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To Calculate the Closest Distance of Approach Between the Ions from Study of Reaction in Different Dielectric Constants of Medium

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Abstract: The stability constants of 4-amino-3-naphthol-sulphonic acid with Co (II) metal ions and 3-amino, 4-hydroxy, 5-nitro benzene sulphonic acid with Cu (II) metal ions in different percentage of ethanol-water mixtures having varying dielectric constants and at constant ionic strength (μa=0.01M) have been determined potentiometrically. The logK values found to increase with increase in percentage of ethanol and vary linearly with the reciprocal of the dielectric constant of medium. From the plot of logK versus reciprocal of the dielectric constant, the distance between the centers of reacting ions, d_{AB} has been determined. The values of ΔlogK were calculated to know the exact nature of the electrostatic forces of attraction between metal ion and negatively charged ligand.

Key words: Dielectric constant · LogK · Ethanol-water · Electrostatic forces

INTRODUCTION

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 or methyl alcohol-water and other organic solvent-water mixtures have been made by a number of workers [1-6]. Reddy *et al*. [7] have studied the effect of dielectric constant on the stability of Co (II) and Ni (II) with 2-mercaptoethyl benzimidazole, glycine, ethylene diamine and salicylic acid in various proportions of ethanol-water mixtures at 30°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*. [8]. But the determination of closest distance of approach between the metal ion and ligand was lacking.

Experimental: Metal ion solutions (c = 0.0004 mol dm^{-3}) were prepared from Analar metal salts in bidistilled water and standardized with EDTA [9]. Concentrations of metal nitrate and nitric acid taken were fixed. All the solutions were prepared in double distilled water and the solutions of ligand was always used a fresh in present investigation. The pH measurements were carried out with ELICO-L1-10 (accuracy ±0.05 units) using combined electrode at 28 ± 0.10°C. All chemicals used were of AR grade. Glassware used in these experiments was of Pyrex quality. Ionic strength of the solution was maintained constant at (μa = 0.01M) by adding an appropriate amount of KNO_3 solution. A carbonate free sodium hydroxide solution was used as titrant and standardized against oxalic acid (Analar) [10]. All the calculations were done on personal computer using excel programme.

RESULTS AND DISCUSSION

The present work deals with the study of stability constants of 4-amino, 3-naphthol sulphonic acid with Co (II) and 3-amino, 4-hydroxy, 5-nitro benzene sulphonic acid with Cu (II) metal ions in different dielectric constant (ϵ)_of medium using ethanol-water system. The potentiometric titrations were carried out in different percentage of ethanol-water mixtures by using a pH meter (accuracy ± 0.05 units) with a combined Glass and Calomel

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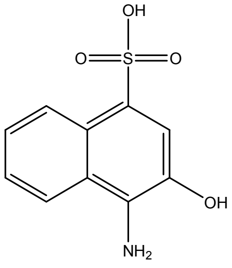
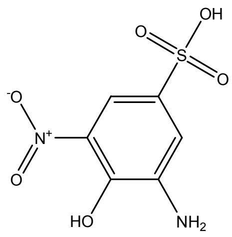
electrode assembly. The electrode system was calibrated with buffer solutions at pH 4.00 and 9.2. The experimental procedure involved in the potentiometric titrations of the mixtures of a) 5 mL 0.01 M HNO_3 solution b) 5 mL 0.01 M HNO_3 and 10 mL 0.002 M ligand solution and c) 5 mL 0.01 M HNO_3, 10mL 0.002 M ligand solution and 5 mL 0.0004 M metal ion solution. The total volume of each mixture was made up to 100 mL and each of the mixture was titrated against standard sodium hydroxide in ethanol-water at 298 K. A constant temperature was maintained at ± 0.05 K by using a thermostat. The ionic strength of solutions was maintained constant by the addition of appropriation amount of 1.0 M KNO_3 stock solution.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions (ñ) versus the free ligand exponent (pL), according to Irving and Rossotti [11]. The maximum value of metal-ligand formation number, ñ was found to extend between 0 and 2 indicating the formation of 1:1 and 1:2 (n (metal): n (ligand)) complexes only. The metal ion solutions used in present study were very dilute (4×10^{-4} mol dm^{-3}); hence there was no possibility of formation of polynuclear complexes [12].

The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves points to the formation of strong metal complexes [13]. The colour of the solution after complex formation was observed to be different from the colour of the ligand at the same pH. The stability constants were calculated using the method of Irving and Rossotti [14] and are presented in Table (1). Structures of ligands used in the present investigation are given below:



4A-3N-SA



3A-4H-5N BSA

The influence of solvent dielectric constant (ϵ) on rates of reactions between the ions is based on electrostatic theory. The model is represented in Figure (1) [15]. The z_Ae and z_Be are the charges on ions, initially, the ions are at infinite distance and then they approach one another and form the activated complex in which the centers of the ions are separated by a distance d_{AB}.

The data of lnk for different values of dielectric constant of medium were employed to calculate d_{AB} by using equation (1).

$$\ln k = \ln k_0 - \frac{z_A \cdot z_B e^2}{4\pi \cdot \varepsilon_0 \cdot \varepsilon \cdot d_{AB} \cdot \mathbf{k} T} \tag{1}$$

Where,

ε= dielectric constant
ε_0= is permittivity of vacuum ($8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$)
z_A and z_B are the charge numbers (may be positive or negative)
e is elementary charge (1.602×10^{-19} C)
k= Boltzmann constant (1.38066×10^{-23} JK^{-1})
k_0 is the value of k in medium of infinite dielectric constant, in which the electrostatic forces have become zero.

Table 1: Metal-ligand stability constants in Ethanol-Water mixtures at 0.01M ionic strength

		Co (II)-4A-3N-SA			Cu (II)-3A-4H-5N-BSA		
% Ethanol	$1/\epsilon$	$LogK_1$	$LogK_2$	$\Delta logK$	$LogK_1$	$LogK_2$	$\Delta logK$
50	0.0204	8.10	6.38	1.82	7.84	5.34	2.50
55	0.0215	8.42	6.88	1.54	8.43	6.03	2.40
60	0.0230	8.80	7.35	1.45	8.82	6.84	1.98
65	0.0244	9.20	7.86	1.34	9.24	7.48	1.76
70	0.0263	9.59	8.48	1.11	9.71	8.21	1.50
75	0.0277	10.23	9.14	1.09	10.37	9.32	1.05

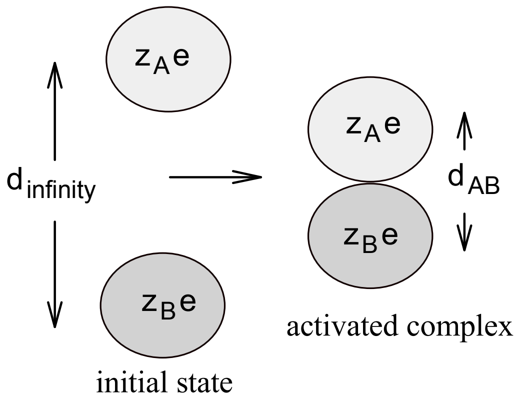


Fig. 1: ‘double sphere model’ for reaction between ions

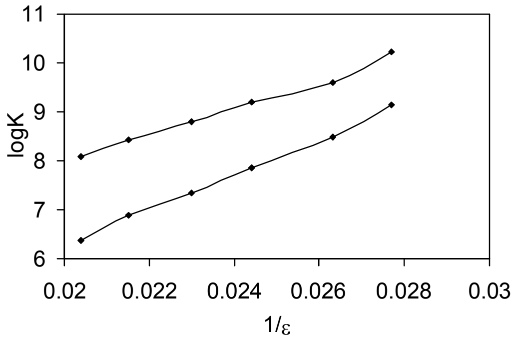


Fig. 2: Plot of 1/ε versus logK of 4A-3N-SA with Co(II) ion in Ethanol-Water mixture

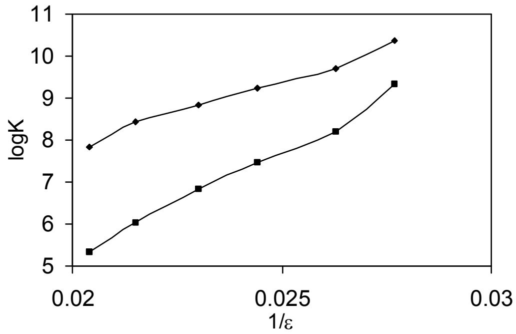


Fig. 3: Plot of 1/ε versus logK of 3A-4H-5N-BSA with Cu(II) ion in Ethanol-Water mixture

According to this equation, the logarithm of the rate constant of the reaction between ions should vary linearly with the reciprocal of the dielectric constant. This relationship can be tested by causing a reaction to occur in a series of ethanol-water mixtures of varying dielectric constants. There are deviations in this relationship at low dielectric constants. Equation (1) is the equation of straight line, so the lnk values have been plotted (Figure 2-3) with reciprocal of dielectric constants. The slope of line obtained is given by equation (2).

$$slope = -\frac{z_A \cdot z_B e^2}{4\pi \cdot \varepsilon_0 \cdot d_{AB} \cdot \mathbf{k}T} \qquad (2)$$

Everything in this equation is known except $d_{AB,}$ it is possible to calculate d_{AB} from the experimental slope by using equation (3)

$$d_{AB} = -\frac{z_A \cdot z_B e^2}{4\pi \cdot \varepsilon_0 \cdot slope \cdot \mathbf{k}T} \qquad (3)$$

This has been done in number of cases and the value obtained is of the order of a few hundred picometers are reasonable. In present investigation the values of distance between centres of ions in activated complex have been calculated using equation (3) and presented in Table (2) along with the intercept of these graphs. The values were found to be in good agreement with the reported values [15].

It can be seen from Table (2) that the values of closest distance of approach for 4-amino, 3-naphthol sulphonic acid with Co (II) ion are larger than for 3-amino, 4-hydroxy, 5-nitro sulphonic acid with Cu (II) ion, which may be due to the large size of former ligand due to the presence of naphthalene ring. Also the values of stability constants (lnk_0) in medium of infinite dielectric constant are smaller which is due to the non-existence of the electrostatic forces.

Table 2: Closest distance of approach between ligands and metal ions

System	Constant	d_{AB} x 10^{-12}	Intercept (lnk_0)
Co (II)-4A-3N-SA	$logK_1$	807	2.42
	$logK_2$	615	1.03
Cu (II)-3A-4H-5N-BSA	$logK_1$	698	1.39
	$logK_2$	435	5.12

Bhattacharya *et al*. [16] have studied equilibrium constants and other properties of ferric salicylate and ferric sulphosalicylate complexes in dioxane-water mixtures. The log K values increases with increase in the percentage of ethanol, this is due to the effect of bulk solvent. Studies on similar lines have been carried out by many workers [17-21] and obtained the similar results.

The difference between log K_1 and log K_2 values are also given in Table (1). It could be seen from this table that this difference continuously decreases with the increase in ethanol percentage. The lowering of dielectric constant would increase the electrostatic forces of attraction between metal ion and negatively charged ligand to from 1:1 complex. The formation of 1:2 complexes on the other hand is due to the reaction, which would probably explain the observed behaviour.

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