis.

The values of n^{-} (metal-ligand formation numbers) were calculated by Irving-Rossotti's expression.

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 calculated from the plots of n^{-} vs pL by half integral method. The accurate values were obtained by pointwise calculations which are presented in Tables 5 and 6. It is observed from these tables that log K_1 and log K_2 values increased with increasing the percentage of acetone-water and ethanol-water mixtures.

This may be due to the fact of the effect of organic bulky solvent which decreases formation constants but increases log K_1/log K_2 values.

TABLE-5
METAL-LIGAND STABILITY CONSTANTS (log K_1/log K_2) IN DIFFERENT PERCENTAGE OF ACETONE-WATER MIXTURES

% Acetone	Dielectric Consant (D)	1/D	log K_1	log K_2	Mole fraction
0	78.0	0.0128	1.2304	0.7782	—
10	73.0	0.0136	1.8195	1.0792	0.036
20	67.0	0.0149	2.0513	1.1015	0.079
30	61.0	0.0163	2.9511	1.6525	0.129
40	55.0	0.0181	3.0550	2.0515	0.185
50	48.0	0.0250	4.5300	4.2539	0.263

TABLE-6
METAL-LIGAND STABILITY CONSTANTS (log K_1/ log K_2) IN DIFFERENT PERCENTAGE OF ETHANOL-WATER MIXTURES

% Ethanol	Dielectric consant (D)	1/D	log K_1	log K_2	Mole fraction
0	78.0	0.0128	1.2055	0.7180	—
10	75.0	0.0133	1.7980	1.0050	0.007
20	69.0	0.0144	1.9950	1.1000	0.015
30	63.5	0.0157	2.6580	2.0155	0.100
40	57.5	0.0173	2.9518	2.1055	0.180
50	52.0	0.0192	3.9183	2.8525	0.265

The plots between pk/log K vs 1/D and mole fraction

The plot between pk/log K *vs.* 1/D showed fairly linear relationship, at low percentage of acetone-water mixture and ethanol-water mixture (Figs. 1–12). But at high percentage of acetone-water and ethanol-water mixtures, it showed non-linearship relation. The plots between pk/log K *vs.* mole fraction of different percentage of acetone and ethanol showed fairly linear relationship.

Narwade *et al.*[13] have studied the same relationship for diketone complexes with transitiom metal ions. The work of Harned and Owen[14] has shown an approximate linear relationship for pk values of acetic acid in different percentage of dioxane-water mixtures. Mandakmare *et al.*[15] have studied the same phenomenon for substituted coumarins in different percentage of dioxane-water, DMF-water and THF-water mixtures.

PLOTS BETWEEN pk/log K *vs*. MOLE FRACTION
(FOR ACETONE-WATER MEXTURE)

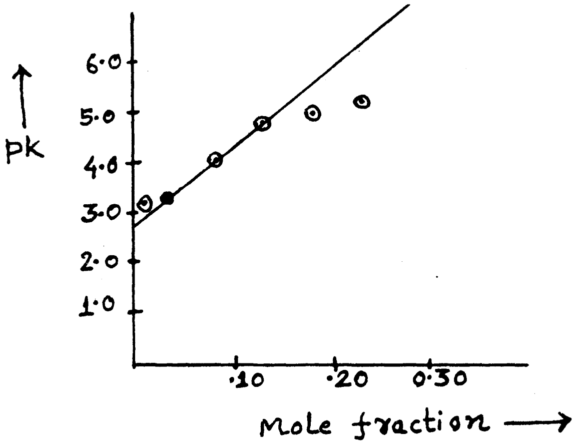

Fig. 1

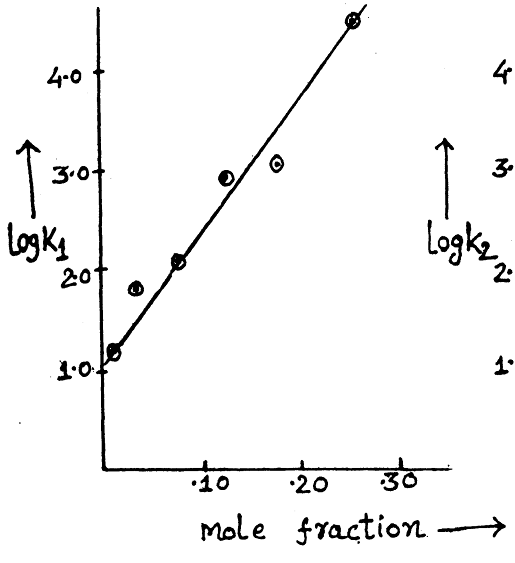

Fig. 2

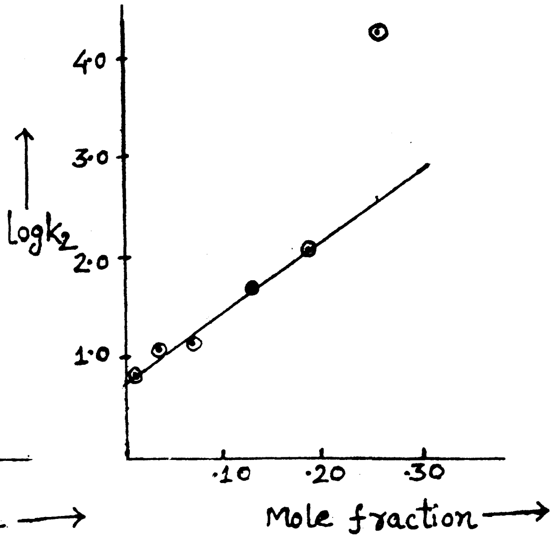

Fig. 3

PLOTS BETWEEN pk/log K *vs.* MOLE FRACTION
(FOR ACETONE-WATER MEXTURE)

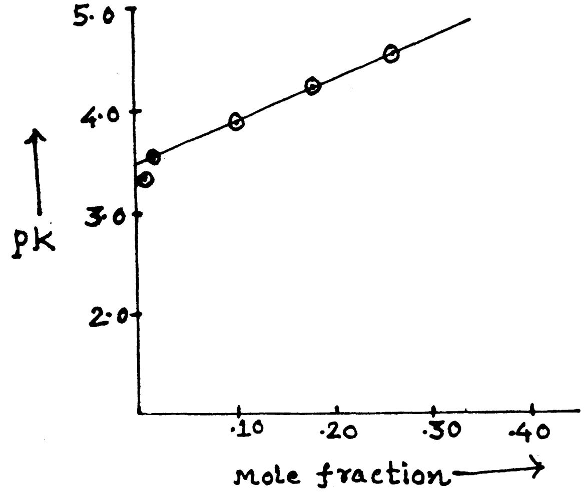

Fig. 4

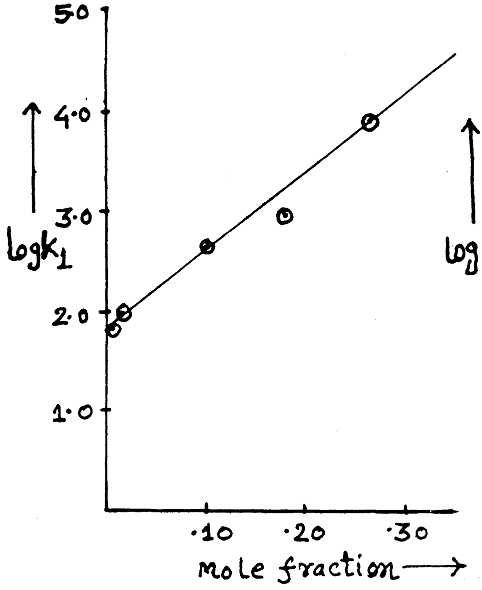

Fig. 5

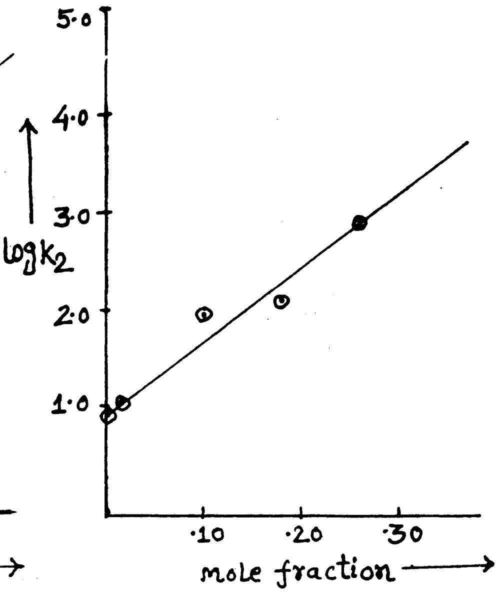

Fig. 6

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

Frank and Ives[16] have shown the addition of first increment of other organic co-solvent to water. The dielectric constant of a medium is not solely responsible

PLOTS BETWEEN pk/log K *vs.* $\frac{1}{D}$ FOR ETHANOL-WATER MIXTURE

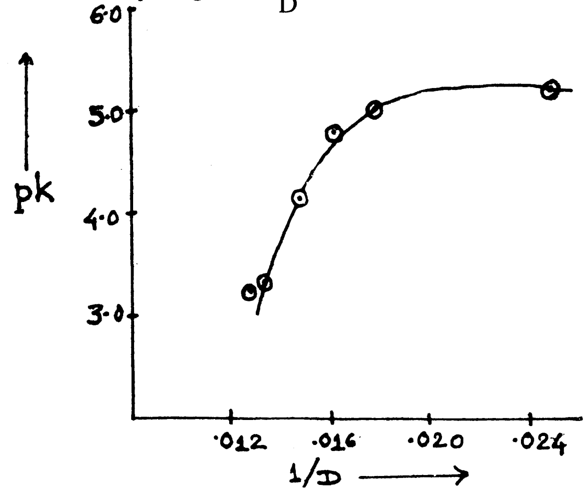

Fig. 7

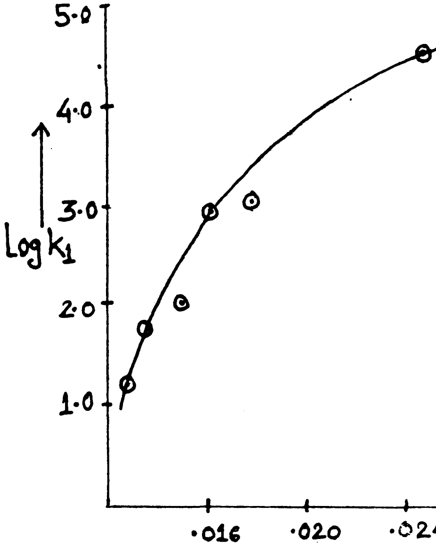

Fig. 8

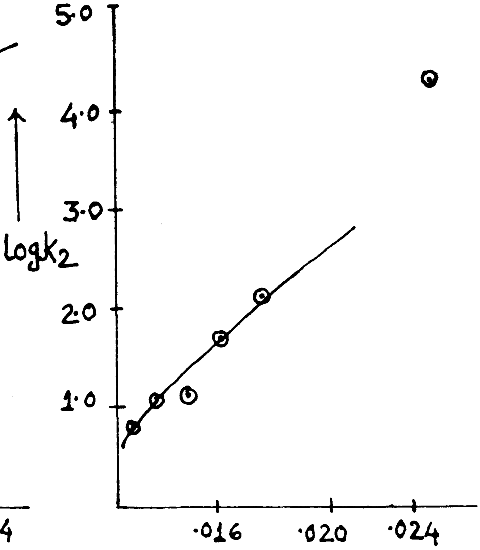

Fig. 9

for the extent of dissociation; there is at least an additional factor of the chemical role of the solvent in most cases. Vasuda[17] has expressed the dissociation constant of some weak acids as a function of dielectric constant of the bulk solvent. Ohtaki[18] showed the solvent effect on dissociation ammonium and pyridinium ions.

PLOTS BETWEEN pk/log K *vs.* $\frac{1}{D}$ FOR ACETONE-WATER MIXTURE

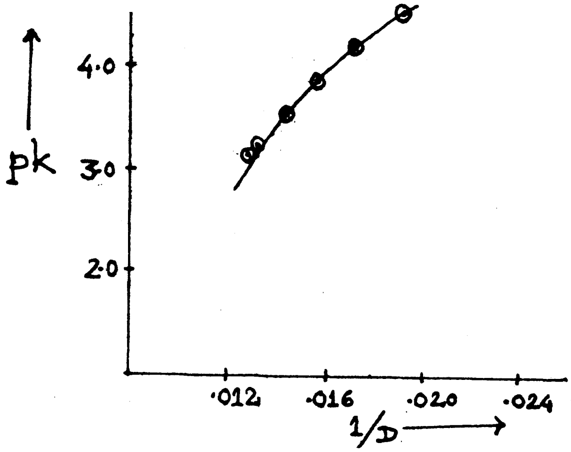

Fig. 10

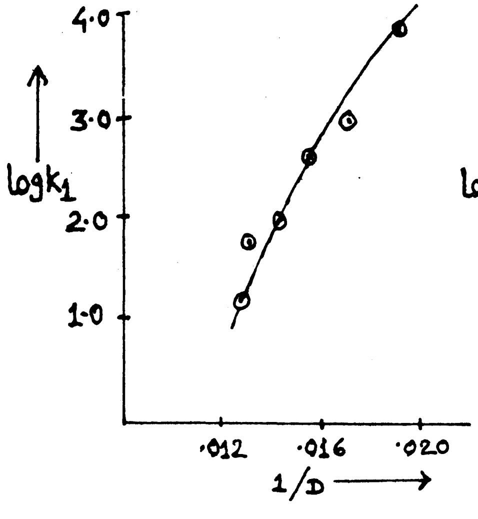

Fig. 11

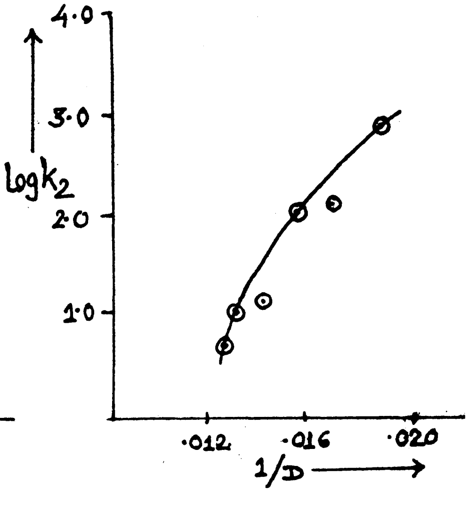

Fig. 12

ACKNOWLEDGEMENTS

Authors are very much thankful to the Principals of Government Polytechnic College and Government Science College, Gadchiroli for providing facilities.

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(*Received*: 7 August 1996; *Accepted*: 16 November 1996) AJC-1185