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STABILITY CONSTANTS OF METAL (II) COMPLEXES WITH SOME DERIVATIVES OF BENZENE SULPHONIC ACID IN DIFFERENT PERCENTAGE OF DIOXANE – WATER MIXTURE

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ABSTRACT

The stability constants of Ni^{2+}, Co^{2+} and Cu^{2+} with p-amino benzene sulphonic acid, p-nitro benzene sulphonic acid and p-chlorobenzene sulphonic acid in different percentage of dioxane-water has been determined pontentiometrically by Calvin-Bjerrum titrations. The titrations were carried out at contstant ionic strength (0.1M) and constant temperature i.e. 27 ± 0.1°C. The data obtained can be used to study the values of porton-ligand and metal ligand stability constants for 1 : 1 and 1 : 2 complexes.

Key words : Stability constant, Metal (II) Ion, Ligands, Water-dioxane mixture.

INTRODUCTION

Salicyclic acid derivatives, amino acid derivatives and sulphonic acid derivatives have considerable interest. However, little information is available on stability constant of these ligands with transition metal ions in dioxane-water mixture. The survey of literature reveals that metal-ligand stability constant of amino acid, adipic and itaconic acid have been studied[1]. Narwade et al.[2] have investigated the stability constants of lanthanide ions with some substituted acids spectrophotometrically. Keeping the importance of substituted sulphonic acids in mind; in the present paper, an effort has been made to study the stability constants of Ni(II), Co(II) and Cu(II) with p-amino benzene sulphonic acid (PABSA), p-chlorobenzene sulphonic acid (PCBSA) and p-nitrobenzene sulphonic acid (PNBSA) in different percentages of dioxane-water mixture (10%, 20%, 30% and 50%). The titrations were carried out using Calvin-Bjerrium[3] titrations technique at 27 ± 0.1°C temperature and

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confirmed spectrophotometrically by isobestic point method.

EXPERIMENTAL

All the chemicals used in present investigation were of analytical grade. Carbonate free NaOH solution was prepared and standardized by potassium hydrogen phthalate. The solutions of ligand was prepared in different percentage of dioxane-water mixture by dissolving requisite amount of p-aminobenzene sulphonic acid (PABSA), p-chlorobenzene sulphonic acid (PCBSA) and p-nitrobenzene sulphonic acid (PNBSA). A digital potentiometer Model Systronics-105 was used for titrations. These titrations were carried out by keeping the ionic strength of medium constant (m = 0.1M) by adding appropriate amount of 1 M KNO_3 solutions. pH –values were calculated by Van-Uitert and Hass[4] equation.

RESULTS AND DISCUSSION

Proton ligand stability constants

The value of proton-ligand stability constant (pK-values) were calculated from the formation curves between pH and proton-ligand formation number $\overline{n}_A$. The proton-ligand formation number ($\overline{n}_A$) were calculated using Irving and Rossottis equation[5,6]. The formations curves were constructed by plotting the values of $\overline{n}_A$ against pH of solution in all the % of dioxane-water mixture. The pK values were estimated by noting the pH at which $\overline{n}_A$ = 0.5 and accurate values were determined by pointwise caluculation method, which are presented in Table 1.

Table 1. pK Values

% of Dioxane	Co (II)			Ni (II)			Cu (II)		
	PABSA	PCBSA	PNBSA	PABSA	PCBSA	PNBSA	PABSA	PCBSA	PNBSA
10%	3.79	3.91	4.31	3.95	4.12	4.10	4.41	5.32	5.57
20%	4.21	4.72	4.89	4.50	4.85	4.95	4.82	5.31	5.62

Cont…

% of Dioxane	Co (II)			Ni (II)			Cu (II)		
	PABSA	**PCBSA**	**PNBSA**	**PABSA**	**PCBSA**	**PNBSA**	**PABSA**	**PCBSA**	**PNBSA**
30%	4.75	5.30	5.65	5.20	5.80	5.17	5.92	6.12	5.98
50%	5.31	5.85	6.22	5.60	5.83	6.32	6.07	6.58	6.72

It is clear from tables that pK-values increases with increasing the percentage of dioxane in dioxane-water mixtures. Sondawale and Narwade[7] have observed the same phenomenon in different percentage of ethanol/acetone–water mixtures. Chachere et al.[8] have also observed the increase in pK – values with increasing percentage of dioxane in dioxane-water mixture for amino acids.

The stability of the different 1 : 1 binary M (II)-ligand complexes increases according to the order –

PNBSA < PCBSA < PABSA

This can be interpreted in terms of the effect of basicity of these compounds.

The stability of the 1 : 1 and 1 : 2 complex containing sulphanilic acid is largely dependent on the nature of the electron withdrawing group. Generally, the complexes containing the NO_2, Cl and NH_2. The order of electron withdrawing tendency is in the order as NO_2, Cl and NH_2, the order of electron withdrawing tendency is in the order as $NO_2 > Cl > NH_2$. Hence, PABSA form more stable complex than the PCBSA; in turn than PNBSA.

The dependence of stability of the complexes studied on the nature of metal ion and is found to follow the trend : Co (II) < Ni (II) << Cu (II). This is in conformity with the lrving – Williams order. The additional high satability of the Cu (II) complex is attributed to the unique electronic configuration ($3d^9$) of Cu (II) ion, which is capable of additional stabilization due to John-teller distortion.

Metal – ligand stability constant

The comparison between acid and the metal titration curves indicates that the metal curves are well separated from ligand curves. This suggests the formation of metal-ligand complex in the solution. The metal-ligand formation constant $\overline{n}$ and pL values were calculated using two different methods i.e.

(i) Half integral method i.e. form graph of $\overline{n}$ vs. pL at $\overline{n} = 0.05$ and $\overline{n} = 1.5$

(ii) Pointwise calculation method i.e. as suggested by lrving and Rossotti.

The value of $\overline{n}_A$ at various pH have been calculated from free acid and ligand titration curves. The following equation is used to calculated the values of $\overline{n}_A$, which has been employed by lrving and Rossoti.

$$\overline{n}_{A} = V - \frac{(E^{O} + N)(V_2 - V_1)}{(V^{O} + V_1)\, T^{O}_{L}}$$

Where V^o is the initial volume of solution, V_1 and V_2 denote the volumes of alkali needed to reach the same value of pH in the titration of acid and ligand, respectively. T^o_L is the total concentration of ligand. N is the normally of alkali solution. E^o is the initial concentration of free acid. From the values of $\overline{n}_A$ so obtained, P_L was calculated using the equation.

$$p_L = \log_{10}\left[\frac{\dfrac{1+[H^+]}{K}}{[T^{O}_{L} - T^{O}_{m}] \times n} \text{ X } \frac{(V^{O} + V_3)}{V^{O}}\right]$$

Where K and $[H^+]$ are the stability constant and hydrogen ion concentration for pH values, respectively. The values of n varies between $0.2 < n < 4.5$, which indicates that there is formation of 1 : 1 and 1 : 2 complexes in the solution.

It was found that Log K_1 and Log K_2 values increased with increasing percentage of dioxane in dioxane–water mixture. The change in colour during the titration showed the commencement of complex formation. The increase in pK and log K values may be due to the effect of bulk solvent. The data obtained in present investigations were found to be in good agreement with the values obtained by Yasuda[9] and Narware and Jahagirdar[10].

Isobestic point method (spectrophotometrically)

The spectrophotometric study was carried out for confirmation of complex formation between metal ion and ligands by isobestic point method.

The equimolar solution of Ni^{2+}, Co^{2+} and Cu^{2+} in (10^{-2} M) and p-aminobenzene sulphonic acid (PABSA), p-chlorobenzene sulphonic acid and p-nitrobenzene sulphonic acid (10^{-2} M) were mixed in 1 : 20 ratio. The pH of the solution was varied from 2.5 to 5.5.

It has been observed that all the curves were passing through one point at different wavelengths for different metal (II) ions with different ligands. (Isobestic point). This confirms the formation of 1 : 1 and 1 : 2 complexes. These complexes were also studied pH-metrically.

Thus, from the results, we conclude that certain metal-ligand complexes are not stable in water or stability constant have low value but stability of complex is enhanced as the percentage of dioxane was increased in the mixture.

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