Rafidain Journal of Science
https://rsci.mosuljournals.com
Vol. 31, No.1, pp. 47-61, 2022

Study of Electrical Conductivity for Salt Diclofenac Potassium in Water and Water-Methanol Mixtures at Different Temperatures

Hakam A. Alhayaly **Mohammed Y. Al-Tamer**
Department of Chemistry/ College of Science/ University of Mosul

Article information

p-ISSN: 1608-9391
e -ISSN: 2664-2786

Received: 31/10/2021
Accepted: 12/12/2021

DOI: 10.33899/rjs.2022.172932

corresponding author:

Hakam A. Alhayaly
hakam2027@gmail.com

Mohammed Y. Al-Tamer
d.altamer56@gmail.com

ABSTRACT

This paper traces the conductivity of diclofenac potassium salts in the low concentrations in water and mixtures of water and methanol (10%, 20% and 30% aqueous methanol) at different temperatures (288.15, 293.15, 298.15, 303.15 and 308.15 K). The conductivity data were analyzed using the Lee-Wheaton conductivity equation to obtain the values of equivalent conductivity at infinite dilution “Λo”, association constants (K_A), the association diameter (R) and Walden product ($\Lambda_0\eta_0$). The results showed that diclofenac potassium salt behaves as weak electrolytes in the solvents used. Moreover, standard thermodynamic parameters of the association (change value in: Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated and discussed. The results showed that the values of molar conductivity, the distance parameter between the ions (R) and association constants (KA) increase with increasing temperature at the best fit value of the standard deviation (σ). The thermodynamic results also indicated that the ion association process is endothermic (+ΔH) and spontaneous (- ΔG) and increasing degrees of freedom (+ΔS).

Keywords: Equivalent conductivity, Lee- Wheaton model, Association constants, Diclofenac potassium.

INTRODUCTION

Diclofenac potassium is the potassium salt form of diclofenac acid, a benzene acetic acid derivative and nonsteroidal anti-inflammatory drug (NSAID) with analgesic, antipyretic and anti-inflammatory activity.

It is available as a medicine in the form of tablets 50 mg (light brown) and as an effervescent powder to be given orally, the chemical name is 2-[(2,6-dichlorophenyl) amino] benzeneacetic acid, mono salt potassium; Molecular weight 334.25 g/mol. Its molecular formula is $C_{14}H_{10}C_{l2}NKO_2$, and it has the following structural formula: (Helmy *et al*., 2015)

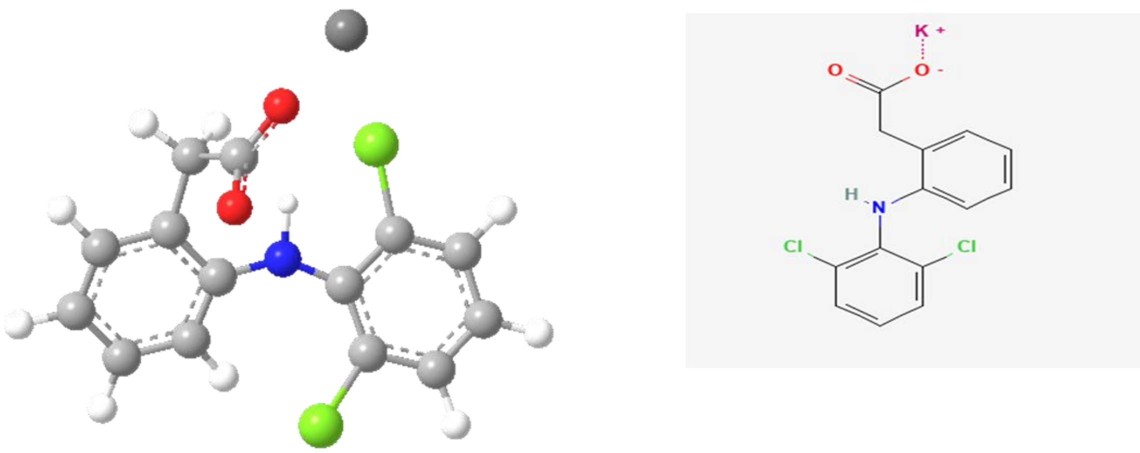

Fig. 1: The structural formula of Diclofenac potassium salt

Many medicines are weak acids or bases that are in the form of salts to improve their solubility. Diclofenac acid is one of these compounds, and it has a very low solubility in water (17.8 mg / L). The high hydrophobicity of diclofenac is partially preserved even if the drug is in salt form. (Shmukler *et al*., 2015)

The interactions between (ion -ion) and (ion- solvent) or the behavior of electrolytes in solution can be useful in scientific studies depending on the transport properties (conductivity and movement of ions) of such electrolytes in solutions.

One of the most important methods for studying the interactions of ion-ioni, ion- solvent, and solvents - solvent in solution is the study of the electrical conductivity of electrolytes depending on the temperature change at a range of dilute concentrations. (Bešter, 2009)

Mixtures of methanol and water at different temperatures exhibit a wide range of relative permittivity and viscosity that affect the conductivity and thermodynamic parameter. (El-Dossoki, 2010). Ion mobility in aqueous solutions, equivalent conductivity, association constants (K_A), all these data are very important to learn about therapeutic efficacy of drugs. (Manca *et al*., 2005; Chadha *et al*., 2003)

The drug-drug and drug-solvent interactions may be of great importance to understand their physiological action and identify the therapeutic efficacy of drugs. (Shmukler *et al*., 2015).

EXPERIMENTAL

Materials

The chemicals used were: - Diclofenac potassium powder (Pioneer company for pharmaceutical industries-Iraq), Methanol (Fluka Switzerland, 99.8%), Potassium Chloride (Merck, Germany, 99.99%) and water (The freshly prepared bidistilled water was used as the solvent with the specific conductivity of less than 1.5×10^{-6} S/cm).

Apparatus

The devices and tools that have been used to determine the conductivity of Diclofenac potassium in the range of low concentrations and at different temperatures are: - Professional Benchtop conductivity meter BC3020 (Singapore) (±0.2% μS cm^{-1}) connected to the thermostatic water bath of type (HAKKE -NK22) to maintain the temperature constant at the desired temperature (±0.15 °C). A closed Jacket cell connected to the thermostat using isolated rubber tubes was used. 30ml of solvents was placed in conductimetric cell pyrex and then the stock solution was added using plastic syringe. After each addition the solution was mixed using magnetic stirrer. Distillation system (GFL model 2001/4) Germany. Analytical balance (Sartorius) Germany sensitive (±0.0001).

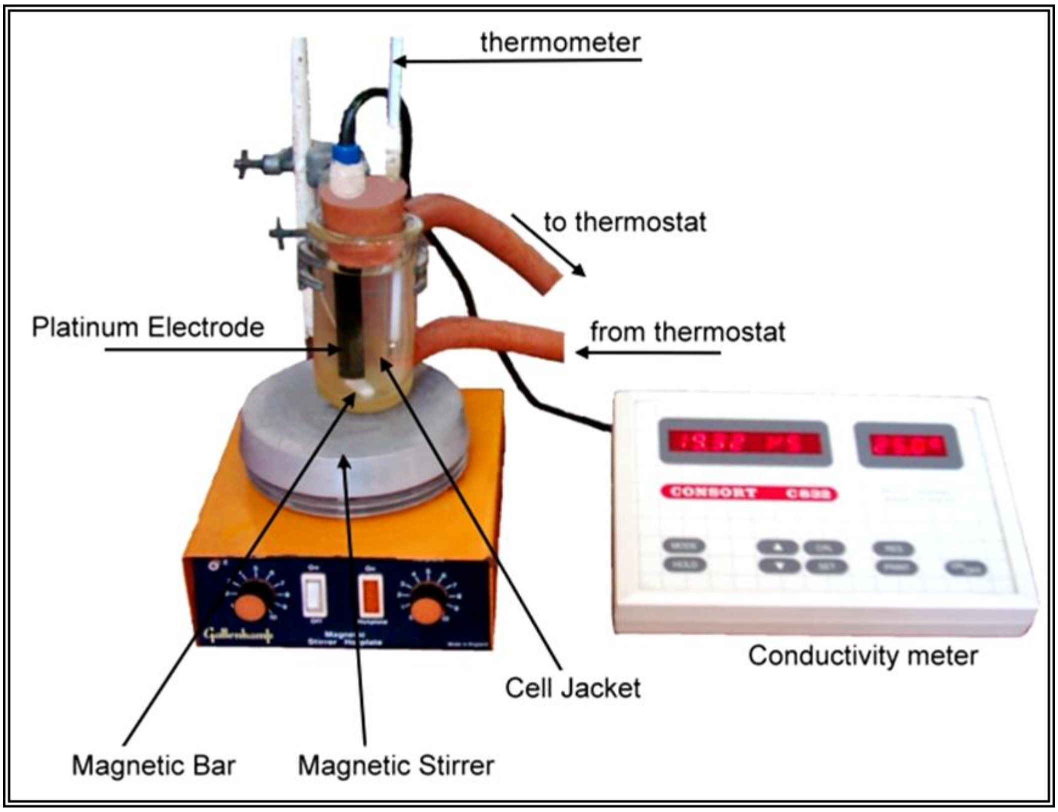

Fig. 2: Basic devices and tools used for conductivity measurement

RESULTS AND DISCUSSION

Physical properties

For procedure accurate measurements to the conductivity of electrolyte should know some of the properties of the solvent used as density (ρ), viscosity (η) and relative permittivity (ε). Pevious values of the100% water and 10, 20 and 30% (MeOH-H2O) mixtures at different temperature (288.15,293.15,298.15,303.15 and 308.15K) were tabulated in (Table 1). (Stokes and Mills, 1965; Wensink *et al*., 2003; Hus *et al*., 2015; González *et al*., 2007)

Table 1: Physical properties of the solvents used at different temperatures

Solvent	T	density (ρ, g cm−3)	viscosity (η, cP)	The relative permittivity (ε)
100% water	288.15 K	0.9993	1.123	82.31
	293.15 K	0.9983	1.002	80.37
	298.15K	0.9971	0.895	78.51
	303.15K	0.9957	0.8	76.73
	308.15K	0.9941	0.712	74.9
10% methanol–water	288.15 K	0.9828	1.49	78.07
	293.15 K	0.9816	1.312	75.84
	298.15K	0.9802	1.155	73.54
	303.15K	0.9786	1.015	72.37
	308.15K	0.9768	0.894	70.43
20% methanol–water	288.15 K	0.9678	1.815	72.89
	293.15 K	0.9664	1.589	71.02
	298.15K	0.9647	1.392	69.22
	303.15K	0.9628	1.206	67.48
	308.15K	0.9604	1.062	65.78
30% methanol–water	288.15 K	0.9543	2.007	67.75
	293.15 K	0.9518	1.759	66.01
	298.15K	0.9492	1.54	64.33
	303.15K	0.9467	1.336	62.71
	308.15K	0.944	1.172	61.1

Data analysis

When solution contain only electrolytes of type (1:1), then:

Λequiv. = f (Λo , R, KA)

Where:

Λequiv:- is the equivalent conductivity.

Λo is the equivalent conductivity at infinite dilution.

KA, is the association constants

$$\mathbf{M^{+}_{(aq.)} + X^{-}_{(aq.)} \rightleftharpoons (M^{+}_{n.aq}X^{-})^{\circ}}$$

R is the distance between the cation and anion.

When the short-range forces are strong enough that they induce closer proximity of the ions to allow the formation of either contact ion pair (CIP) or separated solvent ion pair (SSIP).

The value of R depends on the exchange reactions between the ion and the solvent (Ion-solvent) in the solution. The simplest form of Lee-Wheaton equation for electrolyte solutions of type (1:1) is: (Lee and Wheaton, 1979); (Al-Healy and Hameed, 2020)

$$\Lambda=\Lambda^{\circ}\{1+C1(KR)(\varepsilon K)+C2(KR)(\varepsilon K)^{2} +C3(KR)(\varepsilon K)3 -PK/(1+KR)(1+C4(KR)(\varepsilon R) +C5(KR)(\varepsilon K)2 +KR/12\} \quad ....1$$

where C1 to C5 are complex functions.

$\epsilon = (|Z|2\ e\ 2\ /DKT)$ $\quad K\ 2 = (8\pi N2\ e|Z|2C/1000DKT)$ $\quad P= (F\varsigma|Z|/3\pi\eta)$

ζ = conversion factor; C=concentration (mole/liter); D=Dielectric constant of solvent.

F=Faraday's constant = $9.64867\ x10^{4}$; η: Viscosity of the Solvent.

The electrical conductivity of solution of Diclofenac potassium was studied using conductivity water and mixture from water and methanol (10%, 20% and 30%) whose conductivity of solvent was subtracted from the conductivity values of Diclofenac potassium at different temperature.

These solutions were considered homogeneous electrolytes of type (1:1), we can express it by the following Equation: (Al-Obaidi, 2010)

$$M^{+}_{aq} \quad + \quad X^{-}_{aq} \xrightleftharpoons{K_A} (M^{+}_{n.aq} X^{-})^{\circ}$$

Kohlorousch equation was used, after the conductance was measured, and then the equivalent conductance was calculated at different concentration as shown in (Table 2).

Table 2: The molar conductance of Diclofenac potassium at different temperatures in water and (10%, 20% and 30% methanol–water) solvent

Solvent	100% water		10% Meth		20% Meth		30% Meth	
T(K)	C (mole/liter)	Λequiv (S.equiv⁻.cm2)	C (mole/liter)	Λequiv (S.equiv⁻.cm2)	C (mole/liter)	Λequiv (S.equiv⁻.cm2)	C (mole/liter)	Λequiv (S.equiv⁻.cm2)
28815	8.63E-05	87.64585	4.03E-05	80.14586	1.82E-04	66.47423	1.87E-04	58.19891
	1.72E-04	84.6451	7.25E-05	70.88542	2.69E-04	60.81303	2.68E-04	53.55725
	2.57E-04	78.43317	1.07E-04	66.39023	3.54E-04	57.89018	3.46E-04	50.52699
	3.35E-04	75.15205	1.38E-04	64.10107	4.32E-04	56.1886	4.27E-04	49.80926
	4.19E-04	73.63491	1.74E-04	63.26673	5.92E-04	55.16228	5.14E-04	49.43933
	4.99E-04	73.6417	2.06E-04	62.68361	6.75E-04	54.9998	5.91E-04	49.26941
	5.82E-04	72.70303	2.34E-04	61.67613	7.53E-04	55.03412	6.67E-04	49.31839
	6.51E-04	73.17126	2.64E-04	61.43739	8.95E-04	54.37727	7.54E-04	49.2819
	8.05E-04	73.08926	2.97E-04	61.25581	9.73E-04	54.60066	8.27E-04	47.91835
	9.01E-04	72.98434	3.28E-04	59.66903	1.05E-03	54.62977	9.16E-04	48.75655
	9.66E-04	73.20428	3.63E-04	60.49308	1.12E-03	54.55025	9.81E-04	48.92406
	1.04E-03	72.63157	3.97E-04	60.96997	1.20E-03	54.39255	1.06E-03	48.98709
	1.12E-03	72.16303	4.28E-04	61.07938			1.13E-03	49.19021
293.15	9.88E-05	87.28532	4.21E-05	92.8388	1.06E-04	63.75758	4.44E-05	59.31176
	1.23E-04	83.79334	6.34E-05	80.19717	1.59E-04	57.50468	6.18E-05	54.76722
	2.59E-04	75.04855	8.26E-05	76.43727	2.68E-04	54.97912	8.43E-05	53.04078
	3.41E-04	73.68658	1.00E-04	75.0593	3.58E-04	52.48871	1.04E-04	52.19524
	4.19E-04	73.01937	1.19E-04	75.37219	4.34E-04	51.60061	1.23E-04	52.41548
	5.04E-04	72.83938	1.38E-04	75.03417	5.21E-04	51.78626	1.43E-04	52.41867
	5.81E-04	72.6124	1.57E-04	74.48288	5.96E-04	52.04521	1.60E-04	52.18758
	6.56E-04	72.62997	1.77E-04	74.45673	6.72E-04	52.05239	1.72E-04	52.24405
	7.58E-04	72.48463	1.93E-04	74.28164	7.51E-04	52.23834	1.79E-04	52.34652
	8.10E-04	72.34635	2.13E-04	69.87041	8.21E-04	51.12292	1.89E-04	52.26467
	8.92E-04	72.21595	2.30E-04	67.69263	9.10E-04	52.00274		
	9.68E-04	72.16948			9.92E-04	52.1213		
298.15	9.76E-05	89.4587	9.77E-05	75.32412	1.72E-04	64.67501	3.40E-04	56.08505
	1.33E-04	84.47565	1.77E-04	66.98251	2.55E-04	54.41604	4.27E-04	54.41803
	2.65E-04	74.67847	2.53E-04	64.62766	3.45E-04	51.93612	5.03E-04	52.58809
	3.46E-04	74.01402	3.26E-04	63.5922	4.20E-04	51.95567	5.76E-04	51.50545
	4.28E-04	73.96739	4.12E-04	63.32148	4.93E-04	51.56812	6.67E-04	51.02706
	5.08E-04	73.65202	4.89E-04	63.001	5.75E-04	53.94753	7.38E-04	50.79057
	5.81E-04	73.59734	5.59E-04	62.87061	7.36E-04	51.37437	8.10E-04	50.73663
	6.65E-04	73.27056	6.29E-04	61.11866	8.08E-04	48.42509	8.97E-04	50.71968
	7.44E-04	72.94209	7.85E-04	61.58354	8.76E-04	51.29957	9.74E-04	50.7921
	8.08E-04	73.07905	8.64E-04	62.08322	9.61E-04	51.38008	1.05E-03	50.8815
	9.00E-04	72.77969	9.46E-04	61.95442	1.03E-03	51.41738	1.13E-03	50.86857
	9.74E-04	72.31242	1.09E-03	62.26717	1.10E-03	51.43669	1.20E-03	50.83333
	1.05E-03	72.42836	1.16E-03	61.95539	1.18E-03	51.54445		
303.15	9.74E-05	82.74757	3.80E-05	84.95746	4.19E-05	62.5667	3.89E-05	61.32838
	1.42E-04	78.32183	7.16E-05	73.46722	7.33E-05	58.11476	7.15E-05	57.00163
	2.59E-04	72.7915	1.02E-04	68.37089	1.08E-04	56.3268	1.02E-04	56.17469
	4.15E-04	72.5915	1.38E-04	67.45391	1.39E-04	55.3092	1.36E-04	56.05907
	5.05E-04	71.15426	1.72E-04	66.87936	1.75E-04	53.95464	1.71E-04	56.18723
	5.78E-04	72.28275	2.03E-04	65.68069	2.04E-04	53.56897	2.03E-04	56.16982
	6.56E-04	70.8042	2.35E-04	65.56628	2.41E-04	53.00209	2.35E-04	56.31382
	7.33E-04	70.69492	2.68E-04	65.41002	2.65E-04	52.43197	2.65E-04	52.76448
	8.04E-04	70.66191	2.96E-04	61.22606	3.01E-04	52.32358	2.99E-04	49.88702

	8.87E-04	**70.78146**	**3.28E-04**	**60.62115**	**3.28E-04**	**52.13819**	**3.26E-04**	**46.31955**
	9.63E-04	**70.70882**	**3.63E-04**	**60.6129**	**3.62E-04**	**52.2362**	**3.63E-04**	**46.33974**
	1.04E-03	**71.3856**	**3.94E-04**	**61.00443**	**3.95E-04**	**52.30511**	**3.93E-04**	**46.5089**
	1.11E-03	**71.11324**	**4.24E-04**	**61.07092**	**4.24E-04**	**52.72794**	**4.24E-04**	**46.57046**
	1.19E-03	**71.32127**	**4.57E-04**	**61.23907**	**4.51E-04**	**52.47088**	**0.0004537**	**46.73568**
308.15	**1.70E-04**	**82.03594**	**3.92E-05**	**87.88307**	**4.257E-05**	**70.06728**	**3.90E-05**	**60.71413**
	2.52E-04	**74.23088**	**7.29E-05**	**77.61433**	**7.138E-05**	**67.02161**	**7.55E-05**	**55.55461**
	3.34E-04	**72.36039**	**1.03E-04**	**74.50345**	**0.0001059**	**62.0778**	**1.07E-04**	**52.15571**
	4.14E-04	**71.81355**	**1.33E-04**	**72.87931**	**0.0001386**	**60.0054**	**1.38E-04**	**49.52**
	4.93E-04	**71.57088**	**1.68E-04**	**71.94149**	**0.0001724**	**58.55949**	**1.69E-04**	**48.7396**
	5.69E-04	**71.33062**	**1.97E-04**	**71.84979**	**0.0002032**	**57.43962**	**2.05E-04**	**48.03304**
	6.54E-04	**71.12009**	**2.29E-04**	**67.1743**	**0.0002336**	**57.31936**	**2.36E-04**	**48.01368**
	7.25E-04	**70.86712**	**2.63E-04**	**62.74911**	**0.0002671**	**56.98801**	**2.66E-04**	**48.01619**
	8.84E-04	**69.62074**	**2.93E-04**	**62.8795**	**0.0002963**	**56.61822**	**2.96E-04**	**48.00373**
	9.62E-04	**70.51985**	**3.21E-04**	**62.946**	**0.0003261**	**56.40763**	**3.24E-04**	**48.08899**
	1.03E-03	**70.64028**	**3.58E-04**	**63.17783**	**0.000362**	**55.86967**	**3.62E-04**	**48.14004**
	1.11E-03	**69.92769**	**3.82E-04**	**63.00533**	**0.0003885**	**55.5988**	**3.91E-04**	**48.54184**
	1.18E-03	**70.10368**					**4.25E-04**	**48.49985**
Solvent	**100% water**		**10% Meth**		**20% Meth**		**30% Meth**	
T(K)	**C (mole/liter)**	**Λequiv (S.equiv¯.cm2)**	**C (mole/liter)**	**Λequiv (S.equiv¯.cm2)**	**C (mole/liter)**	**Λequiv (S.equiv¯.cm2)**	**C (mole/liter)**	**Λequiv (S.equiv¯.cm2)**
28815	**8.63E-05**	**87.64585**	**4.03E-05**	**80.14586**	**1.82E-04**	**66.47423**	**1.87E-04**	**58.19891**
	1.72E-04	**84.6451**	**7.25E-05**	**70.88542**	**2.69E-04**	**60.81303**	**2.68E-04**	**53.55725**
	2.57E-04	**78.43317**	**1.07E-04**	**66.39023**	**3.54E-04**	**57.89018**	**3.46E-04**	**50.52699**
	3.35E-04	**75.15205**	**1.38E-04**	**64.10107**	**4.32E-04**	**56.1886**	**4.27E-04**	**49.80926**
	4.19E-04	**73.63491**	**1.74E-04**	**63.26673**	**5.92E-04**	**55.16228**	**5.14E-04**	**49.43933**
	4.99E-04	**73.6417**	**2.06E-04**	**62.68361**	**6.75E-04**	**54.9998**	**5.91E-04**	**49.26941**
	5.82E-04	**72.70303**	**2.34E-04**	**61.67613**	**7.53E-04**	**55.03412**	**6.67E-04**	**49.31839**
	6.51E-04	**73.17126**	**2.64E-04**	**61.43739**	**8.95E-04**	**54.37727**	**7.54E-04**	**49.2819**
	8.05E-04	**73.08926**	**2.97E-04**	**61.25581**	**9.73E-04**	**54.60066**	**8.27E-04**	**47.91835**
	9.01E-04	**72.98434**	**3.28E-04**	**59.66903**	**1.05E-03**	**54.62977**	**9.16E-04**	**48.75655**
	9.66E-04	**73.20428**	**3.63E-04**	**60.49308**	**1.12E-03**	**54.55025**	**9.81E-04**	**48.92406**
	1.04E-03	**72.63157**	**3.97E-04**	**60.96997**	**1.20E-03**	**54.39255**	**1.06E-03**	**48.98709**
	1.12E-03	**72.16303**	**4.28E-04**	**61.07938**			**1.13E-03**	**49.19021**
293.15	**9.88E-05**	**87.28532**	**4.21E-05**	**92.8388**	**1.06E-04**	**63.75758**	**4.44E-05**	**59.31176**
	1.23E-04	**83.79334**	**6.34E-05**	**80.19717**	**1.59E-04**	**57.50468**	**6.18E-05**	**54.76722**
	2.59E-04	**75.04855**	**8.26E-05**	**76.43727**	**2.68E-04**	**54.97912**	**8.43E-05**	**53.04078**
	3.41E-04	**73.68658**	**1.00E-04**	**75.0593**	**3.58E-04**	**52.48871**	**1.04E-04**	**52.19524**
	4.19E-04	**73.01937**	**1.19E-04**	**75.37219**	**4.34E-04**	**51.60061**	**1.23E-04**	**52.41548**
	5.04E-04	**72.83938**	**1.38E-04**	**75.03417**	**5.21E-04**	**51.78626**	**1.43E-04**	**52.41867**
	5.81E-04	**72.6124**	**1.57E-04**	**74.48288**	**5.96E-04**	**52.04521**	**1.60E-04**	**52.18758**
	6.56E-04	**72.62997**	**1.77E-04**	**74.45673**	**6.72E-04**	**52.05239**	**1.72E-04**	**52.24405**
	7.58E-04	**72.48463**	**1.93E-04**	**74.28164**	**7.51E-04**	**52.23834**	**1.79E-04**	**52.34652**
	8.10E-04	**72.34635**	**2.13E-04**	**69.87041**	**8.21E-04**	**51.12292**	**1.89E-04**	**52.26467**
	8.92E-04	**72.21595**	**2.30E-04**	**67.69263**	**9.10E-04**	**52.00274**		
	9.68E-04	**72.16948**			**9.92E-04**	**52.1213**		
298.15	**9.76E-05**	**89.4587**	**9.77E-05**	**75.32412**	**1.72E-04**	**64.67501**	**3.40E-04**	**56.08505**
	1.33E-04	**84.47565**	**1.77E-04**	**66.98251**	**2.55E-04**	**54.41604**	**4.27E-04**	**54.41803**
	2.65E-04	**74.67847**	**2.53E-04**	**64.62766**	**3.45E-04**	**51.93612**	**5.03E-04**	**52.58809**
	3.46E-04	**74.01402**	**3.26E-04**	**63.5922**	**4.20E-04**	**51.95567**	**5.76E-04**	**51.50545**
	4.28E-04	**73.96739**	**4.12E-04**	**63.32148**	**4.93E-04**	**51.56812**	**6.67E-04**	**51.02706**
	5.08E-04	**73.65202**	**4.89E-04**	**63.001**	**5.75E-04**	**53.94753**	**7.38E-04**	**50.79057**
	5.81E-04	**73.59734**	**5.59E-04**	**62.87061**	**7.36E-04**	**51.37437**	**8.10E-04**	**50.73663**
	6.65E-04	**73.27056**	**6.29E-04**	**61.11866**	**8.08E-04**	**48.42509**	**8.97E-04**	**50.71968**
	7.44E-04	**72.94209**	**7.85E-04**	**61.58354**	**8.76E-04**	**51.29957**	**9.74E-04**	**50.7921**
	8.08E-04	**73.07905**	**8.64E-04**	**62.08322**	**9.61E-04**	**51.38008**	**1.05E-03**	**50.8815**
	9.00E-04	**72.77969**	**9.46E-04**	**61.95442**	**1.03E-03**	**51.41738**	**1.13E-03**	**50.86857**
	9.74E-04	**72.31242**	**1.09E-03**	**62.26717**	**1.10E-03**	**51.43669**	**1.20E-03**	**50.83333**
	1.05E-03	**72.42836**	**1.16E-03**	**61.95539**	**1.18E-03**	**51.54445**		
303.15	**9.74E-05**	**82.74757**	**3.80E-05**	**84.95746**	**4.19E-05**	**62.5667**	**3.89E-05**	**61.32838**
	1.42E-04	**78.32183**	**7.16E-05**	**73.46722**	**7.33E-05**	**58.11476**	**7.15E-05**	**57.00163**
	2.59E-04	**72.7915**	**1.02E-04**	**68.37089**	**1.08E-04**	**56.3268**	**1.02E-04**	**56.17469**
	4.15E-04	**72.5915**	**1.38E-04**	**67.45391**	**1.39E-04**	**55.3092**	**1.36E-04**	**56.05907**
	5.05E-04	**71.15426**	**1.72E-04**	**66.87936**	**1.75E-04**	**53.95464**	**1.71E-04**	**56.18723**

	5.78E-04	72.28275	2.03E-04	65.68069	2.04E-04	53.56897	2.03E-04	56.16982
	6.56E-04	70.8042	2.35E-04	65.56628	2.41E-04	53.00209	2.35E-04	56.31382
	7.33E-04	70.69492	2.68E-04	65.41002	2.65E-04	52.43197	2.65E-04	52.76448
	8.04E-04	70.66191	2.96E-04	61.22606	3.01E-04	52.32358	2.99E-04	49.88702
	8.87E-04	70.78146	3.28E-04	60.62115	3.28E-04	52.13819	3.26E-04	46.31955
	9.63E-04	70.70882	3.63E-04	60.6129	3.62E-04	52.2362	3.63E-04	46.33974
	1.04E-03	71.3856	3.94E-04	61.00443	3.95E-04	52.30511	3.93E-04	46.5089
	1.11E-03	71.11324	4.24E-04	61.07092	4.24E-04	52.72794	4.24E-04	46.57046
	1.19E-03	71.32127	4.57E-04	61.23907	4.51E-04	52.47088	0.0004537	46.73568
308.15	1.70E-04	82.03594	3.92E-05	87.88307	4.257E-05	70.06728	3.90E-05	60.71413
	2.52E-04	74.23088	7.29E-05	77.61433	7.138E-05	67.02161	7.55E-05	55.55461
	3.34E-04	72.36039	1.03E-04	74.50345	0.0001059	62.0778	1.07E-04	52.15571
	4.14E-04	71.81355	1.33E-04	72.87931	0.0001386	60.0054	1.38E-04	49.52
	4.93E-04	71.57088	1.68E-04	71.94149	0.0001724	58.55949	1.69E-04	48.7396
	5.69E-04	71.33062	1.97E-04	71.84979	0.0002032	57.43962	2.05E-04	48.03304
	6.54E-04	71.12009	2.29E-04	67.1743	0.0002336	57.31936	2.36E-04	48.01368
	7.25E-04	70.86712	2.63E-04	62.74911	0.0002671	56.98801	2.66E-04	48.01619
	8.84E-04	69.62074	2.93E-04	62.8795	0.0002963	56.61822	2.96E-04	48.00373
	9.62E-04	70.51985	3.21E-04	62.946	0.0003261	56.40763	3.24E-04	48.08899
	1.03E-03	70.64028	3.58E-04	63.17783	0.000362	55.86967	3.62E-04	48.14004
	1.11E-03	69.92769	3.82E-04	63.00533	0.0003885	55.5988	3.91E-04	48.54184
	1.18E-03	70.10368					4.25E-04	48.49985

It was found that diclofenac potassium salt behaves in all the above measurements as weak electrolytes. This was proved by drawing the relationship between the square root of several concentrations in the dilute range of diclofenac potassium solution versus the equivalent conductivity calculated at different temperatures. Figs. (3, 4, 5, 6) illustrate this behavior and it turned out to be in a curved shape, and none of the solution showed a straight line, indicating that these solutions behave like a weak electrolyte.

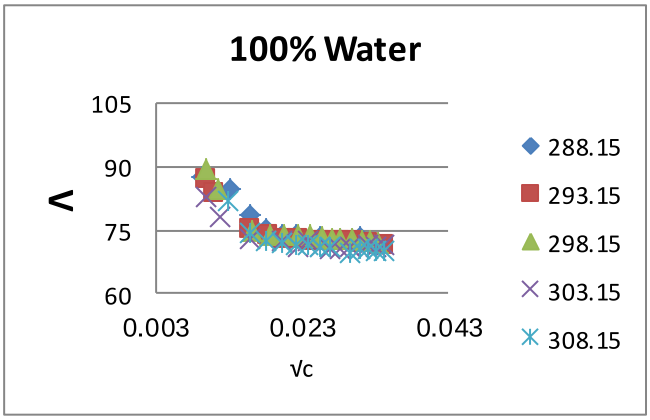

Fig. 3: Relation between Λequiv. ad square root of concentration) in water at different temperatures

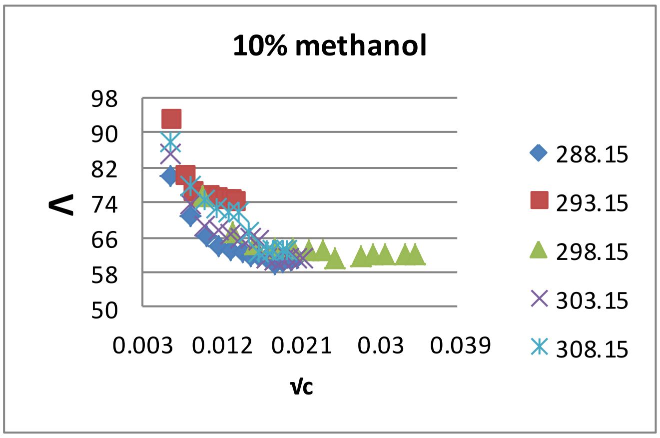

Fig. 4: Relation between Λequiv. and square root of concentration in a mixture of (10 methanol + 90% water) at different temperatures

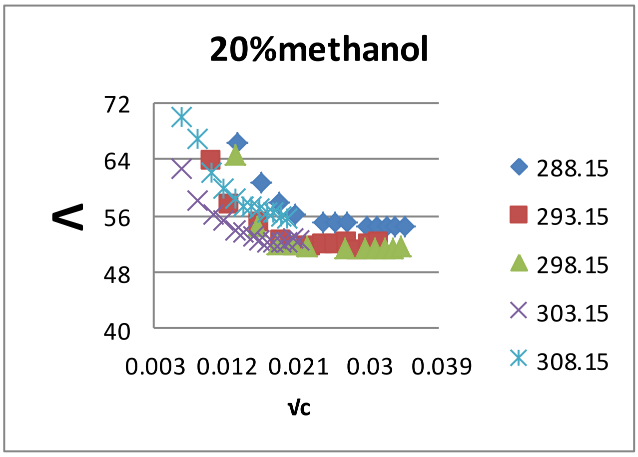

Fig. 5: Relation between Λequiv. and square root of concentration) in a mixture of (20 methanol + 90% water) at different temperatures.

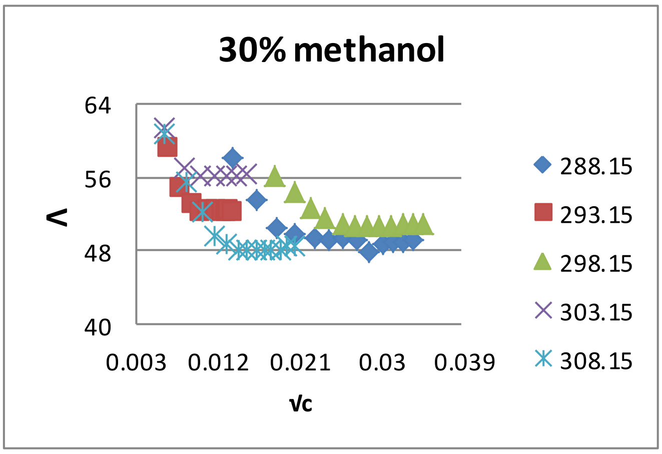

Fig. 6: Relation between concentration) in a mixture of (30 methanol + 90% water) at different temperatures Λequiv. and square root of.

By using the Lee-Wheaton model and data analysis for Diclofenac potassium solution which include the concentrations and equivalent conductivity values using the (RM1) program in (FORTORAN 90 Language) and after giving information about absolute temperature, Solvent viscosity (η), dielectric constant of solvent and the values of KA and R were assumed as Rmin, Rmax, and ΔR with molar solution concentrations with the equivalent conductance of solutions.

After analyzing the information, it was confirmed that the solutions of the drug compound used are weak electrolytes. As a result of the analysis, the values of: the equivalent conductance at infinite dilution(Λ_o), association constants (K_A), the distance parameter between the ions (R), As well as obtaining the values of the Standard Deviation σ: (Al-Obaidi, 2010).

$\sigma_{(\Lambda)}$ =

$$\left[\sum_{n=1}^{Np} \frac{(\Lambda_{calc.} - \Lambda_{expt.})^2}{Np}\right]^{1/2} \quad ....2$$

Table 3 shows the results of the analysis using the equation Lee-Wheaton.

Table 3: The equivalent conductance at infinite dilution(Λ_o), the distance parameter between the ions (R), the standard deviations (σ) and association constants (K_A) of the Diclofenac potassium salt in the used solvents at different temperatures

Solvent	T	Λ_o	R	Σ	K_A
	K	(S.equiv^{-1}.cm^2)	(A°)	S^{-1} mol^{-1} cm^2	dm^{-3}.mol^{-}
100% water	288.2	82.7799	3	0.047461538	205.393
	293.2	86.6946	5	0.041205983	392.2402
	298.2	90.5404	7	0.13447094	661.0432
	303.2	91.6506	8	0.040847863	1211.9011
	308.2	99.505	9	0.206069231	2329.0585
10%Meth	288.2	81.5505	3	0.034788034	2086.75
	293.2	84.4602	4.5	0.369845299	2533.0489
	298.2	84.4925	5	0.445576068	6440.9519
	303.2	93.638	7	0.315722222	8171.8373
	308.2	102.0976	9	0.41232906	12660.4752
20%Meth	288.2	63.415	3	0.15567265	422.4375
	293.2	64.7177	3.9	0.159341026	916.0029
	298.2	65.396	4.4	0.296322222	1544.344
	303.2	65.9996	5.1	0.219953846	2896.0153
	308.2	77.4083	7	0.266209402	5034.9448
30%Meth	288.2	57.4153	3	0.351113675	1308.8446
	293.2	60.255	4	0.092388889	1659.9699
	298.2	62.9423	4.7	0.375544444	2553.4369
	303.2	65.7195	5.1	0.186839316	3300.4638
	308.2	68.4817	5.8	0.072796581	4595.2238

Table (3) show that the equivalent conductance at infinite dilution (Λ_o) values increase with increasing temperature and this is due to the increase in the solvent fluidity with increasing temperature (decreasing viscosity of the medium), which affects the mobility of ions. Equivalent Conductivity at Infinite dilution of Diclofenac Potassium Inversely proportional to the ratios of organic-aqueous property for solvents at the same temperature as follows 30% < 20% < 10%. This behavior is attributed to the formation of a hydrogen bond between water and alcohol molecules leading to the binding of alcohol and H_2O molecules and an increase in the viscosity of the medium this will cause reduce the movement of ions and decrease the values of (Λ_o) with increasing percentages of organic solvent. It may also result from a decrease in the relative permittivity with the increase of the organic percentage in the solvent. It also shows that the values of the association constants (K_A) increase with increasing temperature. This is due to the decrease in the dielectric constant and density of the solvent as the temperature increases. An increase in the value of the association constant with increasing temperature indicates that the association process is endothermic. This behavior is supported by other studies by several authors. (Dash *et al*., 2006; Gomaa and Tahoon, 2016; El-Dossoki *et al*., 2011; Bhat and Shivakumar, 2004).

It was also found that as the temperature increased, the distance parameter between the ions (R) increased (and the state of the ions changed from contact ion pair (CIP) to separated solvent ion pair (SSIP). The higher the percentage of organic solvent (% Methanol), the closer the distance between the ions, while maintaining the separated solvent ion pair (SSIP).

As for the standard deviation values (σ), their values were few, and this confirms that the use of the Lee-Wheaton equation is appropriate in this study.

Thermodynamics of association:

Thermodynamic functions of Diclofenac potassium can be estimated through value of association constants (K_A) at different temperatures by Van 't Hoff equation:

$$\ln K_A = \frac{-\Delta H}{R} \cdot \frac{1}{T} + C \quad \ldots\ldots 3$$

Plotting of ($\ln K_A$) versus the reciprocal (1/T) for all systems results a linear relationship as shown in Fig. (7).

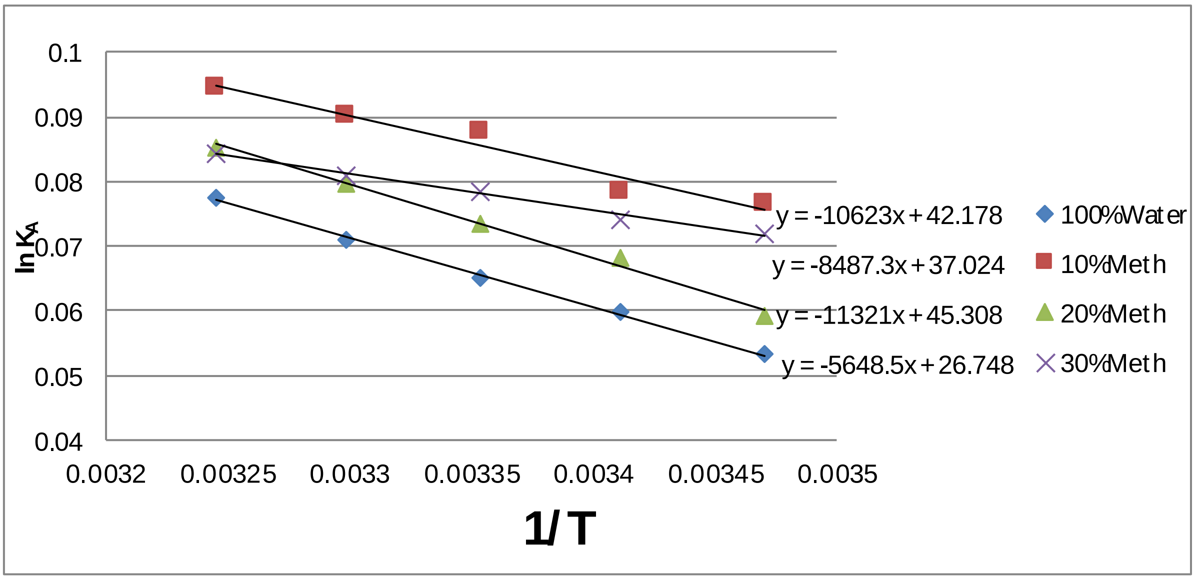

Fig. 7: Relation between (lnkA) and (1/T) in water and mixtures of water and methanol (10%, 20% and 30% aqueous methanol) at different temperatures.

From Fig. (7) it is found that the inverse relationships between (lnkA) and (1/T). This means that the system is endothermic (+ΔH).

Also, the thermodynamic parameters (ΔG) were obtained from (K_A) values with temperatures according to the Gibbs free energy equation

$$\Delta G = -RT \ln K_A \quad \ldots\ldots 4$$

As well as calculating (ΔS) the values obtained from the above equations.

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots 5$$

Table (4) show the Thermodynamic values obtained from the above equations.

Table 4: ΔH, ΔG and ΔS of Diclofenac potassium solution in water solvent and mixtures of water and methanol at different temperatures

100% water				**10%Methanol**		
T	ΔH	ΔG	ΔS	Δ H	ΔG	ΔS
K	(kJ.mole^{-1})	(kJ.mole^{-1})	(J.mole^{-1}. K^{-1})	(kJ.mole^{-1})	(kJ.mole^{-1})	(J.mole^{-1}. K^{-1})
288.15	88.3196	-12.7567	350.7766	70.5634	-18.3108	308.4303
293.15		-14.5547	350.9271		-19.1009	305.8649
298.15		-16.0969	350.2146		-21.7402	309.4683
303.15		-17.8945	350.3681		-22.7046	307.6628
308.15		-19.8663	351.0819		-24.2007	307.5258
20% Metanol				**30%Methanol**		
T	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
K	(kJ.mole^{-1})	(kJ.mole^{-1})	(J.mole^{-1}. K^{-1})	(kJ.mole^{-1})	(kJ.mole^{-1})	(J.mole^{-1}. K^{-1})
288.15	94.1227	-14.174	375.8344	46.9616	-17.1935	222.6448
293.15		-16.622	377.7748		-18.0709	221.8403
298.15		-18.2003	376.7331		-19.4465	222.7338
303.15		-20.09	376.753		-20.4176	222.2635
308.15		-21.8383	376.3134		-21.5816	222.4345

As expected, it is noted from (Table 4) that the value of (ΔH) for ionic association is positive (endothermic).

The obtained values of (ΔG) were negative, which indicates the spontaneous of the association process. Decreased Gibbs free energy by increasing temperatures indicates more spontaneous processes.

While the values of (ΔS) were positive, the reason for this is due to the lack of arrangement or coordination (disorientation) of the solvent molecules when forming the ionic pair. It was noted that the positive values of ΔS° do not vary significantly with increasing temperature this indicates that the number of degrees of freedom during the ionic association process does not change significantly possibly due to the poor solubility of the positive ion. These thermodynamic results are in a good agreement with what many authors have mentioned in other theories and studies. (Bhat and Shivakumar, 2004; Gomaa *et al*., 2016; Gomaa *et al*., 2017; Helmye *et al*., 2015)

Walden product

Walden product ($\Lambda_0\eta_0$) which is an indicator from the point of view of the interaction of ion-solvent (Walden, 1920).

The change in the temperature of the electrolyte solution will lead to a change in the viscosity values. As the temperature increases, the viscosity decreases. Therefore, the transitional movement that causes the equivalent conduction of ions will increase. Therefore, the Walden product ($\Lambda_0\eta_0$) for Diclofenac potassium was calculated at different temperatures. Walden product has formulated its rule (for 1:1electrolyte) in the form as in Eq. (6)

$$\Lambda_0\eta_0 = 0.82\ [1/r^{+}_{s} + r^{-}_{s}] \qquad \ldots\ldots 6$$

the factor $[1/r^{+}_{s} + r^{-}_{s}]$ is a measure of the hydrodynamic radii of the ions.

Table (5) shows the values Walden product and inverted dielectric constant at different temperatures.

Table 5: The Walden product ($\Lambda_0\eta_0$) and inverted dielectric constant of Diclofenac potassium at different temperatures in the used solvents

Solvent	T	η_o	Λ_o	$\eta\Lambda_o$	D	1/D
	(K)	cP	S mol^{-1} cm^2	S mol^{-1} cm^2 cP		
100% Water	288.15	1.123	82.7799	92.9618277	82.31	0.01215
	293.15	1.002	86.6946	86.8679892	80.37	0.01244
	298.15	0.895	90.5404	81.033658	78.51	0.01274
	303.15	0.8	91.6506	73.32048	76.73	0.01303
	308.15	0.712	99.505	70.84756	74.9	0.01335
10% Methanol	288.15	1.49	81.5505	121.510245	78.07	0.01281
	293.15	1.312	84.4602	110.8117824	75.84	0.01319
	298.15	1.155	84.4925	97.5888375	73.54	0.0136
	303.15	1.015	93.638	95.04257	72.37	0.01382
	308.15	0.894	102.0976	91.2752544	70.43	0.0142
20% Methanol	288.15	1.815	63.415	115.098225	72.89	0.01372
	293.15	1.589	64.7177	102.8364253	71.02	0.01408
	298.15	1.392	65.396	91.031232	69.22	0.01445
	303.15	1.206	65.9996	79.5955176	67.48	0.01482
	308.15	1.062	77.4083	82.2076146	65.78	0.0152
30% Methanol	288.15	2.007	57.4153	115.2325071	67.75	0.01476
	293.15	1.759	60.255	105.988545	66.01	0.01515
	298.15	1.54	62.9423	96.931142	64.33	0.01554
	303.15	1.336	65.7195	87.801252	62.71	0.01595
	308.15	1.172	68.4817	80.2605524	61.1	0.01637

From the (Table 5) it was found that the values of Walden's product decrease as the dielectric constant of the solvent decreases as shown in Fig. (8). We also notice from the (Table 5) that Walden's product values decrease with increasing temperature. The reason for this may be related to increase in the diameter of the ions solvated in mixtures with increasing temperature. (Robinson and Stokes, 1965)

Walden's product is mainly affected by two factors. The equivalent conductance at infinite dilution (Λ_0) and viscosity (η_0) whereas η_0 is inversely proportional to temperature, while Λ_0 is directly proportional to temperature, from here we conclude the contribution of the viscosity value is the most influential in the inverse behavior of Walden product with temperature.

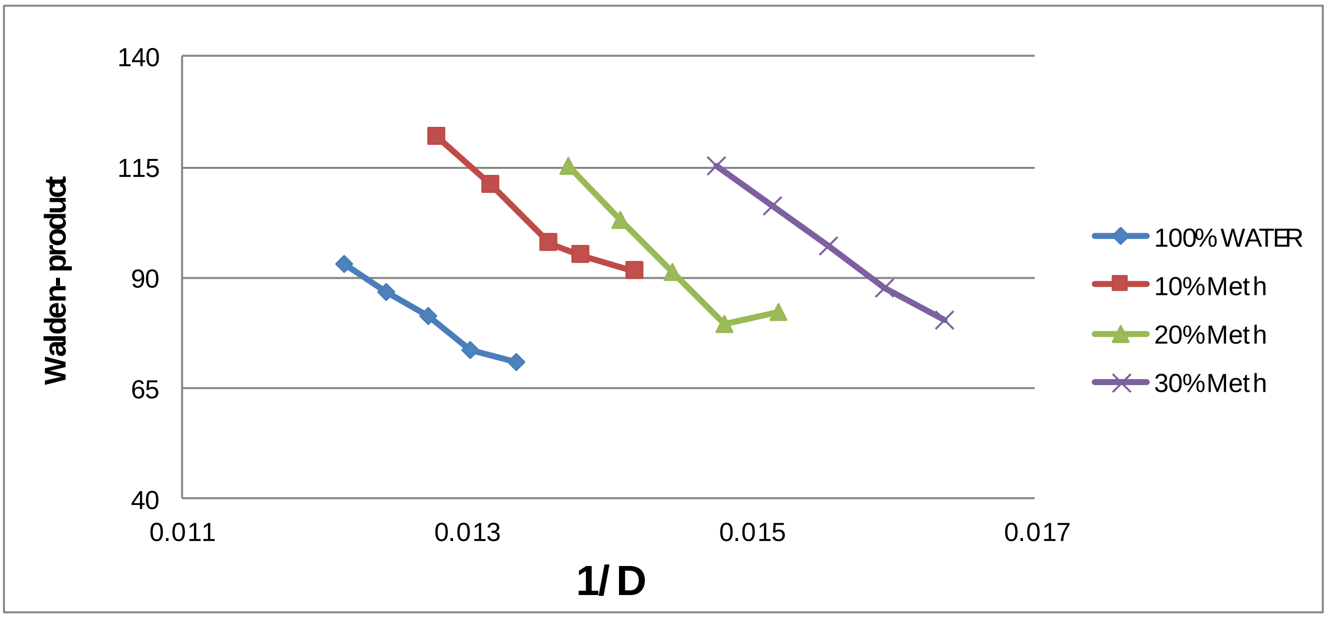

Fig. 8: Relation between Walden-product and (1/D) in water and mixtures of water and methanol (10%, 20% and 30% aqueous methanol).

CONCLUSION

The present study reports to the conductivity data of solutions of diclofenac potassium salts in water and mixtures of water and methanol at different temperatures in the range of low concentrations, which were measured with the help of the Lee-Wheaton equation that diclofenac potassium salt behaves as a weak electrolyte in the above solvents. We observed that the values of conductivity parameters such as K_A, R, Λ_o differ from one solvent to another depending on viscosity and the dielectric constant of the used solvents and interactions in the solution. Ion-association process in the solution is spontaneous process (ΔG= -ve), endothermic (ΔH=+ve) and lead to increased randomness. (ΔS= +ve).

ACKNOWLEDGEMENTS

The authors thank the head of Chemistry Department and the Dean of the College of Science at the University of Mosul for the requirements of the study and for completing it as required.

REFERENCES

Al-Healy, F.M.; Hameed, Y. (2020). Measurement of the electrical conductivity of equivalent a number of aspartic acid complexes in different percentages of water mixture with methanol at 310 absolute temperature. *Raf. J. Sci.*, **29**(1), 80-94.

Al-Obaidi, Z.M. (2010). Study of the electrical conductivity for some drug compounds in different solvents and different temperature and their interaction with albumin. Msc thesis Mosul, University of Mosul.

Bešter, R.M. (2009). Nonsteroidal anti-inflammatory drugs ion mobility: a conductometric study of salicylate, naproxen, diclofenac and ibuprofen dilute aqueous solutions. *Acta Chim. Sloven.*, **56**(1), 70-77.

Bhat, J.I.; Shivakumar, H.R. (2004). Conductometric studies on solvation behaviour of tartaric acid in various solvent mixtures. *J. Molec. Liq.*, **111**(1-3), 101-108.

Chadha, R.; Kashid, N.; Jain, D. (2003). Microcalorimetric studies to determine the enthalpy of solution of diclofenac sodium, paracetamol and their binary mixtures at 310.15 K. *J. Pharma. and Biomed. Analys.*, **30**(5), 1515-1522.

Dash, U.N.; Mahapatra, J.R.; Lal, B. (2006). Ion association and solvation of Co (III) complexes in water+ alcohol mixtures at different temperatures. *J. Molecul. liqu.*, **24**(1-3), 13-18.

El-Dossoki, F.I. (2010). Effect of hydrogen bond, relative permittivity and temperature on the transport properties and the association behavior of some 1: 1 electrolytes in some binary mixed solvents. *J. Molec. Liq.*, **151**(1), 1-8.

El-Dossoki, F.I.; Abdallh, N.E.; Elmasly, S. E. (2011). The transport properties and the association behavior of some 1:1 and 2:1 electrolytes in some binary alcoholic–aqueous mixtures. *J. Molec. Liq.*, **163**(3), 135-140.

Gomaa, E.A.; Tahoon, M.A. (2016). Ion association and solvation behavior of copper sulfate in binary aqueous–methanol mixtures at different temperatures. *J. Molec. Liq.*, **214,** 19-23.

Gomaa, E.A.; Abu-Qarn, R.M. (2017). Ionic association and thermodynamic parameters for solvation of vanadyl sulfate in ethanol-water mixtures at different temperatures. *J. Molecular Liquids*, **232**, 319-324.

Gomaa, E.A.; Tahoon, M.A.; Shokr, A. (2016). Ionic association and solvation study of CoSO4 in aqueous-organic solvents at different temperatures. *Chem. Data Collect.*, **3**, 58-67.

González, B.; Calvar, N.; Gómez, E.; Domínguez, Á. (2007). Density, dynamic viscosity, and derived properties of binary mixtures of methanol or ethanol with water, ethyl acetate, and methyl acetate at T=(293.15, 298.15, and 303.15) K. *J. Chem. Thermodynam.*, **39**(12), 1578-1588.

Helmy, E.T.; Gomaa, E.A.; Abou-Elleef, E.M. (2015). Complexation of 2-mercaptoimidazol with some barium salts conductometrically in various solvents at different temperatures. *International J. Modern Chem.*, **7,** 141-155.

Hus, M.; Žakelj, G.; Urbič, T. (2015). Properties of methanol-water mixtures in a coarse-grained model. *Acta Chim. Sloven.*, **62**(3), 524-530.

Lee, W.H.; Wheaton, R.J. (1979). Conductance of symmetrical, unsymmetrical and mixed electrolytes. Part 3. Examination of new model and analysis of data for symmetrical electrolytes. *J. Chem. Soc., Faraday Transactions 2: Molec. and Chem. Phys.*, **75**, 1128-1145.

Walden, P. (1920). Über die Ionendurchmesser in nichtwässerigen Lösungen. *Z. Anorg. Allg. Chem.*, **113**(1), 125-130.

Robinson, R.A.; Stokes, R.H. (1965). "Electrolyte Solutions. Courier Corporation". London: Butterworths.

Shmukler, L.E.; Manin, N.G.; Safonova, L.P. (2015). Conductometric study of diclofenac salts in water at different temperatures. *J. Molec. Liq.*, **208**, 16-20.

Stokes, R.H.; Mills, R. (1965). "Viscosity of Electrolytes and Related Properties". 1st ed. 1965. London: Pergamon press.

Wensink, E.J.; Hoffmann, A.C.; Van Maaren, P.J.; Van der Spoel, D. (2003). Dynamic properties of water/alcohol mixtures studied by computer simulation. *J. Chem. Phys.*, **119**(14), 7308-7317.

Manca, M. L.; Zaru, M.; Ennas, G.; Valenti, D.; Sinico, C.; Loy, G.; Fadda, A. M. (2005). Diclofenac-β-cyclodextrin binary systems: physicochemical characterization and in vitro dissolution and diffusion studies. *Aaps Pharmscitech*, **6**(3), E464-E472.

دراسة التوصيل الكهربائي لملح بوتاسيوم ديكلوفيناك في الماء ومخاليط الماء والميثانول عند درجات حرارة مختلفة

الملخص

تم تتبع التوصيلية لملح البوتاسيوم ديكلوفيناك في نطاق التراكيز المنخفضة في الماء ومخاليط الماء والميثانول (10٪، 20٪ و 30٪) عند درجات حرارة مختلفة (288.15 ، 293.15 ، 298.15 ، 303.15 ، 308.15 كلفن). تم تحليل بيانات التوصيلية باستخدام معادلة التوصيلية لي – ويتون للحصول على قيم التوصيل المكافئ عند التخفيف اللانهائي "Λ^{o}" وثوابت التجمع (KA) والمسافة بين الايونات (R) بالإضافة الى ناتج والد ($\Lambda 0\eta 0$). أظهرت النتائج أن ملح البوتاسيوم ديكلوفيناك يتصرف كإلكتروليت ضعيف في المذيبات المستخدمة. تم حساب ومناقشة الدوال الثرموديناميكة للتجمع الايوني (التغير في الطاقة الحرة ΔG)، التغير في المحتوى الحراري (ΔH) والتغير في الانتروبي (ΔS). أظهرت النتائج أن قيم التوصيل المولاري (Λ^{o}) والمسافة بين الايونات (R) وثوابت التجمع (KA) تزداد مع زيادة درجة الحرارة عند أفضل قيمة للانحراف المعياري (σ). كما أظهرت نتائج الديناميكية الحرارية أن عملية الارتباط الأيوني ماصة للحرارة (ΔH +) وتحدث بشكل تلقائي (ΔG −) وزيادة في العشوائية ($+\Delta S$).

الكلمات الدالة: التوصيل المكافئ، نظرية لي – ويتون، ثابت التجمع، بوتاسيوم دايكلوفيناك.