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Effect of Temperature and Media on the Complexation of Sm(III) with 5-Bromo-2 Hydroxy Acetophenone

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The present paper deals with the interaction of Sm(III) with 5- bromo-2-hydroxyacetophenone at different temperatures (30, 40, 50 and 60°C). The stability constant of the complex has been studied in 25, 50 and 70% diozane-water mixture. pH-metric data based on Bjerrum Calvin method was employed for the calculation proton-ligand and metal-ligand stability constants. The systems were studied by maintaining M : L ratio 1 : 1 and 1 : 2.

Key words: Samarium(III), 5-bromo-2 hydroxy acetophenone, complexes, stability constant.

INTRODUCTION

Complexation studies are very important from the point of view of analytical and biochemical researchers. Therefore, this study has received the attention of many researchers in recent years[1–3]. The ligand may get attached to metal ions by coordinate bonds. The extent to which the ligand binds to a metal is expressed in terms of stability constants[4, 5]. They are determined by different methods using instruments like polarography, potentiometry, spectrophotometry, etc. In the present paper we are reporting the stability constants of Sm(III) with 5-bromo-2-hydroxy acetophenone using pH-meter.

EXPERIMENTAL

All chemicals used were of S.D. Fine, AnalaR grade. Solutions were prepared in doubly distilled water (pH 6.7–6.8 and specific conductivity 2×10^{-6} mhos). The ligand 5-bromo-2-hydroxy acetophenone was prepared from 4-bromophenol as described in the literature[6]. pH-meter Elico LI-120 with combined electrode CI-51 was used for the pH-metric data.

RESULTS AND DISCUSSION

The determination of proton-ligand stability constant was carried out by point-wise calculations. They were also confirmed by half integral method and least

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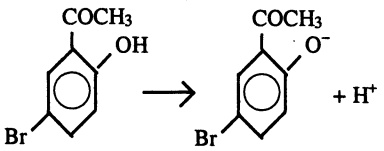
squares method. Since the ligand has only one binding site, we observed only one neutralisation point. Therefore only one pH value was obtained. The ionisation of 5-bromo-2-hydroxy acetophenone can be expressed as:



In the present study we observed that the metal-ligand curve is well separated (Fig. 1) from the ligand curve which proves that the liberation of proton could be due to complex formation. The values of log K are determined by pointwise calculations. log K_1 is assigned to 1 : 1 while log K_2 is assigned to 1 : 2 complexes. The average closely related log K values are taken to represent stability constants of metal-ligand complexes. The results are shown in Tables 1 and 2.

TABLE-1
PROTON-LIGAND STABILITY CONSTANT OF
5-BROMO-2-HYDROXY ACETOPHENONE

pH	n A	pK	
8.50	0.806003	9.118542	
8.65	0.758335	9.146648	
8.75	0.728418	9.178479	
8.90	0.684124	9.235617	
9.00	0.639790	9.249482	Mean pK = 9.26
9.10	0.601037	9.277968	
9.20	0.562291	9.308776	
9.30	0.512496	9.321712	
9.40	0.446072	9.325950	
9.50	0.409609	9.341229	
9.60	0.382025	9.391121	

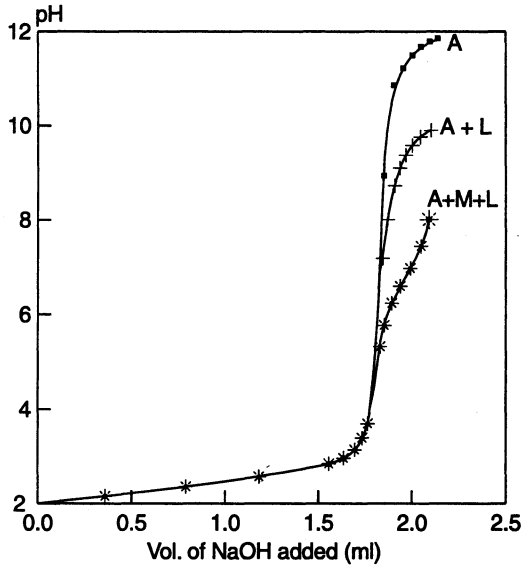
TABLE-2
METAL-LIGAND STABILITY CONSTANT OF
Sm-5-BROMO-2-HYDROXY ACETOPHENONE

Temp. = 30°C, $T_L^0 = 2 \times 10^{-3}$ m, $T_m^0 = 4 \times 10^{-4}$ m, $V_0 = 50$, $\varepsilon_0 = 0.008492$, n = 0.1 m, n = 0.2212.
50% Dioxane : water

n	pL	log k_1		$\bar{n}$	pL	log k_2	
0.27695	7.40856	6.99180	Mean log k_1 = 7.21	1.55078	6.99599	7.08450	
0.36556	7.36686	7.12743	St. dev. = +0.13	1.60616	6.95306	7.14033	Mean log k_2 = 7.21
0.60375	7.33994	7.52282	Least square = 7.13	1.74462	6.87124	7.33600	St.dev. = +0.10
				1.80001	6.77873	7.35543	Least square = 7.09

Effect of Sovent: The proton-ligand and metal-ligand stability constant are determined in 0%, 25%, 50%, 75% dioxane-water mixture using pointwise calculations. Table-3 represents pK values of 5-bromo-2-hydroxy acetophenone.

The practical pK values are converted into thermodynamic pK values using Van Uitert[7] correction factor.



A = Acid ($HClO_4$); L = ligand (5-bromo-2-hydroxy acetophenone);
M = metal (Sm(III) nitrates); ionic strength = 0.1M.

TABLE-3
pK VALUES OF 5-BROMO-2-HYDROXY ACETOPHENONE

Dioxane-water (%)	pK (Experimental value)	pK (Thermodynamic value)	log K_1	log K_2
0	8.76	–	6.28	5.53
25	9.25	9.43	6.76	6.02
50	9.74	10.30	7.73	7.09
75	10.58	12.48	10.63	9.93

The metal-ligand stability constant of Sm(III) 5-bromo-2-hydroxy acetophenone in 0, 25, 50 and 75% dioxane water has been determined by pointwise calculation and these are also presented in Table-3.

It is clear from the data that proton-ligand and metal-ligand stability constants increase with increase in composition of dioxane-water system. In the present investigation, the pK values refer to the release of a proton from phenolic —OH group present in the side chain of the structure. We observed that with increase in dioxane percentage, there is decrease in acidity of ligand. Secondly, metal-ligand stability constant increases with dioxane percentage. This can be explained on the basis of solvation of anion obtained after dissociation and ligand field stabilisation. This is in agreement with other workers.[8,9] Increase in pK values and metal-ligand stability constants might be due to decrease in dielectric constant of medium, effect of bulk solvent and specific solute-solvent interactions.

Effect of temperature: In the present investigation it was decided to study the effect of various temperatures, *viz.*, 30, 40, 50 and 60°C, on the proton-ligand stability constant. A new technique called as continuous titration technique developed by Pethe-Mali[10] was adopted for this purpose. The results are presented in Table-4.

TABLE-4
pK VALUES OF 5-BROMO-2-HYDROXY ACETOPHENONE
AT DIFFERENT TEMPERATURES

Temperature (°C)	pK (Experimental value)	pK (Thermodynamic value)
30	9.74	10.30
40	9.64	10.20
50	9.51	10.07
60	9.39	9.95

The pK values decrease with increase in temperature. This is in agreement with pitzer[11]. The various thermodynamic parameters are calculated using the above data. The value of ΔH (– 4.53 kcal/mole) and positive value of ΔG (14.28 kcal/mole) indicate the dissociation of ligand into ions to be a thermodynamic process but not a spontaneous and favourable process. The negative value of ΔS (–31.6 cal/mol/dye) is expected since after ionisation the water molecule gets systematically oriented around the ions. The formation of ions, therefore, is bound to produce more order in water structure leading to negative values of S.

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