

THERMODYNAMIC STABILITY CONSTANTS AND OTHER RELATED THERMODYNAMIC PROPERTIES FOR Zn(II)-PMBP COMPLEX

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Abstract. The thermodynamic stability constants and other related thermodynamic properties for the complex formed between Zn(II) and 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 have been determined over the temperature range, 5-45° in chloroform phase.

Introduction

1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (PMBP) has been used as an efficient extracting agent.¹⁻⁸ The study of various thermodynamic constants for the formation of chelates during the extraction of various elements with PMBP is, therefore, of significant interest. Work on Zn(II)-PMBP chelate is presented in this paper.

Experimental

All chemicals used were of Analar grade or otherwise purified by recrystallization. Triply distilled water was used for making solutions for the metal ions of required concentration. PMBP was synthesized as described in the literature.⁹ The methods for the measurements of percentage extraction and for the analysis of the samples were similar to those reported in the literature.¹⁰ pH measurements were made using model 23A (Electronic Instruments Ltd.) and a thermostat bath HAAKE Model NK22 was used to obtain the required temperature for the experiment. The partition coefficient measurements were made using method described elsewhere.¹¹ The pK measurement for PMBP were made spectrophotometrically using Zolon Red as reagent for indicating the concentrations for the ionized and unionized species of PMBP. Absorption was measured at wavelength 420 nm and 480 nm.¹²

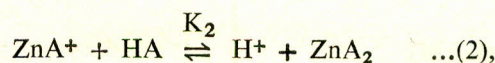
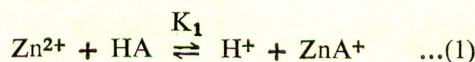
Results and Discussions

The extraction constants (K_{ex}) for Zn(II) with PMBP were measured over the temperature range 5-45° using chloroform as an extracting medium from aqueous solution of the element. The values thus obtained are reported in Table 1. The extractions were carried out over a pH range 1.1 to 2.5 and it was also observed that the value of K_{ex} were independent of hydrogen ion concentration within this pH range.

TABLE 1. EXTRACTION CONSTANTS FOR Zn(II)-PMBP CHELATE AT VARIOUS TEMPERATURES

Temperature (T°C)	Log K_{ex}
5	— 0.274
15	— 0.451
25	— 1.133
35	— 1.770
45	— 2.424

The log-log plot for the percentage extraction in chloroform phase (E) and hydrogen ion concentration gave rise to *c* slope of 1.97 indicating thereby that two hydrogen ions are liberated during the formation of the complex. These results are similar to those reported elsewhere.¹⁰ Thus the reaction can be written as follows:



where HA is PMBP and K_1 and K_2 are the first and second-step stability constants respectively. The extraction constants can be written as :

$$K_{ex} = (\text{ZnA}_2) (\text{H}^+)^2 (\text{Zn}^{2+})^{-1} (\text{HA})^{-2} \quad \dots(3).$$

The extraction constants of the complex ZnA_2 can be expressed through overall stability constant (B_2) of the complex, the distribution constant of the complex (P_{ZnA_2}), dissociation constant of the reagent (K_{HA}) and the distribution constant of the reagent (P_{HA}) as

$$K_{ex} = B_2 K_{\text{HA}}^2 P_{\text{HA}}^{-2} P_{\text{ZnA}_2} \quad \dots(4)$$

Thus for the evaluation of overall stability constants and the other two stability constants, K_1 and K_2 , the partition coefficients and distribution coefficients for the metal complex and reagent and dissociation

constants for the reagent were determined under the experimental conditions employed. The values are shown in Table 2.

TABLE 2. EXPERIMENTALLY DETERMINED VALUES FOR pK_{HA} , $\log P_{HA}$ AND $\log P_{ZnA_2}$ OVER A RANGE OF TEMPERATURE 5-45°.

T°C	5	15	25	35	45
pK_{HA}	4.039	4.040	4.040	4.038	4.036
$\log P_{HA}$	2.311	2.320	2.331	2.346	2.358
$\log P_{ZnA_2}$	2.640	2.646	2.651	2.660	2.667

The values for the stability constants for step (1) and step (2) were obtained by the method reported in the literature¹³ with the help of computer analysis. The values thus obtained for $\log \beta_2$, $\log K_1$ and $\log K_2$ are summarized in Table 3.

TABLE 3. VALUES OBTAINED FOR THE THERMODYNAMIC STABILITY CONSTANTS $\log \beta_2$, $\log K_1$ AND $\log K_2$ AT DIFFERENT TEMPERATURES

T°C	5	15	25	35	45
$\log \beta_2$	10.334	9.623	8.958	8.338	7.701
$\log K_1$	5.787	5.389	5.016	4.669	4.313
$\log K_2$	4.547	4.234	3.942	3.669	3.388

The tendency of a metal ion to take up ligand is proportional to the number of vacant sites.

For the type of ligand such as PMBP coulombic attraction is more for Zn^{2+} as compared to ZnA^+ . Thus $\log K_1 - \log K_2$ is expected to be positive.¹⁴ The values reported in Table 3 are in agreement with it.

From the data on stability constant the standard free energy changes (ΔG°) for the formation of complex were evaluated at various temperatures and are shown in Table 4. Standard heat of formation (ΔH°) were also evaluated from the slope of the plot of $\log K$ or $\log B$ against $1/T$ which were fairly good straight lines over the temperature range studied. The values are also reported in Table 4. From the data on ΔG° and ΔH° (see Table 4) at different temperatures the values for the state function entropy of formation (ΔS°) of the complex were also calculated and the results are reported in Table 4.

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TABLE 4. VALUES OF THE THERMODYNAMIC PROPERTIES ΔH° , ΔG° AND ΔS° OBTAINED FROM THERMODYNAMIC STABILITY CONSTANTS (CF. TABLE 3)

T°C	5	15	25	35	45
$\Delta G_{B_2}^\circ$ (KJ/M)	-197.53	-183.94	-171.23	-159.38	-147.20
$\Delta G_{K_1}^\circ$ (KJ/M)	-110.62	-103.01	-95.88	-89.25	-82.44
$\Delta G_{K_2}^\circ$ (KJ/M)	-86.91	-80.93	-75.35	-70.13	-64.76
$\Delta H_{B_2}^\circ$ (KJ/M)	-108.71	-108.71	-108.71	-108.71	-108.71
$\Delta H_{K_1}^\circ$ (KJ/M)	-60.84	-60.84	-60.84	-60.84	-60.84
$\Delta H_{K_2}^\circ$ (KJ/M)	-47.87	-47.87	-47.87	-47.87	-47.87
$\Delta S_{B_2}^\circ$ (J/MT)	319.49	261.22	209.79	164.51	121.03
$\Delta S_{K_1}^\circ$ (J/MT)	179.06	146.42	117.58	92.24	67.92
$\Delta S_{K_2}^\circ$ (J/MT)	140.43	114.80	92.21	72.27	53.11

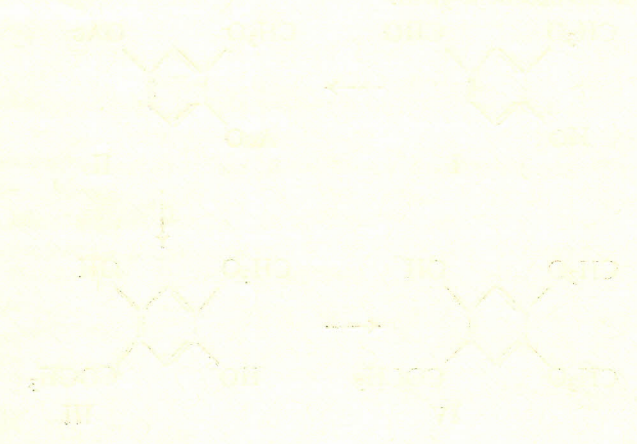
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THE THERMODYNAMIC STABILITY CONSTANTS AND OTHER RELATED THERMODYNAMIC PROPERTIES OF THE COMPLEXES OF URANIUM(VI) WITH 2-AMINO-2-NAPHTHOL-6-SULFONIC ACID AND ITS DERIVATIVES

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