*Tikrit Journal of Pure Science 17 (4) 2012* **ISSN: 1813 - 1662**

# Electrochemical Behaviour of Benzylidene acetophenone and Its Derivatives in methanol at 298.16K

**Laith Waad Allah Abd Allah**

*Dept. Of pharm chem. , College of pharmacy. , Uni. of Tikrit , Tikrit , Iraq*

(**Received:** 15 / 5 / 2011 ---- **Accepted:** 27 / 9 / 2011)

## Abstract

Molar conductance (Λ) of an aqueous solution of benzylidene acetophenone and its derivatives has been determined through accurate conductance measurements. The obtained data were analyzed in accordance to Lee-Wheaton equation taking into account the activity of the electrolyte in the solution. The conductance measurement results were used to determine the association constants ($K_A$) of ion-pairs, the main distance between ions in solution (R), in addition to the molar conductance at infinite dilution ($\Lambda_O$) for the free ion in solution at the best fit value of (σΛ).

Keyword: Benzylidene acetophenone, conductivity, Lee Wheaton equation. Association constant.

## Introduction

The possible importance of such properties as solubility , partition coefficients , surface activity , degree of dissociation of the pH at the body fluid ,interatomic distances between functional groups, redox potential (reduction-oxidation),hydrogen bonding, dimensional factor chelation and the spatial configuration of the molecule are worthy of consideration$^{(1)}$ .

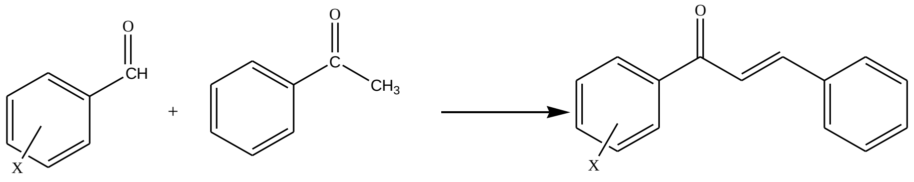
A classic electro analytical technique that finds application in a variety of chemical and biochemical studies is a measurement of solution conductance. For example determination of ionic strengths of solutions, monitor dissolution kinetics and the approach to equilibrium for partially soluble salts , determine critical micelle concentration , follow the course of some enzymatic reaction , as well as to provide basic thermodynamic data of other electrolyte solution from association constant.$^{(2)}$ The conductivity of the complex of (8-hydroxyquinoline) with some transition and alkaline earth metals in methanol were measured, Lee-Wheaton conductance equation was used to analyze the experimental data, and it was found that this equation is very applicable for such type of complexes$^{(3)}$ .The electrical conductivity of the water solutions of o-benzenedisulfonate, m-benzenedisulfonate, 2,6-naphthalenedisulfonate with $[Fe(phen)_3]^{2+}$ was measured at temperatures from 0 °C to 50 °C, to obtain the detailed thermodynamic information of the ion association and examine the nature of the interkaction in these solutions.$^{(4)}$ The electrical conductivity of (Tetracycline,Genlamycine, and stretomycine) complexes with (Ca,Mg,and Fe) have been studred to determine the association constant $K_A$, equivalent conductance($\Lambda_O$) at infinit dilution and the distance parameter R at best fit values of (σΛ) which give agood information abouth the interaction in solution.$^{(5)}$ Measurements of the electrical conductivity of the compounds 2-(2,4-dichlorophenoxy methyl-5-(3-chlorophenyl)-1,3,4-oxadiazole and 2,5-di(2,4-dichlorophenoxy methyl)-1,3,4-oxadiazole in mixture of methanol water as a solvent at different percentages were analyzed by using Lee-Wheaton equation, the values of $\Lambda_o$, $K_A$ and R are calculated$^{(5)}$.

## Experimental

All chemicals were obtained from the usual commercial suppliers and used without further purification. Melting points were measured on electro thermal melting point apparatus 9300 and were uncorrected. The IR spectra (using KBr disc) were recorded with Shimatzu FT/IR spectrophotometer. UV-Visible spectra were measured for ethanolic solutions (25°C) with Zeius PMQ II manual spectrophotometer using matched 10 mm fused silica cells . Conductivity measurements were performed using Jenawy PCM3 conduct meter.

### General procedure for preparation of substituted Benzylidene acetophenone:

To a solution of substituted aldehyeds(0.01 mol) in ethanol (25 mL), a solution of NaOH(6 mL,40%) was added. The reaction mixture was stirred at room temp for a period of 24h, diluted with water (100 mL) and acidified with dil.HCl. The product obtained was filtered, washed with water, and recrystallized from ethanol $^{(6)}$.



X=1-H,2-P-Cl,3-P-NO2,4-m-NO2,5-P-CH3O,6-P-Br,7-P-CH3

**Table(1): Physical properties of substituted benzylidene acetopheneone**

| No. | Name of compound | m.p(C°) | Wt(gm) | colour | % |
|---|---|---|---|---|---|
| 1 | benzylidene acetopheneone | 55-58 | 5.3 | Yellow faint | 60 |
| 2 | p-chloro benzylidene acetopheneone | 102-106 | 7.00 | Greenish-yellow | 63.6 |
| 3 | p-nitro benzylidene acetopheneone | 161-165 | 3.2 | Yellow deep | 64 |
| 4 | m-nitro benzylidene acetopheneone | 143-146 | 4.7 | Green faint | 60 |
| 5 | p-methoxy benzylidene acetopheneone | 72-75 | 4.5 | Green faint | 68 |
| 6 | p-bromo benzylidene acetopheneone | 121-124 | 1.9 | Green faint | 58.5 |
| 7 | p-methyl benzylidene acetopheneone | 95-97 | 3.6 | Green faint | 70 |

**Table (2) : Spectral data of substituted benzylidene acetophenone**

| No. | C=O | C=C | C=C $_{arom}$ | Others |
|---|---|---|---|---|
| 1 | 1663 | 1606 | 1573 | |
| 2 | 1659 | 1595 | 1565 | C-cl=631 |
| 3 | 1658 | 1595 | 1560 | $NO_2$asmy=1514<br>$NO_2$smy=1335 |
| 4 | 1660 | 1607 | 1555 | $NO_2$asmy=1528<br>$NO_2$smy=1349 |
| 5 | 1656 | 1595 | 1512 | C-O-C=1215 |
| 6 | 1657 | 1604 | 1545 | C-Br=550 |
| 7 | 1664 | 1605 | 1490 | |

## Conductivity measurements

The conductivity water was prepared by distilling the water twice to give conductivity water of specific conductance $2 \times 10^{-6}$ μs. The cell constant for the conductive cell was measured according to method of Jones and Bradsaw(7) (Jones and Bradsaw, 1933), by using standar solution from( 0.01 M) KCl solution (BDH reagent ), and it was checked regularly and found to be 1.14cm$^{-1}$. General methods have been used for measuring the conductivity of the electrolytes; the conductivity cell was washed with conductive water, methanol, and dried. The empty cell was weighed, then placed in a thermostated water bath type Haake NK22, with temperature deviation was not greater than ±0.1 °C. A known amount of deionized water (25 ml) was placed in the cell and the conductivity of the solvent (water) was measured whereupon the cell plus contents, a solution of $10^{-3}$ M (0.5ml) was injected into the conductivity cell by a syringe and the conductivity was measured. The measurement was repeated after each addition of 0.5 ml of $10^{-3}$ M of the solution till twelve additions. (8)

## Result and discussion

A series of benzylidene acetophenone (I-VII) were prepared and used to estimate their conductivity. These compounds were prepared from the reaction of benzaldehyde with acetophenone. The structure of these compounds was assigned based on their I.R..UV spectral data.

The measurements of the conductivity of compounds were carried out for their aqueous solutions at room temperature.

The values of the molar conductance (Λ) in deferent concentration of the substituted benzylidene aetophenone (I-VII) were given in Table (1) (A-G). The conductance data obtained in this work were first analyzed in accordance with Lee-Wheaton equation. The correlation between the concentration of the aqueous solution of these compounds and their molar conductance are shown in Fig. (1) (A-G) and they behaves as a weak electrolytes, according to Kaloraoush equation. The oppositely charged ions tend to form ion-pairs in the medium of low relative permitivity.At constant temperature the concentration of free ions (Cα) and ion-pairs C(1- α) are at equilibrium. This state is described by the thermodynamic equilibrium (K) for the ion-association reaction. Since the ion pairs are non-conducting entities, and the degree of their dissociation (α) can be given by the ratio between the molar conductivity of the electrolyte (Λ) and the free ion (Λ-Cα), Then the combination of the expressions for K and α can be given as :

$$\Lambda = \frac{(\Lambda - C\alpha)}{1+K(C/C^{\circ})\,\alpha\, y^{2}\pm} \quad \text{-----}\ (1)$$

Where $^{\circ}C = 1$ mole dm$^{-3}$ , y± is the main activity coefficient which can be obtained from equation 2

$$y\pm = \exp\frac{Kq}{1+KR} \quad \text{------}\ (2)$$

referring to the dissociated part of the electrolyte ,R is the distance parameter which must be the least distance that two free ions can approach before they merge into an ion-pair, or in other words , its the furthest distance that separates two ions. The parameters K and q can be obtained from equation 3 and 4 respectively.

$$K^2 = 16000\,\pi\, N_A\, qC\alpha \qquad \text{----------}\ (3)$$

$$q = \frac{e^2}{8\,\pi\,\varepsilon_\circ\ \varepsilon_r\, KT} \qquad \text{----}\ (4)$$

If it is assumed that the dissociated part of the weak electrolyte acts like a completely hypothetical dissociated strong electrolyte of the same type, $\Lambda_{C\alpha}$ can be replaced by any theoretical equation for conductivity in order to make a conductivity model, which was founded to be the Lee-Wheaton equation (5).

$$\Lambda_{c\alpha} = \Lambda_\circ\,[1+C_1(KR)(\varepsilon K) + C_2(KR)(\varepsilon K)^2 + C_3(KR)(\varepsilon K)^3] - (\rho K)/(1+KR)[\,1+C_4(KR)(\varepsilon K) + C_5(KR)(\varepsilon K)^2 + (KR)/12] \ \text{-------}(5)$$

where the concentration dependent terms are both the plasma parameter (εK) and (KR), while the concentration coefficients ε, K and $\rho$ can be obtained from equation 6-8 respectively .

$$\varepsilon = |Z\acute{i}|^2 e^2 / DKT \quad \text{----------}(6)$$

$$K^2 = 8\,\pi\, Ne^2\ |Z\acute{i}|^2\, C/1000\ DKT \ \text{------------}(7)$$

$$\rho = F\,\zeta\, e\ |Z|\ / 3\,\pi\,\eta \quad \text{----------}(8)$$

Where F is the Faraday constant (9.6486 x $10^4$) , ζ is the a conversion factor (volt $\longrightarrow$ e.s.u.)=1/299.7925, and all other terms have previously been defined in details Lee Wheaton, 1978) $^{(9)}$.

**Table(3) A: The measurement of equivalent conductivity of benzylidene acetophenone**

| **Λ (ohm$^{-1}$.equiv$^{-1}$.cm$^2$)** | **$\sqrt{conc.}\times 10^2$** | **$10^5$ × Conc (mole/L)** |
|---|---|---|
| 44.2 | 0.006202 | 3.8461 |
| 33.6 | 0.007524 | 5.6603 |
| 25.7 | 0.008607 | 7.4074 |
| 22.0 | 0.009535 | 9.0909 |
| 19.6 | 0.010351 | 10.7142 |
| 18.4 | 0.011082 | 12.2807 |
| 17.4 | 0.011744 | 13.7931 |
| 16.6 | 0. 012351 | 15.2542 |
| 16.5 | 0.01291 | 16.6666 |
| 16.0 | 0.013429 | 18.0327 |
| 15.8 | 0.013912 | 19.3548 |
| 15.5 | 0.014365 | 20.6349 |
| 15.3 | 0.01479 | 21.875 |
| 15.1 | 0.015191 | 23.0769 |

**Table (3) B: The measurement of equivalent conductivity of Para chloro benzylidene acetophenone**

| **Λ (ohm$^{-1}$.equiv$^{-1}$.cm$^2$)** | **$\sqrt{conc.}\times 10^2$** | **$10^5$ ×Conc (mole/L)** |
|---|---|---|
| 15.8 | 0.010351 | 10.7142 |
| 13.8 | 0.011082 | 12.2807 |
| 13.0 | 0.011744 | 13.7931 |
| 12.4 | 0.012351 | 15.2542 |
| 12.0 | 0.01291 | 16.6666 |
| 11.6 | 0.013429 | 18.0327 |
| 10.8 | 0.013912 | 19.3548 |
| 10.6 | 0.014365 | 20.6349 |
| 10.5 | 0.01479 | 21.875 |
| 9.9 | 0.015191 | 23.0769 |

**Table (3) C: The measurement of equivalent conductivity of Para nitro benzylidene acetophenone**

| Λ **($ohm^{-1}.equiv^{-1}.cm^{2}$)** | $\sqrt{conc.}\times 10^{2}$ | **$10^{5}$ × Conc (mole/L)** |
|---|---|---|
| 98.99 | 0.008607 | 7.4074 |
| 93.33 | 0.009535 | 9.0909 |
| 89.57 | 0.010351 | 10.7142 |
| 87.0 | 0.011082 | 12.2807 |
| 85.22 | 0.011744 | 13.7931 |
| 83.99 | 0.012351 | 15.2542 |
| 83.18 | 0.01291 | 16.6666 |
| 82.45 | 0.013429 | 18.0327 |
| 81.34 | 0.013912 | 19.3548 |
| 80.8 | 0.014365 | 20.6349 |
| 67.99 | 0.01479 | 21.875 |
| 65.36 | 0.015191 | 23.0769 |

**Table (3) D: The measurement of equivalent conductivity of meta nitro benzylidene acetophenone**

| Λ **($ohm^{-1}.equiv^{-1}.cm^{2}$)** | $\sqrt{conc.}\times 10^{2}$ | **$10^{5}$ × Conc (mole/L)** |
|---|---|---|
| 54.94 | 0.008607 | 7.4074 |
| 48.85 | 0.009535 | 9.0909 |
| 46.66 | 0.010351 | 10.7142 |
| 45.3 | 0.011082 | 12.2807 |
| 43.67 | 0.011744 | 13.7931 |
| 42.3 | 0.012351 | 15.2542 |
| 41.99 | 0.01291 | 16.6666 |
| 40.36 | 0.013429 | 18.0327 |

**Table (3) E: The measurement of equivalent conductivity of para methoxy benzylidene acetophenone.**

| Λ **($ohm^{-1}.equiv^{-1}.cm^{2}$)** | $\sqrt{conc.}\times 10^{2}$ | **10 × Conc (mole/L)** |
|---|---|---|
| 67.49 | 0.008607 | 7.4074 |
| 65.33 | 0.009535 | 9.0909 |
| 58.0 | 0.010351 | 10.7142 |
| 52.44 | 0.011082 | 12.2807 |
| 48.0 | 0.011744 | 13.7931 |
| 46.49 | 0.012351 | 15.2542 |
| 43.61 | 0.01291 | 16.6666 |
| 41.67 | 0.013429 | 18.0327 |
| 41.1 | 0.013912 | 19.3548 |
| 39.94 | 0.014365 | 20.6349 |
| 39.41 | 0.01479 | 21.875 |
| 38.5 | 0.015191 | 23.0769 |

**Table (3) F: The measurement of equivalent conductivity of Para bromo benzylidene acetophenone.**

| **$\Lambda$ ($ohm^{-1}.equiv^{-1}.cm^{2}$)** | **$\sqrt{conc.} \times 10^{2}$** | **$10^{5} \times$ Conc (mole/L)** |
|---|---|---|
| 94.5 | 0.008607 | 7.4074 |
| 88.0 | 0.009535 | 9.0909 |
| 81.0 | 0.010351 | 10.7142 |
| 72.5 | 0.011082 | 12.2807 |
| 66.0 | 0.011744 | 13.7931 |
| 61.0 | 0.012351 | 15.2542 |
| 58.1 | 0.01291 | 16.6666 |
| 56.7 | 0.013429 | 18.0327 |
| 55.1 | 0.013912 | 19.3548 |
| 52.8 | 0.014365 | 20.6349 |
| 52.5 | 0.01479 | 21.9000 |

**Table (3) G: The measurement of equivalent conductivity of Para methyl benzylidene acetophenone.**

| **$\Lambda$ ($ohm^{-1}.equiv^{-1}.cm^{2}$)** | **$\sqrt{conc.} \times 10^{2}$** | **$10^{5} \times$ Conc (mole/L)** |
|---|---|---|
| 88.0 | 0.008607 | 7.4074 |
| 84.0 | 0.009535 | 9.0909 |
| 81.4 | 0.010351 | 10.7142 |
| 79.7 | 0.011082 | 12.2807 |
| 78.0 | 0.011744 | 13.7931 |
| 76.0 | 0.012351 | 15.2542 |
| 74.0 | 0.01291 | 16.6666 |
| 72.3 | 0.013429 | 18.0327 |
| 72.0 | 0.013912 | 19.3548 |
| 71.7 | 0.014365 | 20.6349 |
| 71.0 | 0.01479 | 23.0769 |

**Table (4): The result of analysis of derivatives benzylidene acetophenone.**

| **Compount** | **$R \times 10^{-8}$** | **KA** | **$\Lambda^{o}$** | **$\sigma\Lambda$** |
|---|---|---|---|---|
| unsubstituted | 9.0 | 9802 | 53.27 | 0.003 |
| p- methoxy | 10 | 7477 | 143 | 0.003 |
| p- methyl | 9.5 | 4416 | 111.5 | 0.001 |
| p- chloro | 14 | 30897 | 105 | 0.004 |
| P- Bromo | 13 | 29679 | 115 | 0.005 |
| m- nitro | 10 | 12162 | 82.23 | 0.0015 |
| p- nitro | 10 | 5429 | 128.27 | 0.001 |

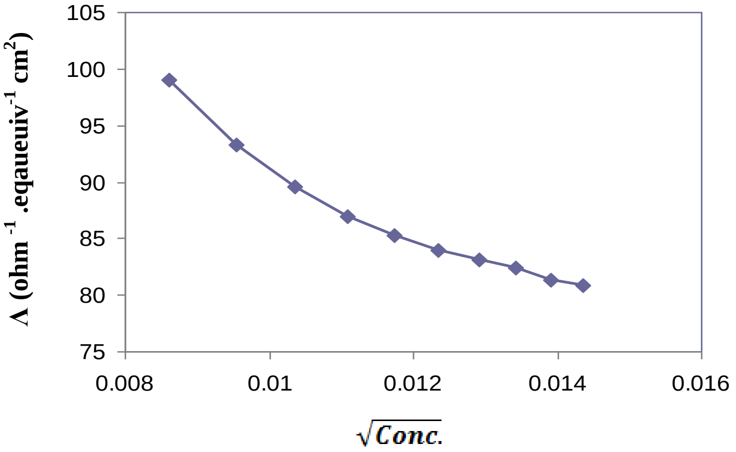


**Figure (1) A:-** **The relation between the square root of conc. Against the equivalent conductance of benzylidene acetophenone.**

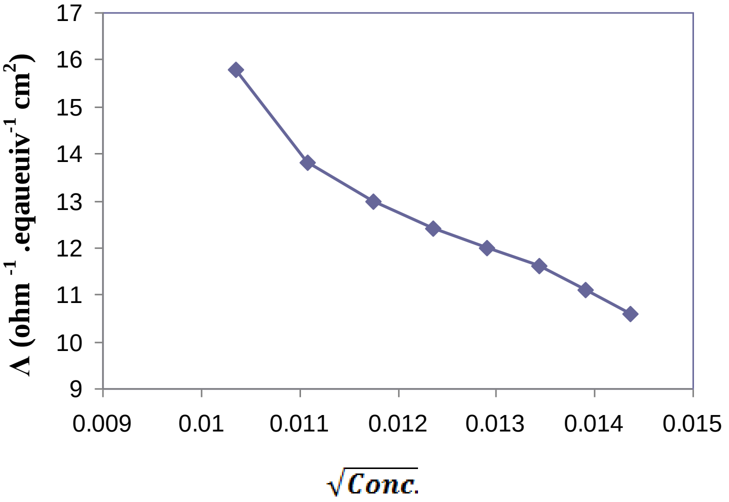


**Figure (1) B:-** **The relation between the square root of conc. Against the equivalent conductance of Para chloro benzylidene acetophenone.**

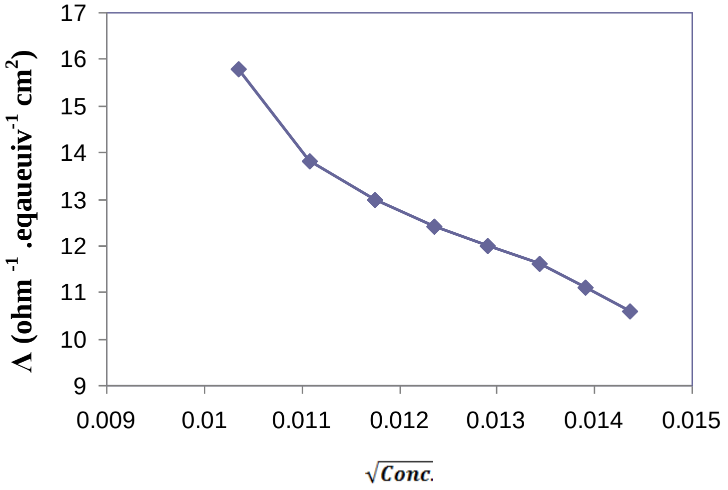


**Figure (1)C :-** **The relation between the square root of conc. Against the equivalent conductance para nitro benzylidene acetophenone.**

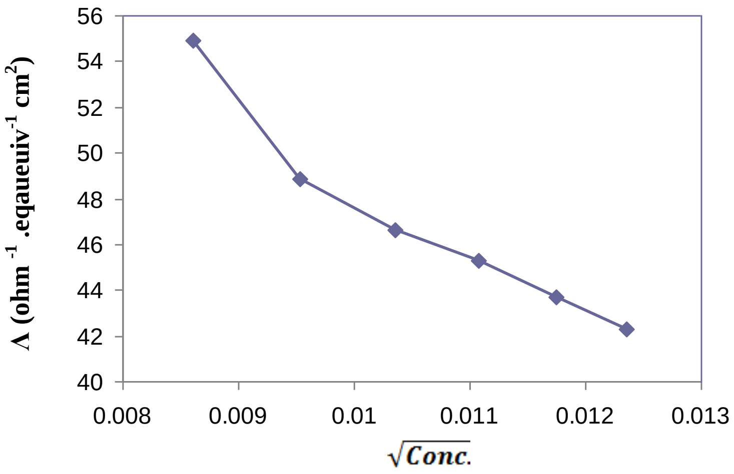


**Figure (1) D:-** **The relation between the square root of conc. Against the equivalent conductance of meta nitro benzylidene acetophenone.**

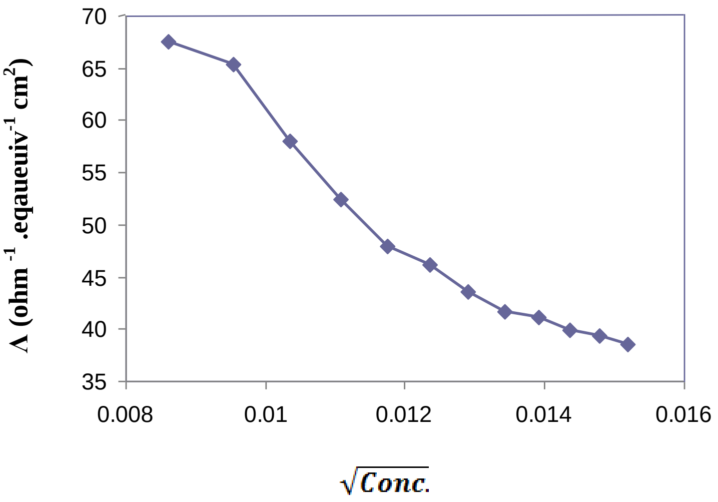


**Figure (1)E :-** **The relation between the square root of conc. Against the equivalent conductance para methoxy benzylidene acetophenone.**

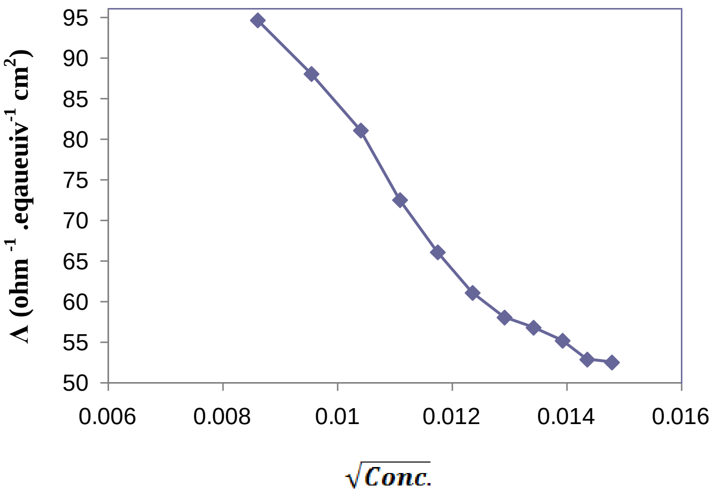


**Figure (1)F :-** **The relation between the square root of conc. Against the equivalent conductance para bromo benzylidene acetophenone.**

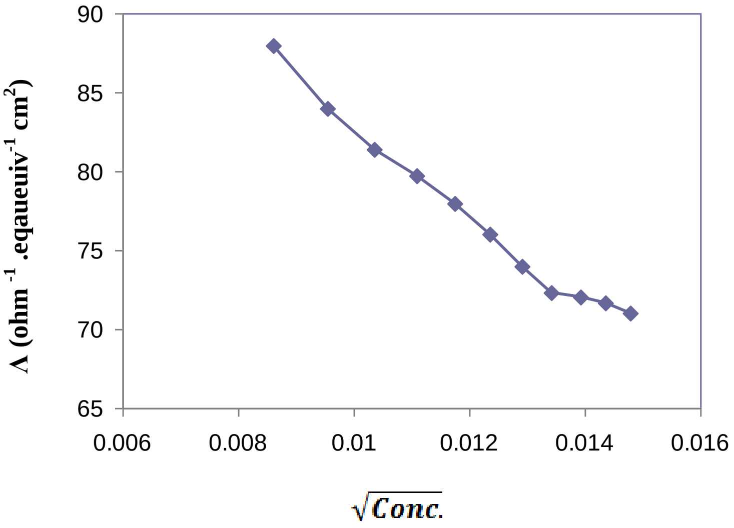


**Figure (1)G :- The relation between the square root of conc. Against the equivalent conductance Para methyl benzylidene acetophenone.**

The value of $K_A$, $\Lambda_o$, R of the aqueous solution the compounds (I-VII) at 298.16K were shown in Table 2. Close inspection of this table shows that all values of $K_A$ follow the sequence p-Cl, p-Br >m-Nitro > unsubstituted >
p-methoxy > p-Nitro > p-methyl. This diversity of the values of $K_A$ may be attributed to the short range interaction and the H-bonding that formed (Yokoyama, H.,1992)(3).

The differences in the $K_A$ values with respect to the above substituent's are explicable in terms of their abilities to form hydrogen bonding and ion-solvent interaction, in addition to their electron donating and with -drawing abilities, since the increase in donor properties of the substituent's will lead to the decrease of association and vice versa. The electrons drawing ability of any group, result in delocalization of the electron density between the substituent's and rest the molecule and accordingly enhances the polarizability of the molecule, giving rise for more association to take place.

## Conclusion:

in this study we went to determine the conductivity behavior of the compound understudy to determine their association constant , equivalent conductance of infinite dilution and the main distance parameters between two solvated ion in solation which gives arecel indication about ion - ion and ion - solvent interaction in solution and to study the behavior of each compound to know the difference in behavior from one to another because of their difference in substitution at room temperature and to examine thier conductivity which is known as weak electrolytes and to apply the Lee - Wheaton equation which is the best equation and modern once in determination of the physical constants (KA, $\Lambda^o$ ,R) of the compound under study.

## References

1- Coury .L. " Biochemistry System " Inc., Coury bioanalytical, **1999**.

2- Wilson and Gisvolds "Text book of organic Medicinal and Pharmaceutical chemistry Twelfth edition **2011 p12**.

3- Akrawi, B.-A.; Sarsem, L.-A. Raf. J. Soc, **2001**, 12, (2), 17.

4- Yokoyama H.; Ohta T.; Iida M. Bull. Chem. Soc. Jp. **1992,** 65, 2901

5- Y.O.AL-ALLaf,R.T. Homeed, H.A. AL -Tai study the biological activity of some antibiotics and their complexes, with som metals Tikrit Journal of pharmaceutical science 2009,5(1): pp 33 -43.

6-B.A. Akrawi , Raf. Jour. Sci, 13, 1, (**2002**) , 63-70

7- Arthur .I.Vogel."Practical Organic Chemistry "Third edition 1956 p718.

8-Jones,G.and Bradsaw,B.C.,**1933**. The measurement of conductance of electrolytes ,J.Amer.Chem.Soc.55,1780-1795.

9-Akrawi,B.A.,and Sarsem,L.A.2001,The electrolytic conductivity of Oxine with transition alkaline earth chloride complexes in methanol at 25°C ,Raf.Jour.Soc vol 12,No.2,PP17-27 .

10-Lee,W.H.and Wheaton,R.J.,**1978** conductance of symmetrical , unsymmetrical and Mixed Electrolytes ,J.Chem.Soc.Faraday Trans .II,74,743.

# سلوك الكيمياء الكهربائي للبنزيليدين اسيتوفينون ومشتقاته في الكحول المثيلي عند درجة حرارة 298.16 كلفن

**ليث وعدالله عبدالله**

*فرع الكيمياء الصيدلانية ، كلية الصيدلة ، جامعة تكريت ، تكريت ، العراق*

( **تاريخ الاستلام:** 15 / 5 / 2011 ---- **تاريخ القبول:** 27 / 9 / 2011 )

## الملخص

تم تقدير التوصيل المولاري ($\Lambda$) للمحلول المائي للبنزيليدين اسيتوفينون مع مشتقاته من خلال دقة قياسات التوصيليه . النتائج التي تم الحصول عليها مطابقة لمعادلة لي ويتون مأخوذا بنظر الاعتبار فعالية الالكتروليت في المحلول.أستعملت نتائج قياس التوصيليه لتقدير ثابت الترابط للأيونات المزدوجة ($K_A$) والمسافة الرئيسية بين الأيونات في المحلول (R) بالأضافه إلى التوصيل المولاري بالتخفيف اللانهائي للأيون الحر في المحلول($\Lambda o$) كانت ملائمة لقيم ($\sigma\Lambda$) .