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THERMODYNAMIC PARAMETERS OF *p*-CHLORO-BENZOYL-ACETONE COMPLEXES FROM A TEMPERATURE VARIATION STUDY

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ABSTRACT

The interactions of certain transition metal ions: Cu(II), Fe(II), Co(II), Cd(II), Ni(II), Zn(II) and Mn(II) with *p*-chloro-benzoylacetone (*p*-CBA) have been studied pH-metrically in a 75% dioxane–water medium at different temperatures and 0.1 M ($NaClO_4$) ionic strength. The order of stability constants was found to be: Cd(II) < Mn(II) < Co(II) < Zn(II) < Ni(II) < Fe(II) < Cu(II).

Thermodynamic parameters (ΔG, ΔH and ΔS) have been calculated at 30°C, maintaining 0.1 M ionic strength. These values show that the interaction between *p*-CBA and the metal ions is a chelation reaction between ionic species. The entropy change plays an important role in stabilising the complexes.

INTRODUCTION

The presence of β-carbonyl groups with at least one proton on the carbon between the two groups allows a keto $\rightleftharpoons$ enol tautomerism [1] to occur. Under appropriate conditions, the enolic proton [2] (Fig. 1) can be removed. The compounds which form when the proton is replaced by a metal ion are metal β-ketoenolate complexes.

β-Diketones are amongst the most versatile and commonly employed chelating agents in the solvent extraction of lanthanides and actinides. The formation constants of these complexes can indicate the relative ease of solvent extraction. Therefore, one of the widely explored areas of metal β-ketoenolate chemistry is that dealing with stability constant measurements.

The present paper deals with the potentiometric determination of stability constants and thermodynamic parameters of the complexes of bivalent metal ions with a β-diketone derived from benzoylacetone.

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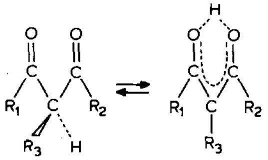

Fig. 1. Keto-enol tautomerism in β-diketones.

EXPERIMENTAL

p-Chloroacetophenone (20 g) was added to 200 ml of absolute ether and 2.5 g of sodium metal. Ethyl acetate (22 g) was then added and the reaction mixture was cooled. On completion of the reaction, the mixture was heated on a water bath for about 2 h and then filtered. The residue was dissolved in water and acidified with acetic acid. White crystals were obtained, which were recrystallised from boiling alcohol. The purity of *p*-chloro-benzoylacetone (*p*-CBA) (Fig. 2) was checked by TLC and elemental analysis.

The ligand solution was prepared in dioxane, purified by the method given in the literature [3]. The medium of titration was 75 : 25 (v/v) dioxane–water mixture. All the metal ion solutions were prepared from their sulphates (BDH, AnalaR). The titrant was a 0.04 M solution of tetramethyl ammonium hydroxide (TMAH) (Merck) in 75% aqueous dioxane (v/v), standardized with a standard solution of oxalic acid. Sodium perchlorate was used to maintain a constant ionic strength. All other reagents were prepared from reagent grade chemicals. An Ecil digital pH-meter (model pH 5651), with a combined electrode of 0–14 pH range, was used for pH measurements.

The stoichiometry of the complexes was ascertained by potentiometric titration. The Bjerrum–Calvin [4,5] pH titration technique, as modified by Irving–Rossotti [6,7], was followed to determine the proton–ligand and the metal–ligand formation constants. For this, the following three solutions, keeping the total volume to 20 ml, were titrated against TMAH at 18, 30, 40 and 50°C.

(i) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml K_2SO_4 (0.02 M) + 15 ml dioxane + 0.5 ml H_2O.

(ii) 3.0 ml $HClO_4$ (0.02M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml K_2SO_4 (0.02 M) + 10 ml ligand (0.01 M) + 5 ml dioxane + 0.5 ml H_2O.

(iii) 3.0 ml $HClO_4$ (0.02 M) + 1.0 ml $NaClO_4$ (2.0 M) + 0.5 ml metal salt solution (0.02 M) + 10 ml ligand (0.01 M) + 5 ml dioxane + 0.5 ml H_2O.

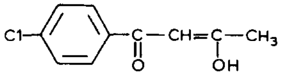

Fig. 2. *p*-CBA.

In all cases corrections for the change in volume on mixing dioxane and water were made (total volume = 19.67 ml).

RESULTS AND DISCUSSION

The pK_a values were obtained from the plot of $\log(\frac{\bar{n}_H}{1-\bar{n}_H})$ versus pH. The values obtained are given in Table 1.

The benzoylacetone radical is univalent so the number of these groups combining with a metal atom will depend upon the principal valency of this atom. Since each benzoylacetone group is equivalent to two associating units it follows that the benzoylacetonates of bivalent metals will be characterised by a molecular arrangement of four points on the sphere of influence of the metallic atom. After complexation a stable six-membered ring is formed and the metal atom serves as the connecting link between the ends of the organic group (the two oxygen atoms).

Thus, the maximum value of $\bar{n}$ obtained should be ~ 2, indicating the formation of 1 : 2 complexes because one replaceable hydrogen is present per ligand molecule. In the present study of bivalent metal complexes, the values of $\bar{n}$ obtained are also ~ 2.

β_n values have been computed from the values of $\bar{n}$ and pL by the weighted-least-squares method of Sullivan et al. [8]. S_{min} values have also been calculated which have the same significance as χ^2, with K degrees of freedom. The values of stability constants obtained are given in Table 1.

The order of increasing stability constants of metal complexes is: Cd(II) < Mn(II) < Co(II) < Zn(II) < Ni(II) < Fe(II) < Cu(II).

The values of stability constants are positive in all cases and increase on decreasing temperature, which shows that a lower temperature is favourable for the formation of complexes.

Thermodynamic parameters

The values of the stepwise and overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of complexation reactions at 30°C and 0.1 M ionic strength were calculated by using the following well-known equations [9]

$$\Delta G = -RT \ln K$$

$$\frac{\mathrm{d} \log K}{\mathrm{d}(1/T)} = \frac{-\Delta H}{4.57}$$

$$\Delta S = \frac{-\Delta H - \Delta G}{T}$$

The values of ΔG, ΔH and ΔS obtained are given in Table 2.

TABLE 1

Protonation and stability constants of bivalent metals at different temperatures

Cation	Temp. 18°C			Temp. 30°C			Temp. 40°C			Temp. 50°C		
	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2	log K_1	log K_2	log β_2
H^+	10.15			9.93			9.85			9.79		
Ni^{2+}	8.4011	7.1473	15.5484	8.1335	6.3979	14.5314	8.0315	6.3497	14.3812	7.6013	6.3472	13.9485
Mn^{2+}	7.0368	3.9945	11.0313	6.8952	3.9196	10.8148	6.7761	3.8035	10.5796	6.6046	3.6744	10.2790
Co^{2+}	7.2465	6.521	13.7675	6.9854	6.3475	13.4229	6.7328	6.3257	13.0585	6.4799	6.1343	12.6142
Fe^{2+}	9.2671	8.1925	17.4596	9.0578	7.9648	17.0226	8.8879	7.7398	16.6277	8.6155	7.5912	16.2067
Cd^{2+}	6.8117	6.0579	12.8696	5.6399	5.1321	19.772	5.6213	4.9661	10.5874	5.5318	4.871	10.4028
Zn^{2+}	8.0165	6.937	14.9535	7.8669	6.433	14.299	7.5155	6.098	13.6135	7.3124	5.4916	12.804
Cu^{2+}	9.3601	8.2853	17.6454	9.0878	8.1577	17.2454	9.0883	7.8829	16.9712	8.7183	7.7418	16.4601

TABLE 2

Thermodynamic parameters for the formation of *p*-CBA complexes at 30°C

Cation	Free energy change (kcal mol^{-1})			Enthalpy change (kcal mol^{-1})			Entropy change (cal mol^{-1} K^{-1})		
	$-\Delta G_1$	$-\Delta G_2$	$-\Delta G$	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H$	ΔS_1	ΔS_2	ΔS
Ni^{2+}	11.277	8.8709	20.148	9.14	2.218	12.694	7.0528	21.956	24.60
Mn^{2+}	9.5605	5.434	14.995	5.712	5.193	11.146	12.701	0.7953	12.702
Co^{2+}	9.685	8.925	18.611	9.520	5.077	13.710	0.5445	12.699	16.174
Cd^{2+}	7.819	7.115	14.935	4.231	5.858	10.080	11.841	4.148	16.023
Zn^{2+}	10.907	8.919	19.826	9.14	2.211	19.041	5.831	22.138	2.590
Fe^{2+}	12.559	11.043	23.602	7.030	7.745	15.758	18.247	10.884	25.887
Cu^{2+}	12.6006	11.311	23.9115	9.14	7.616	17.921	11.421	12.194	19.77

The thermodynamic parameters show that these reactions are exothermic. The values of enthalpy change (ΔH) are negative in all cases, indicating the release of energy during chelation. The values of entropy change (ΔS) accompanying the formation of complexes are positive. As a result of this, the entropy term strongly favours complex formation and accordingly, the chelation effect is essentially an entropy effect. The high positive values of entropy are also justified by considering the greater availability of coordination sites on these metal ions. These metal ions have vacant *d*-orbitals available for the electrons of the ligand. The values of ΔH, ΔG and ΔS are comparable [10] with other ligands having oxygen–oxygen donor sites.

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