

NOTE

Potentiometric Studies of Complex Formation between Ce(III) and 3-Chloro-2-hydroxy Acetophenone

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Stability constants of binary complex of Ce(III) with 3-chloro-2-hydroxy acetophenone at different temperature and in different ratio of water to dioxane has been determined. The thermodynamic parameters ΔH , ΔG and ΔS values are reported.

Key Words: Potentiometric, Complex, Formation, Ce(III), 3-Chloro-2-hydroxy acetophenone.

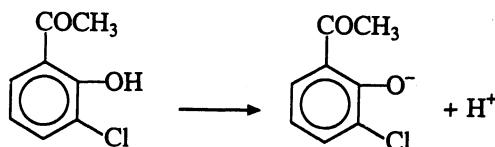
Potentiometric measurements are frequently used to study the binary and tertiary complex formation. The general methods for determining the stepwise stability constants for complexes containing simple nonchelating ligand was first described by Bjerrum¹. Many researchers used this technique later on to study complexation^{2,3}. In the present paper we report the proton-ligand and metal-ligand stability constant of Ce(III) with 3-chloro-2-hydroxy acetophenone.

All the chemicals used were of AnalaR grade and their solution was prepared in double distilled water. Dioxane used was purified by standard methods.⁴ An Elico made LI-120 [NO 03 (0320)] digital pH-meter with combined glass electrode Elico type CL 51 was used for pH measurements. 3-Chloro-2-hydroxy acetophenone (m.p. 55°C) was prepared from 2-chlorophenol using Fries migration method.⁵

Titration were carried out at 30, 40, 50 and 60°C and at ionic strength $\mu = 0.1$ M for studying the effect of medium. The titrations were performed in dioxane-water containing 25, 50 and 75% (v/v) dioxane.

Determinations of proton-ligand stability constants were carried out by point-wise calculation and these are verified by least square methods. The results are presented in Table-1.

The ionisation of 3-chloro-2-hydroxy acetophenone can be represented as:



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Ligand contains only one replaceable hydrogen atom. Hence only one log K value is observed experimentally. The metal-ligand stability constants for Ce(III) and 3-chloro-2-hydroxy acetophenone is given in Table-2. The mean log K_1 value was observed to be 6.95 and log K_2 was 5.77

TABLE-1
PROTON-LIGAND STABILITY CONSTANTS FOR
3-CHLORO-2-HYDROXY ACETOPHENONE

pH	n_A	pK
8.3	0.822871	8.937042
8.4	0.778589	8.946108
8.5	0.759776	9.000069
8.6	0.717714	9.005263
8.7	0.676764	9.020918
8.8	0.636921	9.044084
8.9	0.592651	9.062832
9.0	0.532902	9.067242
9.1	0.467604	9.073644
9.2	0.407839	9.078049
9.3	0.363596	9.080001
9.4	0.324891	9.082363

Mean pK value = 9.03

TABLE-2
log K_1 AND log K_2 VALUES OF Ce(III) 3-Chloro-2-hydroxy acetophenone

n	p^L	log K_1 /log K_2	n	p^L	log K_1 / log K_2
0.25477	7.11652	6.65038	1.21841	6.26583	5.71212
0.36554	7.02685	6.78739	1.32898	6.02894	5.71938
0.49846	6.93958	6.93691	1.43391	5.79188	5.77640
0.66462	6.90603	7.20306	1.64401	5.41919	5.77664
0.72000	6.81165	7.22183	1.76022	5.43459	5.93571

Mean log K_1 = 6.95;
standard deviation = 0.17;
least square method = 6.82

Mean log K_2 = 5.77;
standard deviation = 0.19;
least square method = 6.17

The proton-ligand and metal-ligand constants are generally influenced by dielectric constants. The present study reveals that a linear relation exists between log K and mole fraction of solvents. The pK values increase with increase in percentage of dioxane. This can be explained on the basis of solution of anion obtained after dissociation.

This suggests that ion-ion interaction is more as compared to the ion-dipole interaction between metal ion and solvent molecules.

TABLE-3

Dioxane-water (%)	log K ₁	log K ₂
0	5.52	5.36
25	6.29	6.07
50	6.82	6.17
75	10.03	9.37

For the effect of temperature a new technique developed by Mali *et al.*⁶ was used and practical and thermodynamic proton-ligand stability constants of ligands were reported. (Table 4)

TABLE-4

Temp (°C)	Experimental value pK	Thermodynamic value pK
30	9.72	10.28
40	9.62	10.18
50	9.53	10.09
60	9.45	10.01

It was observed that the pK value decreases with increase in temperature. This may be due to increase in dissociation of ligand at high temperature. At high temperature ligand molecule behaves as a stronger acid (less base)⁷. This is in good agreement with the results obtained by Pitzer.⁸ Different thermodynamic parameters like ΔG , ΔS and ΔH were calculated using the above data. At thermodynamic pK 10.28, ΔH was observed to be +3.03 kcal/mol. ΔG was found to be +14.25 kcal/mol and $\Delta S = -33.72$ cal/mol/°C. The negative value for entropy change may be due to more orderly arrangement of ions in the water structure.

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