

# Synthesis Characterization and a Physical Study of New Polyborate Compounds with Some Transitions Metal Ion

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## Abstract

This Study include preparation of polyborate compounds containing some transition metals cations complexes which are:  $[\text{Ag}(\text{NH}_3)_2][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 7\text{H}_2\text{O}$ (1),  $[\text{Hg}(\text{NH}_3)(\text{H}_2\text{O})][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 10\text{H}_2\text{O}$ (2),  $[\text{Hg}(\text{NH}_3)(\text{H}_2\text{O})][\text{B}_5\text{O}_6(\text{OH})_4][\text{B}_3\text{O}_3(\text{OH})_4] \cdot 9\text{H}_2\text{O}$ (3),  $[\text{Zn}(\text{NH}_3)_3(\text{H}_2\text{O})_3][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ (4),  $[\text{Zn}(\text{NH}_3)_2(\text{B}_6\text{O}_7(\text{OH})_6)] \cdot 5\text{H}_2\text{O}$ (5),  $[\text{Zn}(\text{NH}_3)(\text{H}_2\text{O})_5][\text{B}_5\text{O}_6(\text{OH})_4][\text{B}_3\text{O}_6(\text{OH})_4] \cdot 4\text{H}_2\text{O}$ (6),  $[\text{Cd}(\text{en})][\text{B}_6\text{O}_7(\text{OH})_6] \cdot 7\text{H}_2\text{O}$ (7),  $[\text{Cu}(\text{en})_3][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2.4\text{H}_2\text{O}$ (8),  $[\text{Zn}_{2\text{en}_3}(\text{B}_6\text{O}_7(\text{OH})_6)_2] \cdot 3\text{H}_2\text{O}$ (9),  $[\text{Cu}(1,2\text{dmp})_3][\text{B}_5\text{O}_6(\text{OH})_4] \cdot 6\text{H}_2\text{O}$ (10). The prepared polyborate compounds were characterized by elemental analysis (C.H.N), Infrared (FT-IR), Nuclear Magnetic Resonance Spectroscopy ( $^1\text{H}$ -NMR), ( $^{13}\text{C}$ -NMR), ( $^{11}\text{B}$ -NMR). Some of the prepared compounds was a physically studied by measuring the molar conductivity which were used to determine thermodynamic parameters i.e the ion association constant  $K_a$ , Enthalpy  $\Delta H^\circ$ , Entropy  $\Delta S^\circ$  and Gibbs free energy  $\Delta G^\circ$  implenting Shedlovsky technique with matlab program. The values of  $K_a$ ,  $\Delta G^\circ$  for pentaborate compounds were always greater than other compounds, due to the fact the pentaborate compounds more favored in ion-pair formation than other followed by hexaborate compound then the compound that containing double composition of penta and Triborates. All reactions are endothermic which were supported by the positive values of the enthalpy  $\Delta H^\circ$ .

**Keywords:** Pentaborate(2-), hexaborate(2-), polyborate, Shedlovsky technique.

## Introduction

Boron is one of the most extensively studied elements, due to many different industrial applications [1]. Boron is combined with oxygen such as boric acid and polyborate salts [2]. Boron compounds are known as complexes consisting of ions that are bound together by sharing of oxygen atoms with two types of ions through the bonding of the  $\text{BO}_4^-$  ions and the tetrahedron borate ( $\text{BO}_3$ ) [3] is a triangular borate plane together they form isolated chains or cage rings that condense further to form polymer chains or three-dimensional networking [4, 5].

Most of the polyporate compounds consist of a boroxole rings  $\text{B}_3\text{O}_3$  that are common in polyporate compounds [6, 7, 2]. Different types of boric acid in different aqueous solution the main species in solution at low acidity are  $\text{B}(\text{OH})_3$ , high acidity are  $\text{B}(\text{OH})_4^-$  while the borate ions are more complex within the acidity range [8, 15].

The concentrations of borate anions in the aqueous solution vary according to concentration, temperature and pH [8, 3]. There are several types of isolated polyborate anion triangular borate  $\text{B}(\text{OH})_3$  to pentadecaborate anion  $(3-)[\text{B}_{15}\text{O}_{20}(\text{OH})_8]^{3-}$  [16-18].

The hexaborate anion is classified as hexadentate ligand [8]. Shedlovsky equation in form of equations (1-5) were applied to calculate the reaction constant and thermodynamic properties such as  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $\Delta S^\circ$  of some preparation compounds to infer the proceeding of the process of reaction of electrical conductivity in aqueous solutions which is considered one of the most important ways of demonstrating the molecular binding of charged ions in the electrolyte solution to know which of the compounds is more amenable to formation. [14].

$$\frac{\lambda}{\Lambda S(Z)} = \frac{\lambda}{(\Lambda^\circ)} + \left( \frac{KA}{A^\circ} \right) (C_{\Delta F} \pm S(Z)) \dots \dots \dots (1)$$

$$Z = \left[ \frac{\alpha_{\Lambda^\circ} + \beta}{\Lambda^\circ} \right] (C_{\Delta})^{\frac{1}{\tau}}$$

$$\alpha = \frac{\lambda_{\Lambda^\circ, \lambda_{\Delta F} X^{\frac{1}{\tau}}}, \lambda_{\Delta F}^2 W}{(DT)^{\frac{\tau}{\tau}}}$$

$$\beta = \frac{\lambda_{\Delta F, \lambda_{\Delta F}}}{\lambda_{\Delta F} (DT)^{\frac{\tau}{\tau}}}$$

$$W = Z + Z - \frac{\tau q}{1 + q^{\frac{1}{\tau}}}$$

$$q = \frac{z_+ z_-}{z_+ + z_-} \times \frac{\lambda_+ + \lambda_-}{z_+ \lambda_- + z_- \lambda_+}$$

$$-\log f_{\pm} = \frac{AZ_+ Z_- \mu^{\frac{1}{\tau}}}{1 + BR \mu^{\frac{1}{\tau}}} \dots \dots \dots (2)$$

$$A = \frac{\lambda_{\Lambda^\circ, \lambda_{\Delta F} X^{\frac{1}{\tau}}}, \lambda_{\Delta F}^2}{(DT)^{\frac{\tau}{\tau}}}$$

$$B = \frac{\lambda_{\Delta F, \lambda_{\Delta F} X^{\frac{1}{\tau}}}, \lambda_{\Delta F}^2}{(DT)^{\frac{\tau}{\tau}}}$$

$$\mu = \frac{1}{\tau \sum (C_i \tau_i) z_i^{\frac{1}{\tau}}}$$

$$d = \lambda_{\Delta F} (m/p)^{\frac{1}{\tau}} \dots \dots \dots (3)$$

$$\Delta G = -\tau \cdot \tau RT \log_{\lambda} K_a \dots \dots \dots (4)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \dots \dots \dots (5)$$

Where:  $\lambda$  : Molar conductivity,  $\Lambda^\circ$ : infinite Molar Conductivity,  $K_a$ : Equilibrium constant,  $Z$ : equivalent  $\lambda$  : Ion Conductivity,  $D$ : Electrical constant insulation of the medium,  $\mu$ : Viscosity of the solvent,  $f_{\pm}$ : Activity factor for free ions,  $T$  : Absolute temperature,  $R$ : Maximum center to center distance between the ions in the ion-pair,  $a$ : the sum of crystallographic radii of the ions,  $\rho$ : Density of solute,  $m$ : The molecular weight of the solvent,  $\Delta G^\circ, \Delta H^\circ, \Delta S^\circ$  : Gibbs free energy, enthalpy, entropy respectively.

The aim of this paper to preparation of new polyborate compounds with some transitions metal ions than characterized by elemental analysis (C.H.N), Infrared (FT-IR), Nuclear

Magnetic Resonance Spectroscopy ( $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR,  $^{11}\text{B}$ -NMR). Some of the prepared compounds were physically studied used to determine thermodynamic parameters i.e  $\Delta H^\circ, \Delta G^\circ, \Delta S^\circ$  and equilibrium constant  $K_a$  to explain why different formulations of polyborate compound are formed and to infer the proceeding of the process of reactions.

## Materials and Methods

All the chemicals and solvents used were of chemically pure grade, and commercially available.

## General

The melting point or the decomposition temperature of all the prepared ligand and

metal complexes were observed in an electro thermal melting point apparatus model (Melting SMP31), The FT-IR spectra in the rang (200-4000)  $\text{cm}^{-1}$  were recorded as KBr disc using a Shimadzu FT-IR spectrophotometer (Model: IR- affinity, Shimadzu), Carbon and Proton Nuclear Magnetic Resonance Spectra were obtained using Burker DXR System AL500(500 MHz), Boron Nuclear Magnetic Resonance Spectra were obtained using INOVA(500 MHz), Micro-elemental analysis(C.H.N) were obtained using (ThermoFinnigan flash), Molar Electrical conductivity measurements were carried out by using (Inolabcond 720).

### Preparation of the Complexes

#### Preparation of $[\text{Ag}(\text{NH}_3)_2][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 7\text{H}_2\text{O}$

A solution of ammonium hydroxide (0.9 g, 37%, 25.8 mmol) was added to silver oxide (1 gm, 4.3 mmole). The reaction mixture was stirred at room temperature for 60 mints. A solution of boric acid (2.6 g, 43.2 mmol) in distilled water (10 ml) was carefully added to the filtrate. The solution was stirred at room temperature for 3h.

The final solution was distributed over a few small beaker, and left for 14 days to yield a colorless to re crystals of  $[\text{Ag}(\text{NH}_3)_2][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 7\text{H}_2\text{O}$ . (1.3g, 62%) M.P. = 290°C (dec), C.H.N: H= 4.9%, N=5.7%. Found H= 4.6%, N=5.4%.  $^{11}\text{B}$ /PPM: 18.3, 13.4, 1.2. IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3384(s), 3124(s), 1435(s), 1356(s), 1249(s), 1101(s), 1026(s), 926(s), 782(s) and 696(s).

#### Preparation of $[\text{Hg}(\text{NH}_3)(\text{H}_2\text{O})][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 10\text{H}_2\text{O}$

To a mixture of mercuric sulphate (1 gm, 3.37 mmole) with ammonium hydroxide(0.7 g, 20.22 mmol) in (20 ml) in distilled water. Barium hydroxide (1.06 gm, 3.37 mmole) was added. The reaction mixture was stirred for 3 mints then a white precipitate of barium sulphate was filtrate twice to get rid of the precipitate. Boric acid (2.08 g, 33.7 mmol) was carefully added.

The final solution was left at room temperature for several days to yield  $[\text{Hg}(\text{NH}_3)(\text{H}_2\text{O})][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 10\text{H}_2\text{O}$ . (0.95 g, 34%).M.P=185-188°C. C.H.N: H=3.9%, N=1.6%. Found H=4.1%, N=1.6%.  $^{11}\text{B}$ /PPM:

18.0, 13.0, 1.5. IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3379(s), 3232(s), 1437(s), 1358(s), 1195(s), 1092(s), 1022(s), 926(s), 913(s), 781(s) and 694(s). The polyborate compounds **3**, **8**, **9**, **10** and **6** were prepared in the same way as  $[\text{Hg}(\text{NH}_3)(\text{H}_2\text{O})][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 10\text{H}_2\text{O}$  previous compound.

#### Preparation of $[\text{Zn}(\text{NH}_3)_3(\text{H}_2\text{O})_3][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 3\text{H}_2\text{O}$

To a mixture of zinc chloride (0.5 gm, 3.7 mmole) with ammonium hydroxide (0.8g, 22.2 mmol) in (20 ml) in distilled water. Silver dioxide (0.86 g, 3.7 mmole) was added. The reaction mixture was stirred for 3 mints then a white precipitate of silver chloride was filtrate twice to get rid of the precipitate. Boric acid (2.3 g, 37 mmol) was carefully added.

The final solution was left at room temperature for several days to yield  $[\text{Zn}(\text{NH}_3)_3(\text{H}_2\text{O})_3][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 3\text{H}_2\text{O}$ . (0.73g, 77%).M.P=260°C (dec). C.H.N: H=4.4%, N=6.4%.  $^{11}\text{B}$ /PPM: 16.8, 13.3, 1.6. IR ( $\text{KBr}/\text{cm}^{-1}$ ): 3390(s), 3124(s), 1436(s), 1351(s), 1243(s), 1098(s), 1024(s), 922(s), 781(s) and 694(s). polyborate compounds **7** were prepared in the same way as  $[\text{Zn}(\text{NH}_3)_3(\text{H}_2\text{O})_3][\text{B}_5\text{O}_6(\text{OH})_4]\cdot 3\text{H}_2\text{O}$  previous compound.

### Physical Study

Different concentrations of dilute solutions ( $0.569 \times 10^{-3}$ - $1.1 \times 10^{-3}$  M) were prepared by dissolving the required amount of the sample in distilled water, the electrical conductivity is then measured at a temperatures of (10-30C°) the temperature is controlled through a water bath.

The solution conductivity results were then recorded for the required concentrations after the solvent conductivity was subtracted. Then Shedlovsky technique was applied to calculate thermodynamic parameters i.e the ion association constant  $K_a$ , Enthalpy  $\Delta H^\circ$ , Entropy  $\Delta S^\circ$ , and Gibbs free energy  $\Delta G^\circ$ . Conjunction with The matlab program.

### Results and Discussion

#### Physical Properties

The physical properties of the prepared compounds are shown in Table1:

Table 1: Physical properties data of the Compounds (1-10)

Comp.	Calc. M. Wt	Color	M.P. °C
1	486.1	Colorless	290 D
2	851.8	White	185-188
3	764.2	White	180-182
4	660.7	White	260 D
5	631.4	White	258 D
6	609	White	282 D
7	498	White	250 D
8	751.8	Violet	290 D
9	920	White	280 D
10	829.8	Violet	255 D

## Elemental Analyses

Table 2: Elemental microanalysis C.H.N for the Compounds (1-10)

Comp.	Theoretical			Experimental		
	N%	H%	C%	N%	H%	C%
1	5.7	4.9	-	5.4	4.6	-
2	1.6	3.9	-	1.6	4.1	-
3	1.9	4.0	-	2.2	4.1	-
4	6.4	4.4	-	6.4	4.5	-
5	4.3	2.8	-	4.3	2.3	-
6	2.3	4.8	-	2.5	5.0	-
7	6.3	3.2	5.3	6.8	3.7	5.2
8	11.2	5.3	9.6	11.0	5.4	9.3
9	9.2	4.6	7.8	9.7	5.1	7.6
10	10.1	6.1	13.0	10.1	5.8	13.2

## FT-IR Spectra

The FT-IR spectra and their tentative assignment for the prepared polyborate salts (1-10) are shown in Table 3. FT-IR

investigation of the compounds confirmed the formation of FT-IR polyborate salt. These data of compounds (1-10) have been assigned by comparison with assignment of Jun et al for related polyborate anions [11, 12].

Table 3: The FT-IR spectra of the selected wave numbers of the polyborate salts (1-10)

Comp.	$\nu(\text{O-H})$ $\nu(\text{N-H})$	$\nu$ (C-H)	$\nu_{\text{as}}$ $\text{B}_3\text{-O}$ (	$\delta$ B-O-H) (	$\nu_{\text{as}}$ $\text{B}_4\text{-O}$ (	$\nu_{\text{s}}$ $\text{B}_3\text{-O}$ (	$\nu_{\text{s}}$ $\text{B}_4\text{-O}$ (	$\gamma$ $\text{B}_3\text{-O}$ (
1	3384 s 3124 s	-	1435 s 1356 s	1249 s	1101s 1026 s	926 s	782 s	696 w
2	3379 s 3232 s	-	1437 s 1358 s	1195s	1092 s 1022 s	926 s 913 s	781s	694 m
3	3216 s 3167 s	-	1444 s	1194s	1103 s 1026 s	926 s 884 m	783 m	647 w
4	3390 s 3124 s	-	1436 s 1351 s	1243 s	1098 s 1024 s	922 m	781s	694 w
5	3346 s 3186 s	-	1348 s	1167 s	1089 s 1042 s	941s	775s	670 w
6	3379 s 3220 s	-	1437 s 1361 s	1195 s	1105 s 1027 s	926 s 884 m	783 s	650 m
7	3363s	2971w 2857w	1469 m 1359 s	1248 m	1118 s 1011s	956 s	854 s 808 s	696 w
8	3250s 3167s	2960w 2890w	1465 m 1363 m	1219 m	1042 s 1006 s	931 m	883 w 809 s	700 w
9	3268s	2975w 2855w	1356 s	1162 m	104 1s	953 s	886 w 857 s	694 m
10	3317 s 3271 s	2978w	1427 s 1350 s	1165 m	1072 m	933 w	856 s 810 s	702 m

## B<sup>11</sup>-NMR Spectra

Boron NMR spectra used boron trifluorid diethyl etherate (BF<sub>3</sub>.OEt<sub>2</sub>) as a reference to analyses borate compounds, showed singlet signal at (0 ppm), the spectra of borate compounds are characterized by the appearance of absorption packages at the site (1-20 ppm), The pentaborate compounds show three sinagls associated with an

equilibrium mixture at (~18 ppm) due to B(OH)<sub>3</sub> / B(OH)<sub>4</sub><sup>-</sup>, (~13 ppm) B<sub>3</sub>O<sub>3</sub>(OH)<sub>4</sub><sup>-</sup>, and at (~1.3 ppm) due to [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>-</sup> as in compounds (1,2,4,10), The hexaborate compounds are quantitatively different from the spectrum observed in the pentaborate compounds showing a single signal at (~16.0ppm) as in the compounds (5,7,9),

while compounds (3,6) which consisting of double borate salts Penta and triborates

which correspond to pentatborates [14, 15, 19]. As shown in the Table4.

Table 4: Values of  $^{11}\text{B}$ -NMR for polyborate compounds (1-10)

Comp.	$^{11}\text{B}$ -NMR
1	18.3, 13.4, 1.2
2	18.0, 13.0, 1.5
3	17.4, 13.4, 1.3
4	16.8, 13.3, 1.6
5	16.6
6	16.1, 13.3, 1.2
7	16.6
8	15.2
9	16.8
10	18.0, 12.5, 1.7

### $^{13}\text{C}$ -NMR, $^1\text{H}$ - NMR spectra

$^{13}\text{C}$ -NMR spectra of compound (7) shows singlate at 40 ppm due to carbon atom of the (-CH<sub>2</sub>-) group while  $^1\text{H}$ - NMR spectra shows

two signals [15] at 2.7 ppm refer to -CH<sub>2</sub>-methylene protons and at 4.7 ppm related to exchanging protons of BOH, NH<sub>2</sub>, H<sub>2</sub>O.

Table 5:  $^1\text{H}$ - NMR,  $^{13}\text{C}$ -NMR data for compound 7

Comp.	$^1\text{H}$ - NMR	$^{13}\text{C}$ -NMR
7	2.7 (t, 4H, CH <sub>2</sub> of en), 4.7(s, 10H, exchanging BOH/NH <sub>2</sub> / H <sub>2</sub> O)	40 (CH <sub>2</sub> groups of en)

### Physical Study

From the table 6 the values of  $K_a$  increase in aqueous medium with temperature elevation [20]. The values of  $K_a$  variation values of  $K_a$  for compound (8) are noticeably high this is due to the fact that (en) ethylene diamine ligands are stronger than both (NH<sub>3</sub>) and (1,2-diaminopropane) ligands. All values of  $K_a$  for the pentaborate compounds increase with the

rising temperature. The positive value of  $\Delta H^\circ$  due to the reaction is an endothermic reaction [20]. From variation change of free energy  $\Delta G^\circ$  which is calculated from  $\Delta G^\circ = -RT \ln K_a$  showed negative values of  $\Delta G^\circ$  which is more pronouncel in Pentaborate compound (8) referring to possibility ion-pair of formation among other compounds pentaborate (1, 2, 4, 10).

Table 6: Thermodynamic values  $\Delta G^\circ$  kJmol<sup>-1</sup>,  $\Delta S^\circ$  kJk<sup>-1</sup>mol<sup>-1</sup>,  $\Delta H^\circ$  kJmol<sup>-1</sup> and the values of the reaction constant  $K_a$  dm<sup>3</sup>mol<sup>-1</sup> obtained from the application of the Shedlovsky equation for compounds in aqueous solution at different temperatures

Comp.	$K_a$ dm <sup>3</sup> mol <sup>-1</sup>	$\Delta G^\circ$ kJmol <sup>-1</sup>	$\Delta S^\circ$ kJk <sup>-1</sup> mol <sup>-1</sup> $\times 10^3$	$\Delta H^\circ$ kJmol <sup>-1</sup>
1	670 1590 10625	2.4- 2.9- 3.5-	64.0 63.5 63.4	15.714
2	345 1514 3910	-3.2 -4.1 -4.8	50.2 51.5 52.1	11.000
4	748 3785 13600	-3.6 -4.6 -5.5	55.1 56.6 57.7	12.000
8	2875 10192 29141	-4.3 -5.2 -6.0	85.6 86.0 85.8	20.000
10	920 4910 13851	-3.7 -4.8 -5.5	55.4 57.3 57.7	12.000

The experimental constants data used for calculations are  $D$ , is the dielectric constant of medium at different temperature (10C°, 20C°, 30C° as following 83.832, 80.103, 76.516).  $\eta$ , the viscosity of medium (c.p) at different temperature (10C°, 20C°, 30C° were as following 1.3059, 1.0016, 0.7972 and density ( $\rho$ ) of medium were as a following 0.9997, 0.9982, 0.9956 g/cm<sup>3</sup>) the other variables were calculated by applying equations. Where  $a$ , the sum of crystallographic radii of the ions,  $d$ : is given by equation  $d = 1.183(M/\rho)^{1/3}$  to calculate  $R$  equation  $R = a + d$  was applied,  $R$ , The distance between the ions in ion-pair from

center to center. Then we extract values of  $W, A, B$  applying  $-\log f_{\pm}$ , after that we calculate  $\beta, \alpha, Z, S(Z)$  from stated equations. Then applied all values in equation (1) which represents the function of Shedlovsky. The heat of association enthalpy  $\Delta H^\circ$  was obtained from the slope of the plot  $\log K_a$  vs  $\frac{1}{T}$  the positive values of enthalpy  $\Delta H^\circ$  reveals that ion association processes are endothermic at all temperatures [21]. Molar conductivity limits increase linearly with rise in temperature. The entropy change  $\Delta S^\circ$  are calculated from the Gibbs Helmholtz equation  $\Delta S^\circ = \frac{(\Delta H - \Delta G)}{T}$ . [22, 24].

Table 7: Thermodynamic values  $\Delta G^\circ$  kJmol<sup>-1</sup>,  $\Delta S^\circ$  kJk<sup>-1</sup>mol<sup>-1</sup>,  $\Delta H^\circ$  kJmol<sup>-1</sup> and the values of the reaction constant  $K_a$  dm<sup>3</sup>mol<sup>-1</sup> obtained from the application of the Shedlovsky equation for compounds in aqueous solution at different temperatures

Comp.	$K_a$ dm <sup>3</sup> mol <sup>-1</sup>	$\Delta G^\circ$ kJmol <sup>-1</sup>	$\Delta S^\circ$ kJk <sup>-1</sup> mol <sup>-1</sup> × 10 <sup>3</sup>	$\Delta H^\circ$ kJmol <sup>-1</sup>
3	230	-2.9	49.1	11.000
	1358	-4.0	51.2	
	3400	-4.7	51.8	
6	115	-2.6	33.4	6.875
	623	-3.6	35.7	
	1700	-4.3	36.9	

From tables 7 variation free energy  $\Delta G^\circ$  which is calculated from  $\Delta G^\circ = -RT \ln K_a$  have negative values of  $\Delta G^\circ$  compound (3) is

superior in the possibility of formation in ion- pair other compound (6) due to the large size of the ion mercury compared to zinc ion [22].

Table 8: Thermodynamic values  $\Delta G^\circ$  kJmol<sup>-1</sup>,  $\Delta S^\circ$  kJk<sup>-1</sup>mol<sup>-1</sup>,  $\Delta H^\circ$  kJmol<sup>-1</sup> and the values of the reaction constant  $K_a$  dm<sup>3</sup>mol<sup>-1</sup> obtained from the application of the Shedlovsky equation for compounds in aqueous solution at different temperatures

Comp.	$K_a$ dm <sup>3</sup> mol <sup>-1</sup>	$\Delta G^\circ$ kJmol <sup>-1</sup>	$\Delta S^\circ$ kJk <sup>-1</sup> mol <sup>-1</sup> × 10 <sup>3</sup>	$\Delta H^\circ$ kJmol <sup>-1</sup>
5	149	2.2-	43.1	10.000
	662	-2.7	43.3	
	1190	-4.1	46.5	
7	525	-3.4	54.4	12.000
	1766	-4.2	55.2	
	4352	-4.9	55.8	
9	766	2.3-	52.2	12.500
	2385	-4.4	57.6	
	13600	-5.5	95.4	

From the table 8 Variation of values  $K_a$  for the hexaborate compounds increases with rise in temperature the values of  $K_a$  in increasing in compound (9). From variation free energy  $\Delta G^\circ$  which is calculated from  $\Delta G^\circ = -RT \ln K_a$  negative values of  $\Delta G^\circ$  is high in hexaborate compound (9) which were more possible in ion- pair formation from

other hexaborate compounds (5,7). From the above result it found the pentaborate compound is more possible formation in ion-pair from the other polyborate compound. Molar conductivity limits increasing linearly with increasing temperature as well the values of  $K_a$ . All reaction was endothermic which supported by the positive values  $\Delta H^\circ$  [25, 26, 27].

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