Mansoura Journal of Chemistry V. 39 (1) 2012

# THE ASSOCIATION AND FORMATION CONSTANTS FOR $NaBPh_4$ STOICHIOMETRIC COMPLEXES WITH 2-HYDROXYIMINO-3-(2'-HYDRAZONOPYRIDYL)-BUTANE (HL).

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Received: (26/ 4/ 2012)

## ABSTRACT

The association constant ,formation constants and Gibbs free energies are calculated from the conductometric titration curves of $NaBPh_4$ with 2-hydroxyimino-3-(2'-hydrazonopyridyl)-butane (HL) in absolute ethanol at different temperatures( 293.15 K , 298.15 K , 303.15 K and 308.15 K). On drawing the relation between molar conductance and the ratio of metal to ligand concentrations, different lines are obtained indicating the formation of 1:2 , 1:1 and 2:1 (M:L) stoichiometric complexes. The formation constants of different complexes in absolute ethanol follow the order: $K_f$ (2:1) › $K_f$ (1:1) >$K_f$ (1:2) for (M:L). As the temperature increases, the formation constants and association constants of different complexes increase. The enthalpy and the activation energies were also estimated and their values were also discussed.

**Key words:** Association constants; formation constants; Gibbs free energies; activation energies.

## INTRODUCTION

The long range ion – ion interactions due to screened columbic forces are the most important features of electrolyte in solutions. These act together with shorter – ranged forces between the solvent molecules and between the solvent molecules and ion. Electrical conductivity (EC) is a measure of solvent to conduct electric current and depends on: concentration of the ions, ligand and temperature in solutions. Current is

carried out by both cations and anions, but to different degree. Metal cations with $d^0$ noble gas electron configuration (alkali and alkaline earth) metal ions together with the inert molecular ions like tetraalkylammonium,-phosphonium,-arsonium , and trialkylsulfonium ions exhibit properties mainly determined by their charge and size **[Robison et al., (2002)]**. Solvation of such cations in protic and polar solvents is due to electrostatic ion-dipole and ion induced dipole interactions. Most alkali metals have many different applications. Sodium has a biological role; it is an essential nutrient that regulates blood volume, blood pressure, osmotic equilibrium and PH. Sodium tetraphenyl borate is commercially useful for various purposes. It may be included polymeric composition to impart electrical conductivity. It has been used to precipitate radio active cesium 137 impurities from waste water. Complexes of sodium, potassium and cesium with a range of cyclic polyethers have been synthesized using tetraphenyl borate as the counter ion. While some complexes are found to have similar metal co-ordination to compounds studied previously, the non co-ordination of the tetraphenyl borate anion enables new products to be obtained when reaction conditions are varied. Thus, the sandwich compound Na(benzo-15- crown-5)$_2$BPh$_4$ crystallizes in high yield when appropriate reactant ratios are empoyed, and dibenzo-30-crown-10 is found to co-ordinate either one or two sodium ions depending on the solvent conditions used **[Parsons et al., (1975)]**.

The aim of this work, is to evaluate of the non-covalent behavior of NaBPh$_4$ in presence of 2-hydroxyimino-3-(2'-hydrazonopyridyl)-butane (HL) in absolute ethanol solutions at different temperatures. These non-covalent interactions can help to analyze the role of salts influence in bodies and environment.

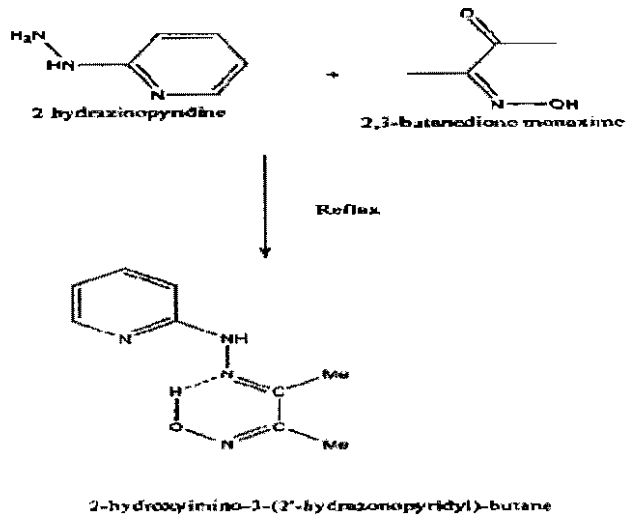
## EXPERIMENTAL

### Materials and Methods

All manipulations were performed under aerobic conditions. The Sodium tetraphenylborate and the used reagents were Merck pure.

**Preparation of Ligand**

2-hydroxyimino-3-(2'-hydrazonopyridyl)-butane (HL) (scheme 1) was prepared by boiling an EtOH solution of 2-hydrazino pyridine (Aldrich) with 2, 3-butanedione monoxime (1:1) under reflux. The product was recrystallized from hot absolute EtOH **[Kamal et al.,(1991)]**. (M.p: 220 °C; yield 80%). The purity of the compound was checked by TLC.




**Scheme. (1):** The outline of the synthesis of 2-hydroxyimino-3-(2'-hydrazonopyridyl)-butane (HL).

**Conductometric titration**

The conductometric titration of the $NaBPh_4$ ($1x10^{-4}$) mole/L against the ligand ($1x10^{-3}$) mole/L in absolute ethanol was performed with 0.2 ml interval additions from HL solution. The specific conductance values were recorded using conductivity bridge AdWa, AD 3000 with a cell constant equal to 1 $cm^{-1}$. The temperature was adjusted at 293.15 K, 298.15 K, 303.15 K and 308.15 K.

## RESULTS AND DISCUSSION

The specific conductance values ($K_s$) of different concentrations of $NaBPh_4$ in absolute ethanol were measured experimentally in absence

and in the presence of ligand at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

The molar conductance ($\Lambda_m$) values were calculated **[Gryzybkowski et al., (1980)]** using equation (1):

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \qquad (1)$$

Where $K_s$ and $K_{solv}$ are the specific conductance of the solution and the solvent, respectively ; $K_{cell}$ is the cell constant and C is the molar concentration of the $NaBPh_4$ solutions.
The limiting molar conductances ($\Lambda_M$) at infinite dilutions were estimated for $NaBPh_4$ in absolute ethanol alone at different temperatures by extrapolating the relation between $\Lambda_m$ and $C_m^{1/2}$ to zero concentration as shown in **Fig.(1)** .

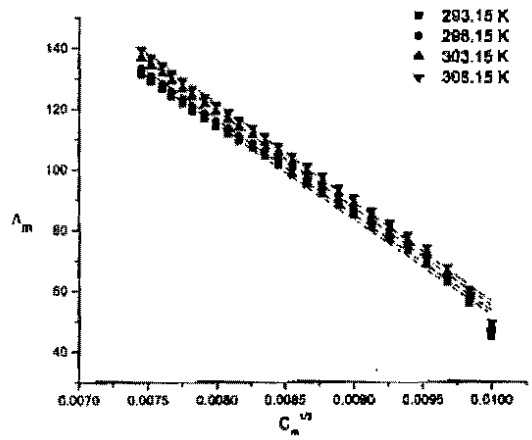



**Fig. (1):** The relation between molar conductance ($\Lambda_m$) and ($C_m^{1/2}$) of $NaBPh_4$ alone in absolute ethanol at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K).

The limiting molar conductances ($\Lambda_0$) at infinite dilutions were estimated for $NaBPh_4$ in the presence of the ligand (HL) by extrapolating the relation between $\Lambda_m$ and $C_m^{1/2}$ to zero concentration Fig. (2).

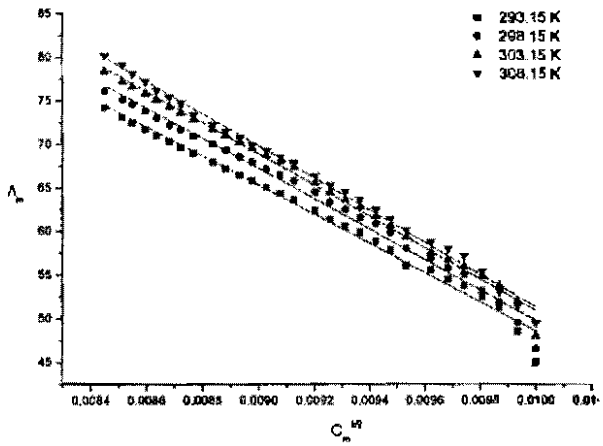



**Fig. (2):** The relation between molar conductance ($\Lambda_m$) and ($C_m^{1/2}$) of $NaBPh_4$ in presence of HL in absolute ethanol at different temperatures (293.15K, 298.15 K, 303.15 K and 308.15 K).

By drawing the relation between molar conductance ($\Lambda_m$) and the molar ratio of metal to ligand (M/L) concentrations **(fig. (3), (4), (5), (6))**, different lines are obtained with sharp breaks indicating the formation of 1:2, 1:1 and 2:1 (M:L) stoichiometric complexes.

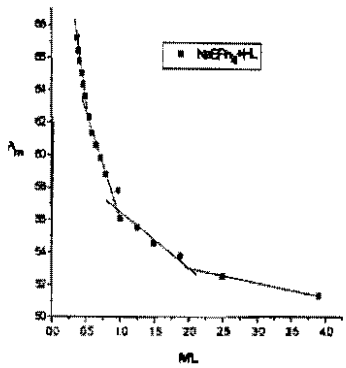


**Fig. (3):** The relation between $\Lambda_m$ and M/L at 293.15 K

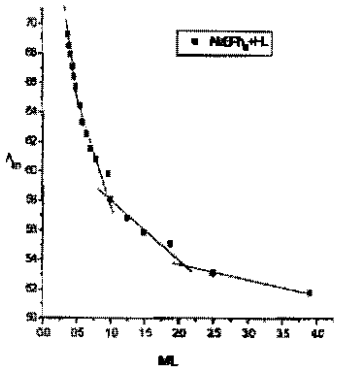


**Fig. (4):** The relation between $\Lambda_m$ and M/L at 298.15 K.

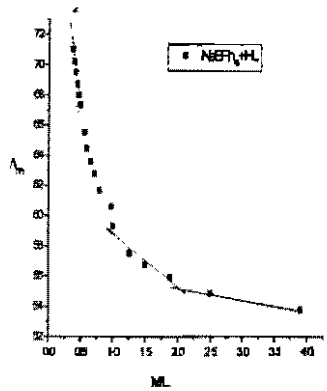


**Fig. (5):** The relation between $\Lambda_m$ and M/L at 303.15 K.

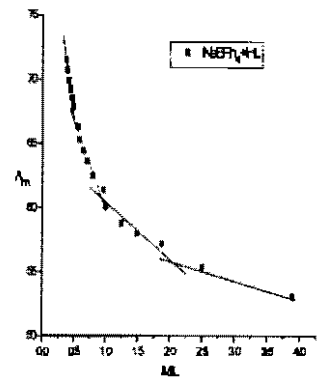


**Fig. (6):** The relation between $\Lambda_m$ and M/L at 308.15 K.

The experimental data of ($\Lambda_M$) and ($\Lambda_o$) were analyzed for the determination of association and formation constants for each type of the stoichiometric complexes.

The association constants of $NaBPh_4$ in the presence of ligand (HL) in absolute ethanol at different temperatures ( 293.15 K , 298.15 K , 303.15K and 308.15 K) for 2:1 ,1:1 and 1:2 (M:L) were calculated **[El-Shishtawi et al., (2010) and Hamada et al.,(2009)]** by using equation(2):

$$K_A = \frac{\Lambda_o (\Lambda_o - S(Z)\Lambda_m)}{C_m \Lambda_m^2 S(Z)^2 \gamma_\pm^2} \qquad (2)$$

Where ($\Lambda_m$, $\Lambda_0$) are the molar and limiting molar conductance of $NaBPh_4$ in presence of Hl respectively; $C_m$ is molar concentration of $NaBPh_4$ , S(Z) is Fuoss-shedlovsky factor, equal with unity for strong electrolytes **[Gomaa, (1987)]** ,$\gamma\pm$ is the mean activity coefficient. The calculated association constants are shown in **Table (1)**.

**Table (1):** Association constants ($K_A$) of NaBPh4 with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

| [M] (NaBPh4) | [ HL ] | $K_A$ | | | |
|---|---|---|---|---|---|
| | | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| $9.52x10^{-5}$ | $4.76x10^{-5}$ | $1.31x10^{5}$ | $1.35x10^{5}$ | $1.39x10^{5}$ | $1.39x10^{5}$ |
| $9.38x10^{-5}$ | $6.25x10^{-5}$ | $1.28x10^{5}$ | $1.32x10^{5}$ | $1.36x10^{5}$ | $1.36x10^{5}$ |
| $9.26x10^{-5}$ | $7.41x10^{-5}$ | $1.24x10^{5}$ | $1.29x10^{5}$ | $1.33x10^{5}$ | $1.34x10^{5}$ |
| $9.09x10^{-5}$ | $9.09x10^{-5}$ | $1.24x10^{5}$ | $1.25x10^{5}$ | $1.26x10^{5}$ | $1.29x10^{5}$ |
| $8.88x10^{-5}$ | $1.12x10^{-4}$ | $1.13x10^{5}$ | $1.14x10^{5}$ | $1.18x10^{5}$ | $1.21x10^{5}$ |
| $8.67x10^{-5}$ | $1.33x10^{-4}$ | $1.08x10^{5}$ | $1.10x10^{5}$ | $1.12x10^{5}$ | $1.15x10^{5}$ |
| $8.47x10^{-5}$ | $1.53x10^{-4}$ | $1.03x10^{5}$ | $1.04x10^{5}$ | $1.07x10^{5}$ | $1.10x10^{5}$ |
| $8.33x10^{-5}$ | $1.67x10^{-4}$ | $9.98x10^{4}$ | $1.01x10^{5}$ | $1.02x10^{5}$ | $1.06x10^{5}$ |
| $8.15x10^{-5}$ | $1.85x10^{-4}$ | $9.67x10^{4}$ | $9.81x10^{4}$ | $9.92x10^{4}$ | $1.03x10^{5}$ |
| $7.98x10^{-5}$ | $2.02x10^{-4}$ | $9.38x10^{4}$ | $9.53x10^{4}$ | $9.61x10^{4}$ | $9.99x10^{4}$ |

The Gibbs free energies of association ($\Delta G_A$) were calculated from the association constant **[Gomaa, (1988) and El-Doussoki, (2008)]** by applying equation (3):

$$\Delta G_A = - R T \ln K_A \qquad (3)$$

Where R is the gas constant (8.341 J) and T is the absolute temperature. The calculated Gibbs free energies were presented in **Table (2)**.

**Table (2):** Gibbs free energies of association $\Delta G_A$ (k J/mol) of NaBPh4 with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

| [M] (NaBPh4) | [HL] | $\Delta G_A$ | | | |
|---|---|---|---|---|---|
| | | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| $9.52x10^{-5}$ | $4.76x10^{-5}$ | -28.7184 | -29.2881 | -29.8407 | -30.3379 |
| $9.38x10^{-5}$ | $6.25x10^{-5}$ | -28.6604 | -29.2337 | -29.7442 | -30.2446 |
| $9.26x10^{-5}$ | $7.41x10^{-5}$ | -28.5877 | -29.1624 | -29.6057 | -30.1545 |
| $9.09x10^{-5}$ | $9.09x10^{-5}$ | -28.5801 | -29.0834 | -29.6057 | -30.1545 |
| $8.88x10^{-5}$ | $1.12x10^{-4}$ | -28.3586 | -28.8679 | -29.4324 | -29.9799 |
| $8.67x10^{-5}$ | $1.33x10^{-4}$ | -28.2451 | -28.7639 | -29.3088 | -29.8542 |
| $8.47x10^{-5}$ | $1.53x10^{-4}$ | -28.1340 | -28.6434 | -29.1879 | -29.7350 |
| $8.33x10^{-5}$ | $1.67x10^{-4}$ | -28.0547 | -28.5622 | -29.0635 | -29.6372 |
| $8.15x10^{-5}$ | $1.85x10^{-4}$ | -27.9786 | -28.4919 | -28.9968 | -29.5736 |
| $7.98x10^{-5}$ | $2.02x10^{-4}$ | -27.9030 | -28.4192 | -28.9172 | -29.4941 |

The formation constants ($K_f$) for $NaBPh_4$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) **[Takeda, (1983) and Rahmi-Nasrabadi et al., (2009)]** by using equation (4):

$$K_f = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (4)$$

Where $\Lambda_M$ is the limiting molar conductance of the $NaBPh_4$ alone, $\Lambda_{obs}$ is the molar conductance of solution during titration and $\Lambda_{ML}$ is the molar conductance of the complex.
The obtained values ($K_f$) for $NaBPh_4$-ligand stoichiometric complexes are presented in **Table (3)**.

**Table (3):** Formation constants ($K_f$) for 1:2, 1:1 and 2:1 (M/L) complexes in absolute ethanol at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

| Complex ratio (M/L) | Concentration | | Temperature | | | |
|---|---|---|---|---|---|---|
| | [M] ($NaBPh_4$) | [HL] | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| 1:2 | $8.33\times10^{-5}$ | $1.67\times10^{-4}$ | $2.25\times10^{7}$ | $2.26\times10^{7}$ | $2.31\times10^{7}$ | $2.45\times10^{7}$ |
| 1:1 | $9.09\times10^{-5}$ | $9.09\times10^{-5}$ | $6.79\times10^{7}$ | $6.81\times10^{7}$ | $6.97\times10^{7}$ | $7.09\times10^{7}$ |
| 2:1 | $9.52\times10^{-5}$ | $4.76\times10^{-5}$ | $7.68\times10^{7}$ | $8.01\times10^{7}$ | $8.41\times10^{7}$ | $8.54\times10^{7}$ |

The Gibbs free energies of formation for each stoichiometric complexes were calculated by using the equation:

$$\Delta G_f = - R\,T \ln K_f \qquad (5)$$

The calculated $\Delta G_f$ values are presented in **Table (4)**.

**Table (4):** Gibbs free energies of formation $\Delta G_f$ (kJ/mol) of NaBPh4 with HL at different temperatures (293.15 K, 298.15 K, 303.15 K and 308.15 K).

| Complex ratio (M/L) | Concentration | | Temperature | | | |
|---|---|---|---|---|---|---|
| | [M] ($NaBPh_4$) | [HL] | 293.15K | 298.15K | 303.15K | 308.15 K |
| 1:2 | $8.33\times10^{5}$ | $1.67\times10^{-4}$ | -41.2632 | -42.6771 | -42.7369 | -43.5857 |
| 1:1 | $9.09\times10^{-5}$ | $9.09\times10^{-5}$ | -43.9516 | -44.7082 | -45.5191 | -46.3127 |
| 2:1 | $9.52\times10^{-5}$ | $4.76\times10^{-5}$ | -44.2540 | -45.1105 | -45.9921 | -46.7893 |

The enthalpy ($\Delta H_A$) for $NaBPh_4$ complexes were calculated for each type of complexes (1:2) , (1:1) and (2:1) (M:L) by using van 't Hoff equation **[Atkins, (1978) and Ives, (1971)]:**

$$d\ln k / dT = \Delta H / RT^2 \qquad (6)$$

Where *R* is the gas constant (8.341 J) and T is the absolute temperature. By drawing the relation between log $K_A$ and 1/T, different lines are obtained indicating the formation of 1:2,1:1 and 2:1 (M:L) stoichiometric complexes **Fig.**(7).

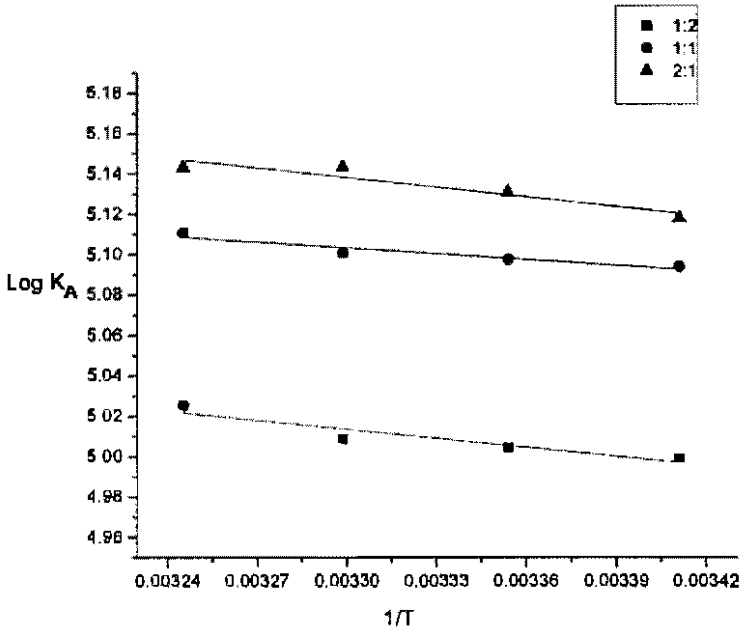



**Fig.** (7): The relation between (log $K_A$) and (1/T).

From the relation between log K and 1/T, $\Delta H_A$ can be calculated for each type of complexes from the slope of each line (-$\Delta H$/2.303R).The entropy ($\Delta S_A$) for $NaBPh_4$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M: L) by using equation (7):

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

Where (S) is the entropy of system.

The calculated values of ($\Delta H_A$) and ($\Delta S_A$) for $NaBPh_4$-ligand stoichiometric complexes are presented in **Table (5).**

**Table (5):** The enthalpies ($\Delta H_A$) (kJ/mol) and entropies ($\Delta S_A$) (J/mol.K) of association for different complexes.

| **Complex ratio** | | **1 : 2 (M/L)** | | |
|---|---|---|---|---|
| **Temp** | **293.15 K** | **298.15 K** | **303.15 K** | **308.15 K** |
| $\Delta H_A$ | 2.8508 | 2.8508 | 2.8508 | 2.8508 |
| $\Delta S_A$ | 105.40 | 105.40 | 105.30 | 105.4 |
| **Complex ratio** | | **1 : 1 (M/L)** | | |
| **Temp** | **293.15 K** | **298.15 K** | **303.15 K** | **308.15 K** |
| $\Delta H_A$ | 1.8934 | 1.8934 | 1.8934 | 1.8934 |
| $\Delta S_A$ | 104.00 | 103.90 | 103.90 | 104.00 |
| **Complex ratio** | | **2 : 1 (M/L)** | | |
| **Temp** | **293.15 K** | **298.15 K** | **303.15 K** | **308.15 K** |
| $\Delta H_A$ | 3.1247 | 3.1247 | 3.1247 | 3.1247 |
| $\Delta S_A$ | 108.60 | 108.70 | 108.70 | 108.60 |

By drawing the relation between log $K_f$ and 1/T, different lines are obtained indicating the formation of 1:2,1:1 and 2:1 (M:L) stoichiometric complexes **Fig.(8).**

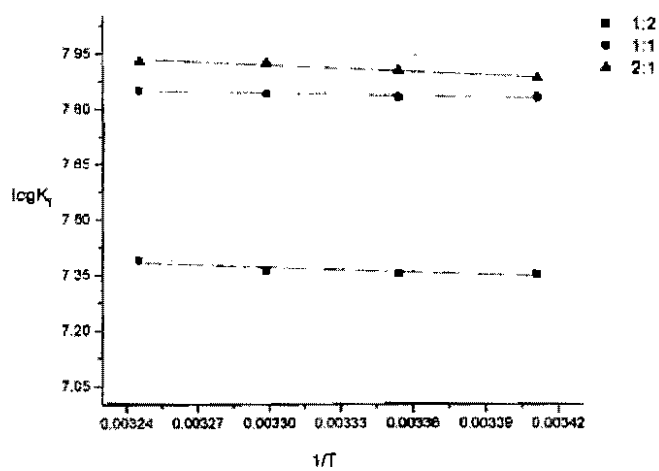



**Fig. (8):** The relation between (log $K_f$) and (1/T).

The enthalpy ($\Delta H_f$) for $NaBPh_4$ complexes were calculated for each type of complexes (1:2), (1:1) and (2:1) (M:L) by using van't Hoff equation.
The calculated values of ($\Delta H_f$) and ($\Delta S_f$) for $NaBPh_4$-ligand stoichiometric complexes are presented in **Table (6)**.

**Table (6):** The enthalpies $\Delta H_f$ (kJ/mol) and entropies ($\Delta S_f$) (J/mol.K) of formation for different complexes.

| Complex ratio | | 1 : 2 (M/L) | | |
|---|---|---|---|---|
| Temp | 293.15K | 298.15 K | 303.15 K | 308.15 K |
| $\Delta H_f$ | 4.1390 | 4.1390 | 4.1390 | 4.1390 |
| $\Delta S_f$ | 154.80 | 157.00 | 154.60 | 154.80 |
| Complex ratio | | 1 : 1 (M/L) | | |
| Temp | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| $\Delta H_f$ | 2.2974 | 2.2974 | 2.2974 | 2.2974 |
| $\Delta S_f$ | 157.70 | 157.60 | 157.70 | 157.70 |
| Complex ratio | | 2 : 1 (M/L) | | |
| Temp | 293.15 K | 298.15 K | 303.15 K | 308.15 K |
| $\Delta H_f$ | 5.5283 | 5.5283 | 5.5283 | 5.5283 |
| $\Delta S_f$ | 169.80 | 169.80 | 169.90 | 169.70 |

The activation energy (Ea) is estimated for $NaBPh_4$ in absolute ethanol alone and in the presence of the ligand (HL) by using Arrhenius equation (8) **[Cox, (1994)]**:

$$k = Ae^{-E_a/RT} \qquad (8)$$

Where $A$ is the pre-exponential factor or simply the *prefactor* and $R$ is the Universal gas constant.

Activation energy in absence of HL can be calculated from the plot of log $\Lambda_M$ and 1/T as shown in **Fig. (9)**, it gives a straight line with a slope (-Ea/2.303R).Activation energy is found to be 2.5116 kJ/mol.

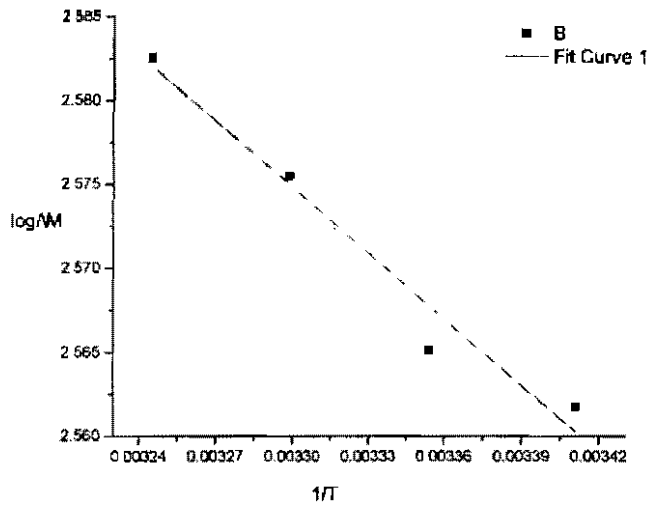



**Fig. (9):** The relation between log $\Lambda_M$ and 1/T.

Activation energy in presence of HL can be calculated from the relation between log $\Lambda_o$ and 1/T as shown in **fig. (10)** .from the slope (-Ea/2.303R), Activation energy is found to be 4.4377 kJ/mol.

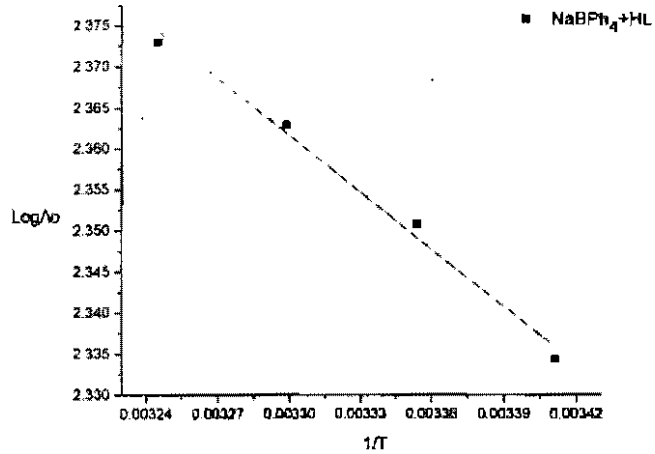



**Fig. (10):** The relation between log $\Lambda_o$ and 1/T.

## CONCLUSION

The association free energies evaluated for $NaBPh_4$-ligand complexes indicating a spontaneous electrostatic attraction.
The formation constants and Gibbs free energies of different complexes in absolute ethanol at different Temperatures (293.15 K, 298.15 K , 303.15 k and 308.15 K) follow the order: $K_f$ (2:1) › $K_f$ (1:1) >$K_f$ (1:2) for (M:L), and $\Delta G_f$(2:1) › $\Delta G_f$(1:1) > $\Delta G_f$ (1:2) for (M:L).

The formation of 1:2, 1:1 and 1:2 (M:L) complexes indicate that (HL) may act as flexidentate ligand.

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## ثوابت التجمع و ثوابت تكوين متراكبات لصوديوم رباعى فينيل البورات مع ٢-هيدروكسى أمينو - ٣- (٢-هيدرازونوبيريدل) بيوتان

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استنتج ثوابت التجمع ، ثوابت التكوين ، الطاقات الحرة و طاقات التنشيط لتفاعل صوديوم رباعى فينيل البورات مع ٢- هيدروكسى أمينو - ٣- (٢-هيدرازونوبيريدل)-بيوتان من القياسات التوصيليةعند درجات حرارة مختلفة و هى ٢٩٣،١٥،٢٩٨،١٥، ٣٠٣،١٥ و٣٠٨،١٥ درجة مطلقة فى الكحول الأيثيلى . عند رسم العلاقة بين التوصيل الجزيئى ونسبة الفلز الى الليجند حصلنا على خطوط مختلفة تدل على تكوين متراكبات بنسبة ٢:١ ، ١:١ و١:٢ (فلز:ليجند) حسبت ثوابت التجمع و التكوين لهذه المتراكبات ووجدت انها تتبع الترتيب : ١:٢<١:١ < ٢:١ (فلز: ليجند). كذلك حسبت الأنثالبى و طاقات التنشيط للتفاعل بين الفلز و الليجند و وجدت أن جميع معاملات الديناميكا الحرارية تزداد بزيادة درجة الحرارة.