Note

CHELATION OF FURAN-2-CARBOXYLIC ACID WITH Ni(II), Cd(II), Zn(II) AND Pb(II) IN 50% v/v DIOXANE—WATER

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Stability constants for complexes of furan-2-carboxylic acid with Cu(II) have been reported in aqueous medium [1] as well as in 50% v/v dioxane—water [2].

In the present study, complexation of this ligand with Ni(II), Zn(II), Cd(II) and Pb(II) has been investigated. The values for the stability constants of metal—benzoic acid complexes have also been determined under similar conditions for comparison.

EXPERIMENTAL

The pH titration technique of Calvin and Wilson [3] as modified by Irving and Rossotti [5] has been used. All chemicals were either B.D.H. or Aldrich analar quality. The dioxane used was purified before use by the recommended procedures [4]. Doubly distilled carbon dioxide-free water was used in all experimental work. Metal nitrate solutions were prepared in doubly distilled water and standardized by EDTA titrations. All pH titrations were carried out in dioxane—water (50% v/v) at $25 \pm 0.1°C$, $35 \pm 0.1°C$ and $45 \pm 0.1°C$ in a thermostated bath. A Toshniwal pH meter CL 46 with a matching glass electrode assembly, of accuracy 0.01 pH unit was used. The meter was calibrated with suitable buffers before each titration.

The mole ratio of metal to ligand was kept at 1 : 5 so that the metal could establish and maintain its maximum coordination number. The following solutions were prepared: 5 ml of 0.01 M HNO_3; 5 ml of 0.01 M HNO_3 + 5 ml of 0.05 M ligand; 5 ml of 0.01 M HNO_3 + 5 ml of 0.05 M ligand + 5 ml of 0.01 M metal nitrate. Ionic strength was maintained by adding calculated amounts of 1.0 M KNO_3. The volume of each of the three solutions was made up to 50.0 ml by adding the calculated amounts of water and dioxane to give a 50% v/v dioxane—water mixture. The solutions were then titrated against standardized potassium hydroxide prepared in 50% v/v dioxane—water. Plots of pH versus volume of alkali used were drawn and from these the volumes of alkali required to obtain the same pH in the three solutions were obtained. The shapes of the titration curves were of the usual form.

RESULTS AND DISCUSSION

Proton—ligand formation curves were obtained by plotting the degree of formation of the proton—ligand complex ($\bar{n}_H$) against the pH. The $\bar{n}_H$ values were obtained by using the relationship of Irving and Rossotti [5]

$$\bar{n} = \frac{V''' - V''}{V^0 + V'} \cdot \frac{N + E^0}{\bar{n}_H T_M^0}$$

The formation curves for the metal—ligand complex were obtained by plotting $\bar{n}$ against P_L. The values of $\bar{n}$, the average number of ligands attached per metal ion, were calculated from the above Irving—Rossotti equation. The proton—ligand and metal—ligand stability constants have been obtained by the Bjerrum half-integral and graphical methods [6,7]. The free ligand exponent P_L was calculated from the equation

$$P_L = \log \frac{\displaystyle\sum_{n=0}^{n=J} {}_n\beta^J \left(\frac{1}{\text{antilog } \bar{B}} \right)^n}{T_L - \bar{n}\, T_m} \cdot \frac{V^0 + V'''}{V^0}$$

where V^c is the total initial volume of the solution. V', V'' and V''' are the volumes of alkali required to obtain the same pH meter reading, B, in three solutions. N is the normality of the mineral acid, E^0 is the normality of the alkali, and T_L and T_m are the total ligand and metal ion concentrations. The results are given in Tables 1, 2 and 3.

Table 1 shows that lead(II) formed the strongest complex with furoic acid. The order of stability is Pb > Cd > Zn ≃ Ni. With increase of temperature, the value of log K_1 first increases (in the range 25—35°C) and then decreases (in the range 35—45°C). This behaviour is analogous to that of the benzoic acid—copper(II) complex [8]. Comparison of the data for metal—furoic acid at 25°C with that for metal—benzoic acid under similar conditions (Table 3) shows that the log K_1 values for metal—furoic acid complexes are lower than those for the metal—benzoic acid complexes. The values reported here for metal—benzoic acid complexes are higher than those

TABLE 1

pK_1^H, log K_1 and ΔG values for metal complexes with furoic acid in dioxane—water (50% v/v) at 0.1 M ionic strength

	Log K_1			$-\Delta G$ (kcal mole^{-1})		
	25°C	35°C	45°C	25°C	35°C	45°C
Furoic acid	4.60	4.68	4.64	—	—	—
Ni	2.494	2.592	2.567	3.401	3.653	3.735
Zn	2.494	2.592	2.533	2.401	3.653	3.686
Cd	2.496	2.623	2.607	3.404	3.697	3.794
Pb	2.712	2.767	2.730	3.698	3.900	3.973

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TABLE 2

Effect of ionic strength on log K_1 dioxane—water (50% v/v) at 25°C

| | Ionic strength (M) | | |
	0.1	0.15	0.2
Furoic acid	4.60	4.65	4.68
Ni	2.494	2.496	2.504
Zn	2.494	2.496	2.504
Cd	2.496	2.523	2.556
Pb	2.712	2.737	2.790

TABLE 3

Log K_1 for metal—benzoic acid complexes in dioxane—water (50% v/v) at 0.1 M ionic strength and 25°C

Benzoic acid	Ni	Zn	Cd	Pb
5.85	2.699	2.699	2.870	3.396

reported by Yasuda et al. [9] in aqueous solutions. The difference is due to the change from aqueous to 50% v/v dioxane—water medium. From this it is concluded that only the carboxylic group of the furoic acid takes part in coordination. The oxygen atom of the heterocyclic ring system, another potential site for donation of electrons, remains unused by the metal ions. Yun et al. [10] have reported that ring oxygen of furan-2-carboxylic acid does not coordinate in complexes with rare earth metal ions.

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