Stability Constants and Thermodynamic Functions of Cobalt(II) and Nickel (II) Chelates of 8-Quinolinyl Mono-Ethyl Ortho-Phosphate

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In previous publication[1] 8-quinolinyl mono-ethyl ortho-phosphate was prepared, its structure was confirmed with IR,UV, NMR and mass spectra, and the halochromic shifts of this parent compound and its complexes with Cu^{2+}, Ni^{2+}. Co^{2+}, Fe^{3+} and Cr^{3+} have been reported.

In the present work, potentiometric studies are performed on 8-quinolinyl ethylphosphate and its cobalt and nickel complexes. The dissociation constant of the ligand, the stability constants of the complexes and the thermodynamic parameters of the formation of these complexes are also determined.

Experimental

Apparatus

All the pH measurements were carried out using Pye Unicam pH meter model 292-MK2.

Reagent and solutions

All solutions were prepared using double distilled water.

8-Quinolinyl mono ethylphosphate, $C_{20}H_{19}O_4N_2P$, (QEP) solution:

A stock solution 5 x 10^{-2}M was prepared by dissolving 1.9100 gm of the solid reagent (prepared as previously described[1]). The required concentrations were made by proper dilutions of the stock soltuion.

Metal-ions solution(0.1 M solution)

Stock solutions of Ni^{2+} and Co^{2+} were prepared from their nitrate hexahydrate salts (Merck) and standardized by complexometric titration[2].

Sodium hydroxide solution

A concentrated solution of sodium hydroxide was prepared in carbon dioxide free bidistilled water. The clear solution was decanted, diluted to proper volume, stored in polyethylene bottle, and standardized by the recommended procedure [3].

Procedure

pH-metric titrations were carried out twice in double Jacketed cell at different ionic strength and temperatures (i.e. 15,20,25,30, and 40°C$\pm$ 0.2°C) under nitrogen atmosphere. The ionic strength was adjusted at μ =0.01, 0.05,0.10 and 0.50 using potassium nitrate. The titration was conducted with standard solution of 0.1 NaOH.

Results and Discussion

The dissociation constants of the ligand at 25°C and 0.1 M ionic strength

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(KNO_3) are log K_1=3.54 and log K_2=8.00.

The potentiometric method requires the calculation of $\bar{L}$ and $\bar{n}$ in order to determine the stability constant of complex formed [4-6] where $\bar{L}$ is the concentration of the free chelating species and $\bar{n}$ is the average number of molecules of ligand bound by one atom of the metal. The detailed method of calculation has previously been reported[7]. The formation curves ($\bar{n}$ vs pL) show that $\bar{n}$ approaches its maximum at 2.

Effect of ionic strength on the stability constant of complexes.

The pH-metric studies on 8-quinolinyl mono-ethyl orthophosphate and its complexes with nickel and cobalt show that the dissociation constant of the ligand and the stability constants of the complexes vary with the change of the ionic strength (cf. Table 1); with the increase of the ionic strength the dissociation constant of the ligand increases, whereas the stability constants of the nickel(II) and cobalt (II) complexes decrease. Stability constants at zero ionic strength were obtained by extrapolation (log K vs $\sqrt{\mu}$) [8].

Effect of temperature on stability constant of complexes:

Table (2) represents the stability constants of nickel (II) and cobalt (II) complexes at constant ionic strength and different temperatures. The results show that the dissociation constant of the ligand and stability constants of the complexes decrease with the increase of temperature.

Thermodynamic parameters for the formation of these complexes are shown in table (3). The values of ΔH were

Table 1: Stability constants of Ni(II) and Co(II) quinolinyl mono ethyl ortho-phosphate chelates at different ionic strength (KNO_3;20°C).

Ion	Constant	μ=0.00	μ=0.01	μ=0.05	μ=0.10	μ=0.50
H^+	log K_1	3.63	3.65	3.65	3.67	3.75
-	log K_2	7.90	7.98	8.05	8.08	8.10
Co^{++}	log K_1	9.20	9.10	8.99	8.90	8.52
-	log K_2	8.65	8.41	8.32	8.15	7.67
Ni^{++}	log K_1	8.88	8.76	8.60	8.49	8.07
-	log K_2	7.75	7.73	7.62	7.49	7.10

Extrapolated values at zero ionic strength (log K vs $\sqrt{\mu}$)

Table 2:Stability constants of Ni(II) and Co(II) quinolinyl mono ethyl phosphate at different temperature (μ =0.1 M KNO_3).

Ion	Constant	To 15°	20°	25°	30°	40°
H^+	log K_1	3.76	3.67	3.54	3.40	3.28
-	log K_2	8.20	8.08	8.00	7.89	7.74
Co^{++}	log K_1	8.98	8.90	8.88	8.87	8.79
-	log K_2	8.21	8.15	8.07	8.05	8.04
Ni^{++}	log K_1	8.51	8.49	8.47	8.42	8.39
-	log K_2	7.53	7.49	7.46	7.46	8.38

Table 3:Thermodynamic parameters for Ni(II) and Co(II) quinolinyl mono ethyl phosphate chelates system (μ =0.1 M KNO_3)

Metal	$-\Delta H_{B_1}$	$-\Delta H_{B_2}$	$-\Delta G_{B_1}$	$-\Delta G_{B_2}$	ΔS_{B_1}	ΔS_{B_2}
Ion	K.Cal.	K.Cal.	K.Cal.	K.Cal	Cal	Cal.
Co(II)	2.28	6.15	11.94	22.87	32.97	57.06
Ni(II)	1.98	4.51	11.38	21.419	32.08	57.71

ΔH and ΔG in K.Cal/mole;ΔS in Cal $mole^{-1}$ $deg.^{-1}$

obtained using the temperature coefficient method and the values of ΔG and ΔS were calculated in the usual way. The reults show that the entropy term makes dominant contribution to the stability of these complexes.

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