

## Studying the thermodynamic dissociation constants of monochloroacetic acid in mixture of ethanol - water

Qhatan Adnan Yousif

*College of Education, Department of Chemistry, Al-Qadisiya University*

(NJC)

(Received on 15/4/2008)

(Accepted for publication 26/10/2008)

### Abstract

This work reports the specific conductivities of monochloroacetic acid electrolyte in a binary mixture solvent of ethanol and water that it covered three solvent compositions ; 0.0586 , 0.0855 and 0.1108 measured in a temperature range from 298.15 to 318.15 K . The molar conductivities of the monochloroacetic acid electrolyte are treated by employing the Debye – Huckel – Onsager ( DHO) equation . The limiting molar conductivities of monochloroacetic acid electrolyte , classical dissociation constants and the degree of dissociation are estimated . Furthermore , the thermodynamic dissociation constants " K " and standard thermodynamic functions of the dissociation process are calculated and discussed . Walden product , corrected Stokes radius and the energy of activation at limiting dilution for the movement of  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions are determined . The results showed the important role for the dielectric constant and the viscosity of mixture of ethanol and water in all values .

	-	-	
( 0.1108	0.0855	0.0586 )	
	.	318.15	298.15
(DHO)	-	-	
		$\text{ClCH}_2\text{COO}^-$	$\text{H}_3\text{O}^+$

## Introduction

The non-aqueous solvent systems have been systematically studied in order not only to measure their physical properties but also to determine their influence on chemical and electrochemical reactions<sup>(1,2)</sup>. The investigations on mixtures of water with an organic solvent as alcohols are particularly important. Later, binary mixtures of organic solvents have been used to study more thoroughly the solvent – solvent interactions and the preferential solvation of ions and molecules<sup>(2)</sup>. Electrostatic phenomena and ion conduction have been considered in terms of ion – solvent and ion – ion interactions<sup>(3)</sup>. The effect of changing solvent composition on the properties of equilibrium systems involving ions is a potentially means of inferring changes in solute – solvent interaction patterns in binary liquid systems<sup>(2)</sup>. The phenomenon termed acidic or basic dissociation is in reality a proton transfer process or protolysis in which the solvent participates. The extent of this acid-base reaction is governed by the acidic or basic properties of the solvent as well as by those of acid or base itself. If ions are formed, the dielectric constant of the solvent also

influence the extent of dissociation<sup>(4)</sup>. Conductivity measurement is of immense important in elucidating not only the behaviour of ions in solution but also in the study of solution structural effects<sup>(5,6)</sup>. Monochloroacetic acid is used in the manufacture of cellulose ethers ( used mainly for drilling muds, detergents, food, pharmaceuticals, manufacture of various dyes, synthetic organic chemicals and as buffer solutions with salicylic acid that it required for calibration of the electrode assembly of the pH-meter )<sup>(7-9)</sup>. A survey of literature<sup>(10-17)</sup> show that conductivity and viscosity studies of electrolytes in several solvent media have been performed in recent years to explore the type and the extent of interactions in electrolyte solution. The limiting molar conductance, the thermodynamic association constant and the Jones – Dole viscosity coefficients are fundamental quantities that have been extracted from these studies. Also, the previous works in the systems of binary mixture that it dependent on the analyzed conductivity data by using Lea – Wheaton conductivity equation<sup>(18-21)</sup> and the values of limiting molar conductance, the association constant and the center - to-center distance of

the formed ions pairs have been derived . The aim of the present work is to study the dissociation constant and the associated thermodynamic properties of monochloroacetic acid in binary mixture system (ethanol+water) in the temperature range (298.15 to 318.15) K and the Debye – Huckel – Onsager ( DHO) equation is applied on this electrolyte .

### Experimental

Monochloroacetic acid with purity more than 99.5% (BDH COMPANY), was used after re-crystallization from ethanol - deionized water mixture ( that it prepared by using the column Resin " from ATA COMPANY " , with specification ; conductivity of purified water quality about 0.1  $\mu\text{S}/\text{cm}^{(22)}$ ). They were dried under vacuum oven and stored in a glass desiccator .Ethanol of purity 99% obtained from FLUKA Company . The solvent composition is expressed in terms of the mole fraction of ethanol in the ethanol – water mixture . The investigation covered three solvent compositions which were : 0.0586 , 0.0855 and 0.1108 .

viscosities of the water ethanol mixtures were determined using a suspended level Ubbelohde viscometer as described elsewhere<sup>(23 24, )</sup> . The

flow times were recorded manually with an electronic timer of precision  $\pm 0.015$  and the temperature of the bath was controlled to be better than  $\pm 0.05$   $^{\circ}\text{C}$  that it supplied by PHYWE company . Digital conductivity meter that it supplier from JCLASSICO company was used to measure the conductivity of the deionized water and of the prepared solutions with an accuracy of  $1 \pm 10^{-9} \text{ Scm}^{-1}$  . Cell used for conductivity measurements is not of accurately known dimensions and consequently they must be calibrated before it is possible to deduce values of the specific conductance from measurements of cell resistance , this is done by means of solutions of accurately known conductivity ( using aqueous KCl solution<sup>(25)</sup> ) at 25  $^{\circ}\text{C}$  , " the cell constant of about  $1.06 \text{ cm}^{-1} \pm 0.01$ ". Some duplicate measurements were made in some solvent composition of mole fraction to check the reproducibility of the results .

The dielectric constants were measured using BI-870 liquid dielectric constant meter<sup>(26)</sup> , BROOKHAVEN INSTRUMENTS CORPORATION , USA ; with full sensitivity 1-200 D and 2% absolute of accuracy . The probe is constructed from two precision cylinders machined from

316 stainless steel . Six 2-25 , 6.4 mm nylon screws maintain the cylinder spacing . The cable consists of two, bundled type 187, low-capacitance, Teflon®- insulated coaxial cables .The outer braid of each cable is grounded . The inner conductors are electrically connected to the two concentric cylinders , which comprise the sensor . The outer cylinder is connected to the measurement signal source : a 7 volt rms , 10 kHz , very low distortion sine wave . The inner cylinder is connected to the detection circuitry.

### Results and Discussion

The viscosity and the dielectric constant data of mixture from ethanol - water at various temperatures range ( 298.15 – 318.15 ) K have been used to estimate the appropriate values of the Debye – Huckel – Onsager constants (DHO)<sup>(3,27-29)</sup> ,  $A$  and  $B$  by using the following relationships :

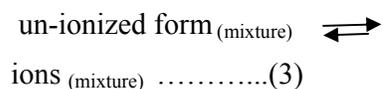
$$A = 82.8 / \eta(\epsilon T)^{1/2} \dots\dots\dots (1)$$

$$B = 8.2 \times 10^5 / (\epsilon T)^{3/2} \dots\dots\dots (2)$$

$A$  accounts for the electrophoretic effect , and  $B$  accounts the relaxation effect . The symbols  $\eta$  ,  $\epsilon$  and  $T$  represent respectively the viscosity ( $\text{cm}^2 \text{s}^{-1}$  unit ) , the dielectric constant ( Debye unit ) and the temperature (K unit ) ; the resulting values of the constants  $A$  and  $B$  are presented in table 1 . The solvent composition was

expressed in terms of the mole fraction of ethanol-water mixture. The investigation covered three solvent compositions which were 0.0586, 0.0855 and 0.1108.

In a weak electrolyte such as monochloroacetic acid the not fully dissociation in solution and an equilibrium exists between the un-ionized form and the ions:



and so , the actual concentration of ions is not equal to the stoichiometric concentration of the ions . In weak electrolyte , the actual concentration of ions only becomes equal to the stoichiometric concentration of the ions in the limiting case of very dilute solutions when the fraction ionized tends to unity . Since  $C_{\text{actual}} = \alpha C_{\text{stoich}}$  , the molar conductivity will depend on the stoichiometric concentration in a precise manner reflecting the fraction ionized . The experimental graph for data of  $\Lambda_{\text{observed}}$  vs.  $\sqrt{C_{\text{stoich}}}$  have been made and at  $C_{\text{stoich}}$  equal zero , the limiting molar conductivity  $\Lambda^0$  is calculated by fitting method<sup>(30)</sup> . The Debye – Huckel - Onsager equation<sup>(28,29,31)</sup> is :-

$$\Lambda_{\text{theoretical}} = \Lambda^0 - (A+B \Lambda^0) \sqrt{C_{\text{actual}}} \dots\dots\dots (4)$$

Where

$$\Lambda_{\text{theoretical}} = \kappa / C_{\text{actual}} = \kappa / \alpha C_{\text{stoich}} = 1 / \Lambda_{\text{observed}} \dots\dots\dots(5)$$

$$\text{So } \Lambda_{\text{theoretical}} = (1 / \alpha) \Lambda_{\text{observed}} \dots\dots\dots(6)$$

$$\text{And } \Lambda_{\text{observed}} = \alpha \Lambda_{\text{theoretical}} \dots\dots\dots(7)$$

$$\text{And the term } (A+B \Lambda^0) \sqrt{\alpha C}_{\text{actual}} = (A+B \Lambda^0) \sqrt{\alpha C}_{\text{stoich}} \dots\dots\dots(8)$$

From this it can be seen , the correct form of The Debye – Huckel - Onsager equation can be used to compare with the experimental results when stoichiometric concentration appear .

$$\text{hence , } \Lambda_{\text{observed}} = \alpha [\Lambda^0 - (A+B \Lambda^0) \sqrt{\alpha C}_{\text{stoich}}] = \alpha \Lambda^0 - \alpha^{3/2} (A+B \Lambda^0) \sqrt{C}_{\text{stoich}} \dots\dots\dots(9)$$

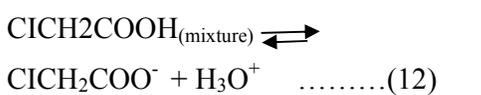
$$\text{Equation ( 9 ) can be written in abbreviated form : } \Lambda_{\text{observed}} = \alpha \Lambda_{\text{correct}} \dots\dots\dots(10)$$

Where

$$\Lambda_{\text{correct}} = \Lambda^0 - (A+B \Lambda^0) \sqrt{\alpha C}_{\text{stoich}} \dots\dots\dots(11)$$

And  $\alpha = \Lambda_{\text{observed}} / \Lambda_{\text{correct}}$  this leads to the understanding of that , the  $\Lambda_{\text{correct}}$  value  $< \Lambda^0$  value and  $\Lambda_{\text{observed}} / \Lambda_{\text{correct}} > \Lambda_{\text{observed}} / \Lambda^0$ . On this principle , the value of  $\alpha$  which to make extent take into account the asymmetry of the ionic atmosphere in a conducting solution via primitive corrections for the electrophoretic and relaxation effects which will be larger than that from the general equation that assuming the ideality . The

correct values of  $\Lambda_{\text{correct}}$  and  $\alpha$  have been calculated by successive cyclic iterations from equation 9 to equation 11 using computer program until  $\Lambda_i - \Lambda_{i+1} < 1 \times 10^{-06}$ . Thus , by using the equation 11 is used to estimate the correct values of the limiting molar conductivity  $\Lambda^0$  . When the monochloroacetic acid is dissolved in mixture of ethanol and water , it yields , as expected , the  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions , as is described in the following equation



By application the law of mass action <sup>(32)</sup>, the apparent equilibrium constant  $K = a_{\text{ClCH}_2\text{COO}^-} \times a_{\text{H}_3\text{O}^+} / a_{\text{ClCH}_2\text{COOH}} \dots\dots\dots(13)$

Where , the "a" terms are the activities of the indicated species. Writing the activity terms in equation (13) as the product of the concentration and the activity coefficient, it becomes:

$$K = C_{\text{ClCH}_2\text{COO}^-} \times C_{\text{H}_3\text{O}^+} / C_{\text{ClCH}_2\text{COOH}} \times f_{\text{ClCH}_2\text{COO}^-} \times f_{\text{H}_3\text{O}^+} / f_{\text{ClCH}_2\text{COOH}} \dots\dots\dots(14)$$

Further, if  $\alpha$  is the degree of dissociation of the monochloroacetic acid whose total concentration is  $C$  moles per liter, then  $C_{\text{ClCH}_2\text{COO}^-}$  and  $C_{\text{H}_3\text{O}^+}$  are each equal to  $\alpha C_{\text{ClCH}_2\text{COOH}}$ , and  $C_{\text{ClCH}_2\text{COOH}}$  is equal to  $C_{\text{ClCH}_2\text{COOH}} (1-\alpha)$  ; it follows,

therefore,  $K = (\alpha^2 C / (1-\alpha)) \times (f_{\text{ClCH}_2\text{COO}^-} \times f_{\text{H}_3\text{O}^+} / f_{\text{ClCH}_2\text{COOH}}) \dots\dots(15)$

If the solution is sufficiently dilute, the activity coefficients are approximately unity, and so equation (15) reduces under these conditions to this form :  $k_a = \alpha^2 C / (1-\alpha) \dots\dots(16)$

It will be noted that in the approximate equation (16) the symbol  $k_a$  has been used; this quantity is often called the "classical dissociation constant," but as it cannot be a true constant it is preferable to refer to it as the "classical dissociation function" or, in brief, as the "dissociation function." , see tables " 3-4" .

The relation between the function  $k_a$  and the true or " thermodynamic" dissociation constant  $K$  is obtained by combining equations (15) and (16); thus :  $K = k_a \times f_{\text{ClCH}_2\text{COO}^-} \times f_{\text{H}_3\text{O}^+} / f_{\text{ClCH}_2\text{COOH}} \dots\dots\dots(17)$

Provided the ionic strength of the medium is not too high, the activity coefficients of the undissociated molecules never differs greatly from unity; hence, equation (17) may be written as :

$$K = k_a \times (f_{\text{ClCH}_2\text{COO}^-} \times f_{\text{H}_3\text{O}^+}) \dots\dots\dots(18)$$

If the solution is sufficiently diluted , the Debye-Huckel limiting law<sup>(31,32)</sup> to be applicable, it follows , that :

$$\text{Log } f_{\text{H}^+} = \text{log } f_{\text{ClCH}_2\text{COO}^-} = - A \sqrt{\alpha C} \text{ stoich} \dots\dots\dots(19)$$

The ionic strength  $1/2 \sum C_i Z_i^2$  , being equal to  $\frac{1}{2} [(\alpha C \times (-1)^2) + (\alpha C \times 1^2)] \dots\dots(20)$  , i.e. , to  $\alpha C \text{ stoich}$  , the equation 18 may be expressed as :

$$\text{Log } K = \text{log } k_a - 2 A \sqrt{\alpha C} \text{ stoich} \dots\dots\dots(21)$$

The true or "thermodynamic" dissociation constant of monochloroacetic acid in a range of temperature ( 298.15 – 318.15 )K in mixture of ethanol and water can be found by equation (21) as is shown in table 5 and figure 1 .

It is clear from table (4) and figure (2), the limiting molar conductivity values for the monochloroacetic acid electrolyte are found to increase in ethanol and water mixture with the increase of temperature from 298.15 to 318.15 K . This is due to the fact that the increased thermal energy results in greater bond breaking and vibrational , rotational and translational energy of the molecule that leads to higher frequency and mobility of the ions . The decrease in the values of limiting molar conductivity ( shown in table 4 , and figure 3 ) with the increase in ethanol content is due to the fact that , with decrease in dielectric constant of the medium , " see table 1 " , the electrostatic attraction between the

ions increase and hence reduce the probability of their existence in the free state and decrease the extent of solvation. The distance of closest approach of the ions becomes smaller. Taking into account as is reported in tables (1 and 4), that the limiting molar conductivity is a measure of the mobility of ion, one can conclude, that the mobility of the ions decrease as the solvent becomes more viscous. Walden product<sup>(33)</sup> is calculated in the range of temperature (298.15-318.15)K in ethanol – water mixture as shown in figure 3 and table 6. The Walden products decrease continuously over the range of mole fraction at fixed temperature. Furthermore, the Walden product is inversely related to Stokes radius. The corrected Stokes<sup>(17)</sup> radius is calculated using the expression:

$$r_i = 0.82Z/\Lambda^0 \eta_0 + 0.0103\varepsilon + r_y \dots(22)$$

where  $r_y = 1.13A^0$  for ethanol as co-solvent with water and  $\varepsilon$  the dielectric constant, as it can be seen, the corrected Stokes radius increases gradually over the mole fraction. The highest Stock radius is, indication maximum solvation. This is in accordance with the experimentally observed minimum value of limiting molar conductivity as it shown in tables 4,6.

Since conductance of an ion depends on its rate of movement, it is quite reasonable to treat conductance in a similar way to the process taking place at a definite rate increase with temperature<sup>(17)</sup>.

$$\Lambda^0 = A_f e^{-E_s/RT} \dots\dots\dots(23)$$

Where  $A_f$  is the frequency factor,  $R$  is the gas constant and  $E_s$  is the Arrhenius activation energy of the transport process. The  $E_s$  values "table 7, figure 4" for all the monochloroacetic acid electrolyte are found to increase with increase in the value of mole fraction. Since the reaction which requires higher activation energy is slow at ordinary temperature, the increase in the values of the activation energy indicates the decrease in the mobility of the ions in the ethanol and water mixture and hence a decrease in the limiting molar conductivity values as it appeared from "table 4". Furthermore, the activation energy for the viscous flow of water<sup>(32-34)</sup> is about, 3.6 kcal which equal to 15.0625 k J mole<sup>-1</sup> and the rate-determining step was assumed to be the jump of the water molecule from one equilibrium position to another. The lower energy of activation for the movement of  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions than that for the viscous flow of water suggests

that the flow of water molecules cannot be the slow stage for the ion movement. On the other hand, the movement of ions in ethanol-water mixture is expected to be considerably slower than that in water and therefore should be excluded as a slow stage throughout the movement of  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions. It is more likely that the rate-determining step in the conductance of the ions is the movement of  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions under the influence of the applied electric field. The pK values for the monochloroacetic acid electrolyte are found in ethanol-water mixture in range (1.53 – 1.66) over temperature range (298.15 – 318.15) K, the value cited in literature cited pK value is 2.82<sup>(35-36)</sup> in aqueous solvent at 25°C which is expected because of the influence of co-solvent. Thus, the pK values increase at the temperature range (298.15 - 318.15) K with increasing values of mole fraction, this means the acidity of monochloroacetic acid is decrease " as is seen in table 5 and figure 5 " and also, indicate to the decrease of the dissociation constant, this behaviour corresponding with the acid-base theory<sup>(34)</sup>, when the basicity is decreased the extents of acid dissociation is become less. At any

value of mole fraction over the temperature range (298.15-318.15)K, the pK values change with temperature as appeared in table 5 and figure 6 which suggests a relatively small dependence of pK on temperature. This means, the value of  $\Delta\text{pK}$  of about  $0.05 \pm 0.02$  could be estimated from a temperature change  $\Delta T$  of about 20K. The dependence of the logarithm of the dissociation constant of monochloroacetic acid in ethanol-water mixture on the dielectric constant, which is shown in figure 7, clearly demonstrates that a larger dielectric constant of the solvent medium leads to a greater dissociation constant of monochloroacetic acid electrolyte.

The dependence of pK values for monochloroacetic acid dissociation in different mole fractions of ethanol-water mixture can be represented by an empirical relation<sup>(2,27,34)</sup>:

$$\text{pK} = A / T - B + C T \dots\dots\dots(24)$$

where A, B and C are constants for a given solvent composition over the temperature range (298.15-318.15)K. The values of constants (A, B and C) are shown in table 8 that it important to found the standard thermodynamic functions for monochloroacetic acid dissociation in different mole fractions

of ethanol - water mixture by the following equations :

$$\Delta G^0 = 2.303 \log (A - BT + CT^2) \dots\dots(25)$$

$$\Delta H^0 = 2.303 \log (A - CT^2) \dots\dots\dots(26)$$

$$\Delta S^0 = 2.303 \log (B - 2CT) \dots\dots\dots(27)$$

$$\Delta C_p^0 = 2.303 \log (-2AT) \dots\dots\dots(28)$$

The standard thermodynamic functions values are collected in "table 9" that have been derived by equations 22, 23, 24 and 25 . The values of  $\Delta G^0$  is negative this refer to the reaction is spontaneous . In other words , the negative value indicates the feasibility of reaction . This behaviour is evident in mole fraction one . But in other mole fractions, the values of  $\Delta G^0$  are positive refer to non-spontaneous reaction over the temperature range ( 298.15 – 318.15 )K , the results reflect the nature of interactions in ethanol - water mixture and corresponding with the values of dielectric constant follows the sequence :  $X = 0.0586 > X = 0.0855 > X = 0.1108$  . In most cases , the  $\Delta H^0$  value is found to be positive indicating the involvement of endothermic character of reaction and the negative value of  $\Delta H^0$  refer to exothermic of reaction . The value of  $\Delta H^0$  is higher positive , especially in mole fraction ,  $X = 0.0586$  is large the endothermic behaviour of the monochloroacetic acid dissociation in ethanol - water

mixture . The positive values of  $\Delta S^0$  in mole fraction ,  $X = 0.0586$  refer to random state to be high of binary mixture from ethanol - water , this values is agreed with the values of  $\Delta G^0$  and  $\Delta H^0$  . The variation of  $\Delta S^0$  with temperature was significant . The negative values of  $\Delta S^0$  in mole fractions  $X = 0.0855$  and  $X = 0.1108$  refer to the increase in order of the system . That proved the presence of interactions of solvent – solute and solvent – solvent are become high . The values of  $\Delta C_p^0$  were negative for mole fraction  $X = 0.0855$  and  $X = 0.1108$  and positive with respect to the solvent composition  $X = 0.0586$  as a consequence of the negative sign of the constant  $C = -0.01898$  . Thus , the  $\Delta C_p^0$  reflects the effect of temperature on  $dH^0$  so that one can write :  $\Delta C_p^0 = dH^0 / dT$  , where the  $\Delta C_p^0$  represents the temperature coefficient of  $\Delta H^0$  . The positive values is an indication for the increasing behaviour of  $\Delta H^0$  with the rise of temperature from (298.15-318) K. On the other hand , the negative sign of  $\Delta C_p^0$  , at the remaining solvent compositions , is due to the decreasing tendency of  $\Delta H^0$  with the increase temperature. Furthermore, the relatively more endothermic and the greater increase in change of entropy

in mole fraction,  $X = 0.0586$ , if it compared with mole fractions  $X = 0.0855$  and  $X = 0.1108$ , includes the loss of complexation which results from the interactions of  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions with the ethanol and water solvents molecules. Thus, the high positive values at this stage of  $\Delta H^0$  values indicates that the undissociation acid molecules are highly stable so that the release of these molecules and the subsequent dissociation stage should highly be endothermic.

### Conclusion

In the present work, conductance, viscosity and dielectric constant measurements have been performed in a range of temperatures ( 298.15 – 318.15 ) K in binary mixture from ethanol and water for monochloroacetic acid electrolyte. The Debye – Huckel – Onsager ( DHO) conductivity equation has been used to determine the limiting molar conductivities and dissociation constants for this electrolyte. Thus, The thermodynamic dissociation constant of monochloroacetic acid has

been estimated by using the  $\text{Log } K = \log k_a - 2 A \sqrt{\alpha C}$  stoich equation. The limiting molar conductivity values for the monochloroacetic acid electrolyte is increased with the increase of temperature and decreased with the increase in ethanol content in mixture. The lower energy of activation for the movement of  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions than that for the viscous flow of water suggests that the flow of water molecules cannot be considered as the slow stage for the ion movement. The dependence of pK values for monochloroacetic acid dissociation in different mole fractions of ethanol + water mixture have been represented by an empirical relation to determine the standard thermodynamic functions. The complexation resulting from  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions have been loosed with the ethanol - water solvents molecules in mole fraction, 0.0586 which denote to higher spontaneous dissociation process, more endothermic and the greater increase in change of entropy.

**Table 1 : Viscosities (  $\text{cm}^2 \text{s}^{-1}$  ), dielectric constants ( Debye ) and the Onsager constants " *A* and *B* " for ethanol + water mixtures at three compositions " *X* " over the temperature range ( 298.15 – 318.15 ) K**

Mole Fraction , <i>X</i>	Temperature , K	Dielectric constant , <i>D</i>	Viscosity , $\text{cm}^2 \text{s}^{-1}$	Constant , <i>A</i>	Constant , <i>B</i>
0.0586	298.15	75	1.478	0.037	0.245
	303.15	73	1.387	0.039	0.249
	308.15	71.3	1.285	0.043	0.251
	313.15	69.9	1.163	0.047	0.253
	318.15	68.3	1.117	0.050	0.256
0.0855	298.15	72.9	1.655	0.033	0.256
	303.15	71.4	1.488	0.037	0.257
	308.15	69.6	1.361	0.041	0.261
	313.15	67.9	1.266	0.044	0.264
	318.15	66.4	1.182	0.048	0.267
0.1108	298.15	70	1.872	0.030	0.272
	303.15	68.1	1.720	0.033	0.276
	308.15	66.6	1.574	0.036	0.279
	313.15	65.1	1.438	0.040	0.281
	318.15	63.5	1.231	0.047	0.285

**Table 2 : Conductance  $\kappa$  ( $S\text{ cm}^{-1}$ ), Molar conductivity  $\Lambda$  ( $S\text{ mol}^{-1}\text{ cm}^2$ ) and acid concentration ( moles per liter) of monochloroacetic acid electrolyte in ethanol + water mixtures at three solvent compositions ( X ) and over temperatures range ( 298.15 – 318.15 ) K .**

X	Concentration	Conductance , $S\text{ cm}^{-1}\times 10^4$					Molar conductivity , $S\text{ mol}^{-1}\text{ cm}^2$				
		298.15	303.15	308.15	313.15	318.15	298.15	303.15	308.15	313.15	318.15
0.0586	$3.2\times 10^{-3}$	5.60	5.87	6.26	6.53	6.65	175	183	196	204	208
	$6.0\times 10^{-3}$	7.85	8.26	8.65	9.30	9.72	131	138	144	155	162
	$8.0\times 10^{-3}$	9.28	9.77	10.60	11.10	11.60	116	122	132	139	145
	$1.0\times 10^{-2}$	10.70	11.30	12.20	12.80	13.30	107	113	122	128	133
	$2.0\times 10^{-2}$	15.40	16.20	17.10	18.20	19.10	76.8	81.1	85.4	91	95.4
X	Concentration	Conductance , $S\text{ cm}^{-1}\times 10^4$					Molar conductivity, $S\text{ mol}^{-1}\text{ cm}^2$				
		298.15	303.15	308.15	313.15	318.15	298.15	303.15	308.15	313.15	318.15
0.0855	$3.2\times 10^{-3}$	4.04	4.28	4.60	4.78	5.09	126	134	144	149	159
	$6.0\times 10^{-3}$	5.74	6.17	6.58	6.95	7.33	95.6	103	110	116	122
	$8.0\times 10^{-3}$	6.14	6.62	7.11	7.52	7.98	76.8	82.7	88.9	94	99.8
	$1.0\times 10^{-2}$	7.92	8.49	9.04	9.50	10.00	79.2	84.9	90.4	95	100
	$2.0\times 10^{-2}$	11.20	12.00	13.00	13.70	14.50	56.2	60.2	65	68.4	72.3
X	Concentration	Conductance , $S\text{ cm}^{-1}\times 10^4$					Molar conductivity, $S\text{ mol}^{-1}\text{ cm}^2$				
		298.15	303.15	308.15	313.15	318.15	298.15	303.15	308.15	313.15	318.15
0.1108	$3.2\times 10^{-3}$	3.17	3.44	3.74	3.96	4.18	99.2	107	117	124	131
	$6.0\times 10^{-3}$	4.75	5.11	5.55	5.87	6.14	79.2	85.2	92.5	97.9	102
	$8.0\times 10^{-3}$	5.56	6.08	6.54	6.94	7.35	69.5	75.9	81.7	86.8	91.9
	$1.0\times 10^{-2}$	6.40	6.95	7.53	8.01	8.46	64	69.5	75.3	80.1	84.6
	$2.0\times 10^{-2}$	9.62	10.30	11.20	11.80	12.40	48.1	51.4	55.9	59.1	62

**Table 3 : The values of Molar conductivity ( $S \text{ mol}^{-1} \text{ cm}^2$ ), correct molar conductance ( $S \text{ mol}^{-1} \text{ cm}^2$ ), degree of dissociation and classical dissociation constant ( $\text{mol liter}^{-1}$ ) for various concentrations  $C$  ( $\text{mol liter}^{-1}$ ) of monochloroacetic acid electrolyte in ethanol + water mixtures at three solvent compositions ( $X$ ) over temperatures range ( $298.15 - 318.15$ ) K .**

At  $X = 0.0586$

Concentration	Temperature	$\Lambda$	$\Lambda_{\text{correct}}$	$\alpha$	$k_a$
$3.2 \times 10^{-3}$	298.15	175	220.0058	0.795	0.009
$6.0 \times 10^{-3}$		131	219.4751	0.596	0.005
$8.0 \times 10^{-3}$		116	219.1895	0.529	0.004
$1.0 \times 10^{-2}$		107	218.9246	0.488	0.004
$2.0 \times 10^{-2}$		76.8	218.159	0.352	0.003
$3.2 \times 10^{-3}$	303.15	183	230.0696	0.795	0.009
$6.0 \times 10^{-3}$		138	229.5111	0.601	0.005
$8.0 \times 10^{-3}$		122	229.2095	0.532	0.004
$1.0 \times 10^{-2}$		113	228.9187	0.493	0.004
$2.0 \times 10^{-2}$		81.1	228.1013	0.355	0.003
$3.2 \times 10^{-3}$	308.15	196	246.0153	0.796	0.009
$6.0 \times 10^{-3}$		144	245.4602	0.586	0.004
$8.0 \times 10^{-3}$		132	245.0635	0.538	0.005
$1.0 \times 10^{-2}$		122	244.7521	0.498	0.004
$2.0 \times 10^{-2}$		85.4	243.9307	0.350	0.003
$3.2 \times 10^{-3}$	313.15	204	257.4322	0.792	0.009
$6.0 \times 10^{-3}$		155	256.7827	0.603	0.005
$8.0 \times 10^{-3}$		139	256.4077	0.542	0.005
$1.0 \times 10^{-2}$		128	256.0875	0.499	0.004
$2.0 \times 10^{-2}$		91	255.1782	0.356	0.003
$3.2 \times 10^{-3}$	318.15	208	263.241	0.790	0.009
$6.0 \times 10^{-3}$		162	262.5189	0.617	0.005
$8.0 \times 10^{-3}$		145	262.131	0.553	0.005
$1.0 \times 10^{-2}$		133	261.8062	0.508	0.005
$2.0 \times 10^{-2}$		95.4	260.8444	0.365	0.004

**Continued table 3**

At X = 0.0855

Concentration	Temperature	$\Lambda$	$\Lambda_{\text{correct}}$	$\alpha$	$k_a$
$3.2 \times 10^{-3}$	298.15	126	156.3716	0.805	0.010
$6.0 \times 10^{-3}$		95.6	155.9789	0.612	0.005
$8.0 \times 10^{-3}$		76.8	155.8978	0.492	0.003
$1.0 \times 10^{-2}$		79.2	155.5398	0.509	0.005
$2.0 \times 10^{-2}$		56.2	154.9757	0.362	0.004
$3.2 \times 10^{-3}$	303.15	134	166.9415	0.802	0.010
$6.0 \times 10^{-3}$		103	166.4948	0.618	0.006
$8.0 \times 10^{-3}$		82.7	166.4136	0.496	0.003
$1.0 \times 10^{-2}$		84.9	166.0499	0.511	0.005
$2.0 \times 10^{-2}$		60.2	165.8096	0.363	0.004
$3.2 \times 10^{-3}$	308.15	144	178.676	0.805	0.010
$6.0 \times 10^{-3}$		110	178.1991	0.617	0.005
$8.0 \times 10^{-3}$		88.9	178.1038	0.499	0.003
$1.0 \times 10^{-2}$		90.4	177.7112	0.508	0.005
$2.0 \times 10^{-2}$		65	177.0234	0.367	0.004
$3.2 \times 10^{-3}$	313.15	149	185.6246	0.802	0.010
$6.0 \times 10^{-3}$		116	185.0944	0.626	0.006
$8.0 \times 10^{-3}$		94	184.9729	0.508	0.004
$1.0 \times 10^{-2}$		95	184.5751	0.514	0.005
$2.0 \times 10^{-2}$		68.4	183.8517	0.372	0.004
$3.2 \times 10^{-3}$	318.15	159	197.5065	0.805	0.010
$6.0 \times 10^{-3}$		122	196.69	0.620	0.006
$8.0 \times 10^{-3}$		99.8	196.8278	0.507	0.004
$1.0 \times 10^{-2}$		100	196.4036	0.509	0.005
$2.0 \times 10^{-2}$		72.3	195.6305	0.369	0.004

**Continued table 3**

At X = 0.1108

Concentration	Temperature	$\Lambda$	$\Lambda_{\text{correct}}$	$\alpha$	$k_a$
$3.2 \times 10^{-3}$	298.15	99.2	124.2332	0.798	0.010
$6.0 \times 10^{-3}$		79.2	123.8428	0.639	0.006
$8.0 \times 10^{-3}$		69.5	123.6731	0.561	0.005
$1.0 \times 10^{-2}$		64	123.4953	0.518	0.005
$2.0 \times 10^{-2}$		48.1	122.9328	0.391	0.005
$3.2 \times 10^{-3}$	303.15	107	134.5626	0.795	0.009
$6.0 \times 10^{-3}$		85.2	134.1385	0.635	0.006
$8.0 \times 10^{-3}$		75.9	133.9392	0.566	0.005
$1.0 \times 10^{-2}$		69.5	133.7542	0.519	0.005
$2.0 \times 10^{-2}$		51.4	133.1475	0.386	0.004
$3.2 \times 10^{-3}$	308.15	117	146.639	0.797	0.010
$6.0 \times 10^{-3}$		92.5	146.1849	0.632	0.006
$8.0 \times 10^{-3}$		81.7	145.9576	0.559	0.005
$1.0 \times 10^{-2}$		75.3	145.7514	0.516	0.005
$2.0 \times 10^{-2}$		55.9	145.0901	0.385	0.004
$3.2 \times 10^{-3}$	313.15	124	155.5197	0.797	0.010
$6.0 \times 10^{-3}$		97.9	155.0405	0.631	0.006
$8.0 \times 10^{-3}$		86.8	154.8	0.560	0.005
$1.0 \times 10^{-2}$		80.1	154.5649	0.518	0.005
$2.0 \times 10^{-2}$		59.1	153.8653	0.384	0.004
$3.2 \times 10^{-3}$	318.15	131	163.9319	0.799	0.010
$6.0 \times 10^{-3}$		102	163.4259	0.624	0.006
$8.0 \times 10^{-3}$		91.9	163.1591	0.563	0.005
$1.0 \times 10^{-2}$		84.6	162.9207	0.519	0.005
$2.0 \times 10^{-2}$		62	162.176	0.382	0.004

**Table 4 : The values of limiting molar conductivity ( $\Lambda_0$  S mol<sup>-1</sup> cm<sup>2</sup>) of monochloroacetic acid electrolyte in ethanol + water mixtures at three solvent compositions ( X ) over temperatures range ( 298.15 – 318.15 ) K .**

Mole fraction X	298.15	303.15	308.15	313.15	318.15
0.0586	222.77934	233.0011	249.18697	260.76112	266.65797
0.0855	158.44476	168.52467	181.08554	188.15011	200.01728
0.1108	125.96941	136.47413	148.74512	157.78296	166.34150

**Table 5 : The values of thermodynamics " true " dissociation constant (K) of monochloroacetic acid electrolyte in ethanol - water mixtures at three solvent compositions ( X ) over temperatures range ( 298.15 – 318.15 ) K .**

Mole fraction , X	Temperatures , K	pK
0.0586	298.15	1.5308
	303.15	1.5466
	308.15	1.5374
	313.15	1.5601
	318.15	1.6009
0.0855	298.15	1.6109
	303.15	1.6090
	308.15	1.6157
	313.15	1.6319
	318.15	1.6119
0.1108	298.15	1.6673
	303.15	1.6583
	308.15	1.6488
	313.15	1.6469
	318.15	1.6405

**Table 6 : The values of Walden product and correct Stokes radius ( $r_i$ ,  $\text{\AA}^0$ ) of the conducting molecular species of monochloroacetic acid electrolyte in ethanol + water mixtures at three solvent compositions (X) over temperatures range (298.15 – 318.15) K.**

Temperatures K	X = 0.0586		X = 0.0855		X = 0.1108	
	Walden pro.	Stokes Ra.	Walden pro.	Stokes Ra.	Walden pro. Ra.	Stokes
298.15	0.3293	4.3925	0.2622	5.0077	0.2358	5.3281
303.15	0.3233	4.4181	0.2508	5.1345	0.2348	5.3237
308.15	0.3202	4.4246	0.2465	5.1721	0.2342	5.3168
313.15	0.3032	4.5536	0.2382	5.2712	0.2269	5.4139
318.15	0.2979	4.58558	0.2364	5.2817	0.2047	5.7882

**Table 7 : The values of energies of activation ( $E_s$ ,  $\text{K J mol}^{-1}$ ) and the frequency factors for the movement of  $\text{ClCH}_2\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions in ethanol + water mixtures at three solvent compositions (X) over temperatures range (298.15 – 318.15) K.**

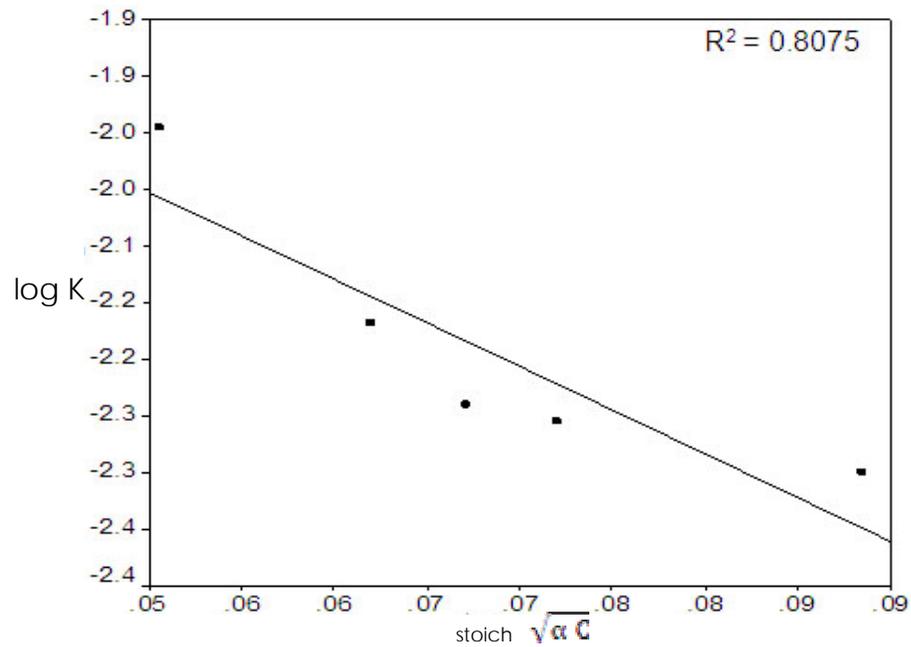
Mole fraction, X	frequency factor, $A_f$	Activation energy, $E_s$
0.0586	3.6558	3.2375
0.0855	3.7937	3.9458
0.1108	4.0431	4.8058

**Table 8 : The values of the temperature dependence constants A, B and C at three different compositions (X) of ethanol + water mixtures**

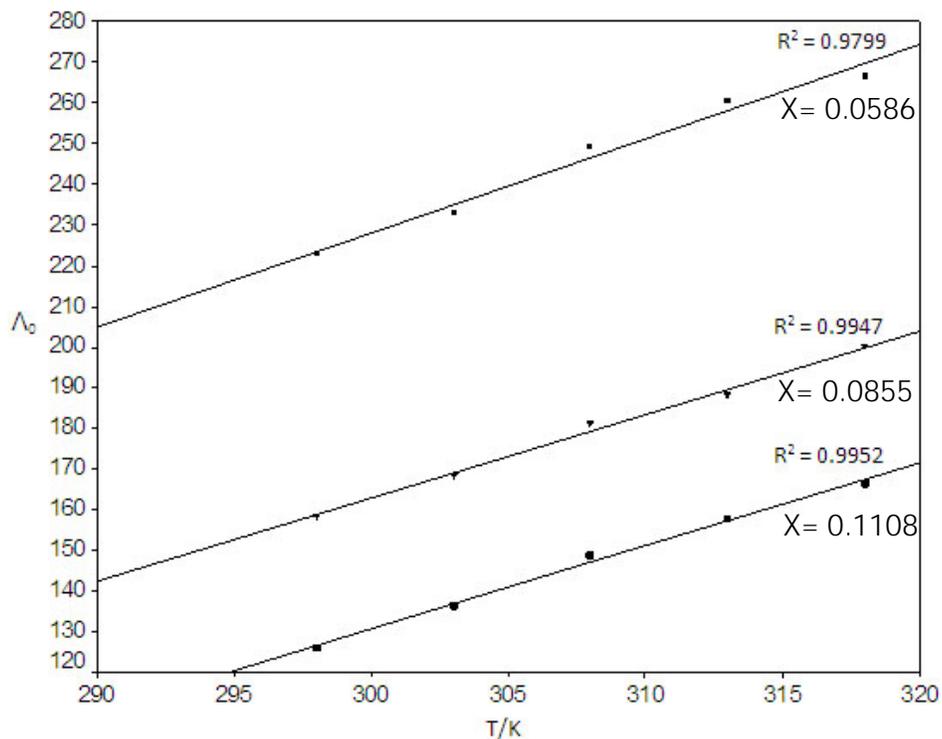
Mole fraction, X	A	B	C	$R^2$
0.0586	-2386	-15.19	-0.0189	0.9405
0.0855	7518	48.03	0.08192	0.9960
0.1108	2500	14.29	0.02538	0.9821

**Table 9 : The values of standard thermodynamics for the dissociation of monochloroacetic acid electrolyte in ethanol + water mixtures at three solvent compositions ( X ) over temperatures range ( 298.15 – 318.15 ) K .**

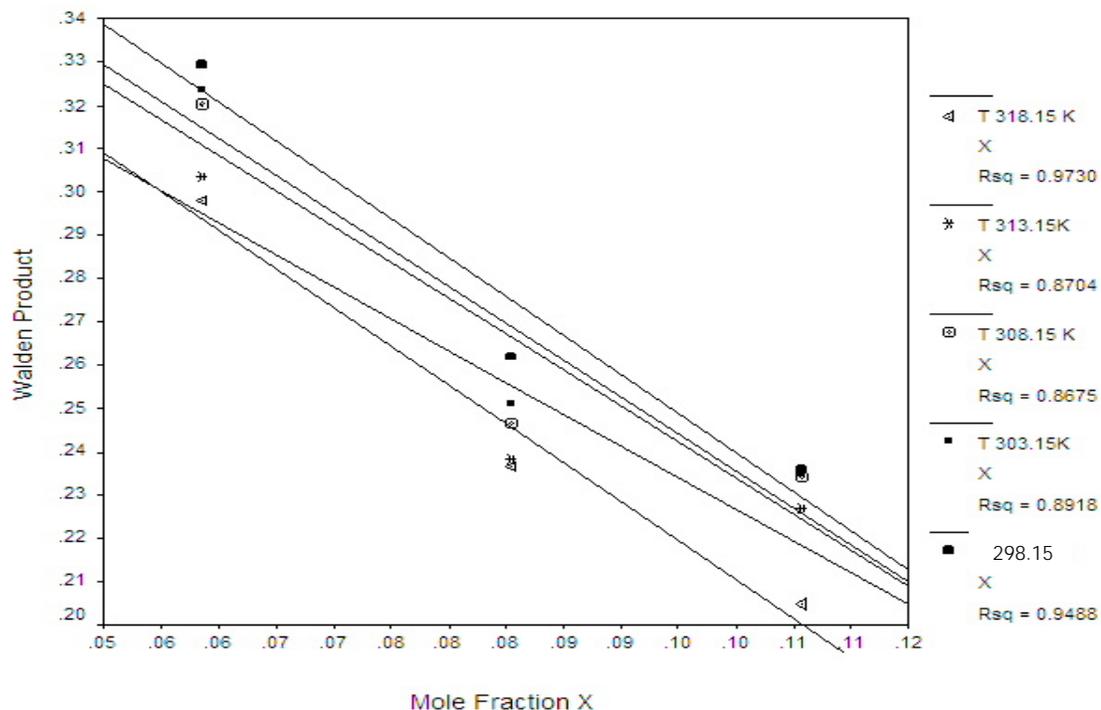
Mole fraction , X	T/K	$\Delta G^0$ , J mol <sup>-1</sup>	$\Delta H^0$ , J mol <sup>-1</sup>	$\Delta S^0$ , JK <sup>-1</sup> mol <sup>-1</sup>	$\Delta c_p^0$ , JK <sup>-1</sup> mol <sup>-1</sup>
0.0586	298.15	-282000	277000.0	1874.8247	2165.6279
	303.15	-291000	288000.0	1911.1608	2201.9639
	308.15	-301000	299000.0	1947.4968	2238.3000
	313.15	-311000	310000.0	1983.8328	2274.6360
	318.15	-321000	322000.0	2020.1689	231 0.9721
0.0855	298.15	9190.00	4660.00	-15.2067	-934.7114
	303.15	9300.00	-57.30	-30.8898	-950.3945
	308.15	9500.00	-4850.00	-46.5729	-966.0776
	313.15	9770.00	-9720.00	-62.2560	-981.7607
	318.15	10100.00	-14700.0	-77.9390	-997.4438
0.1108	298.15	9480.00	4710.00	-661.1382	-289.5871
	303.15	9580.00	3250.00	-676.8213	-294.4459
	308.15	9690.00	1770.00	-692.5044	-299.3048
	313.15	9830.00	259.00	-708.18749	-304.1636
	318.15	10000.00	-1270.00	-723.8705	-309.0225



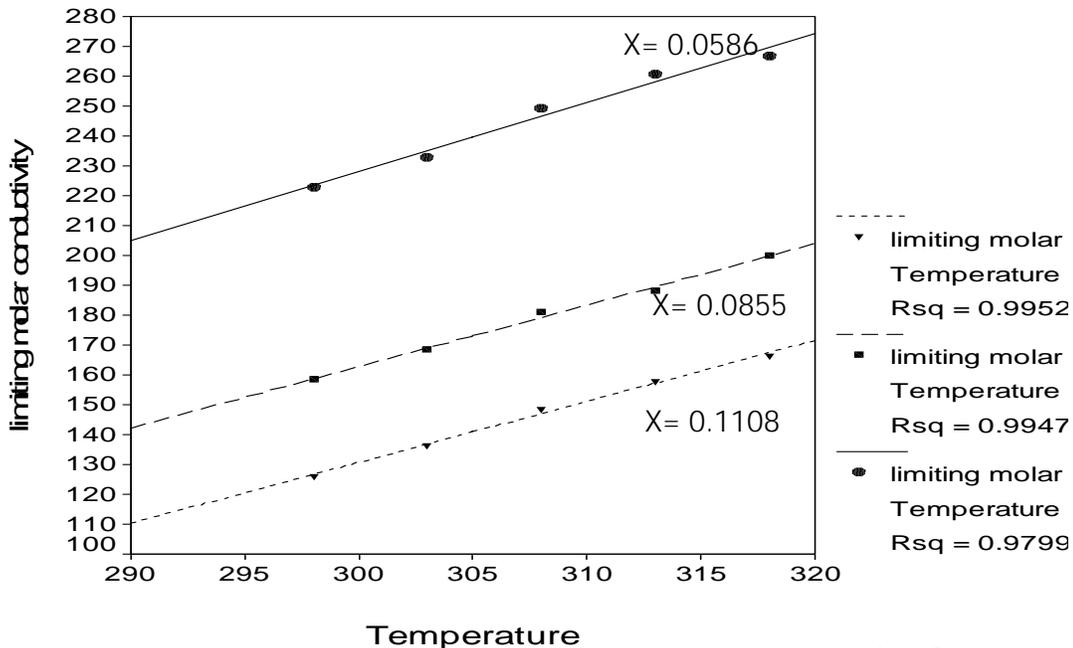
**Figure 1 :** plot the values of  $\log K$  versus to  $\sqrt{\alpha C_{\text{stoich}}}$  at temperature 289.15 K for mole fraction  $X = 0.1108$ .



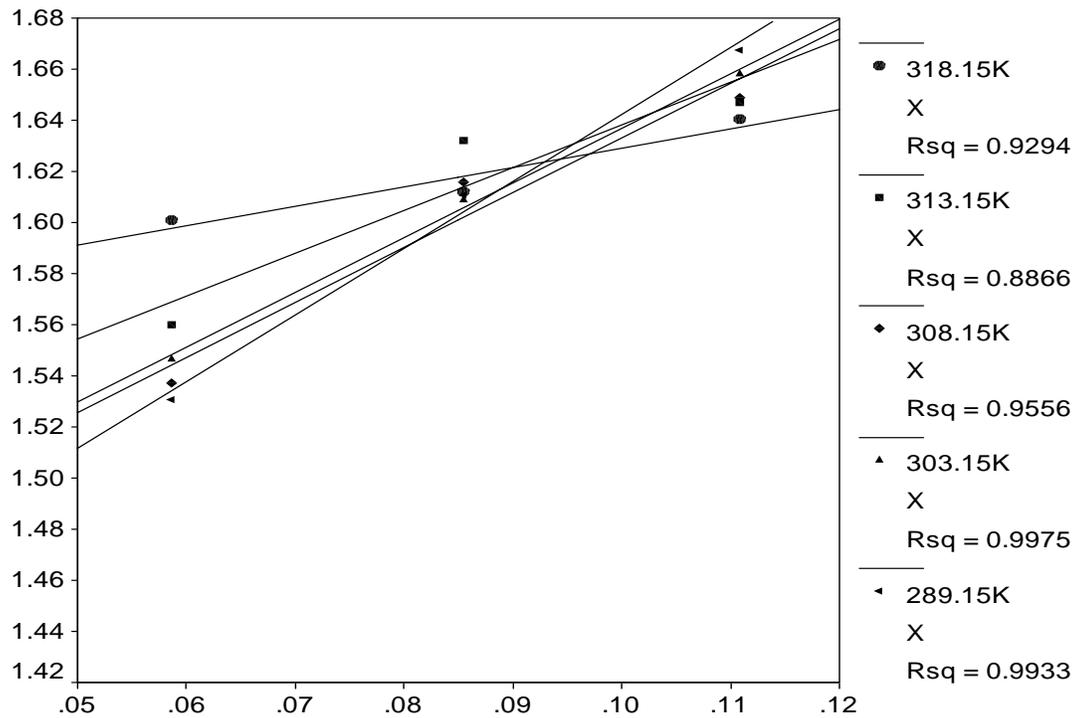
**Figure 2 :** plot the values of limiting molar conductivity ( $\text{S cm}^{-1} \text{mol}^{-1}$ ) of monochloroacetic acid electrolyte in ethanol - water mixtures at three solvent compositions ( $X$ ) over temperatures range (298.15 – 318.15) K.



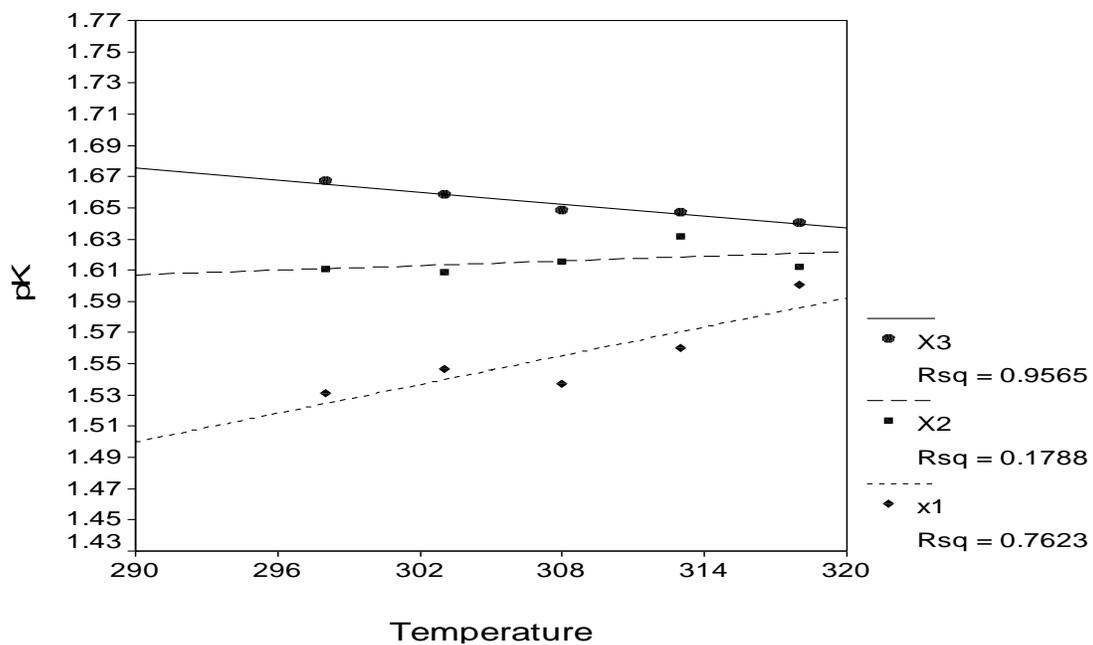
**Figure 3 :** plot the values of Walden product versus the mole fractions (  $X$  ) of monochloroacetic acid electrolyte in ethanol - water mixtures over temperatures range ( 298.15 – 318.15 ) K .



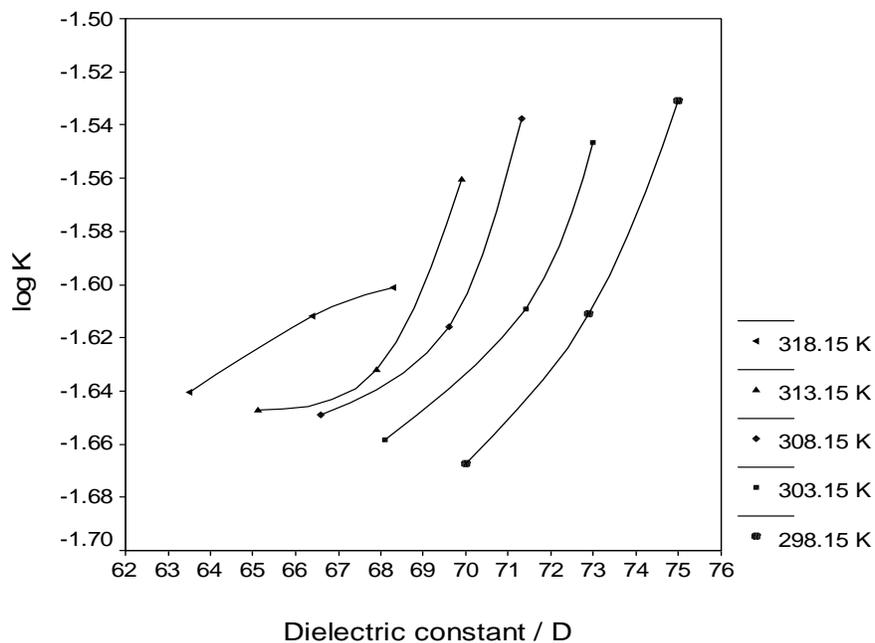
**Figure 4 :** plot the values of limiting molar conductivity ( $\Lambda_0$  S mol<sup>-1</sup> cm<sup>2</sup>) of monochloroacetic acid electrolyte in ethanol - water mixtures at three solvent compositions (  $X$  ) over temperatures range ( 298.15 – 318.15 ) K .



**Figure 5 : plot the values of pK versus the mole fractions ( X ) of monochloroacetic acid electrolyte in ethanol - water mixtures over temperatures range ( 298.15 – 318.15 ) K .**



**Figure 6 :** plot the values of  $pK$  versus the temperatures range over ( 298.15 – 318.15 ) K at three mole fractions (  $X$  ) of monochloroacetic acid electrolyte in ethanol -water mixtures .



**Figure 7 :** plot the values of logarithm  $K$  versus the dielectric constants over the temperatures range ( 298.15 – 318.15 ) K at three mole fractions (  $X$  ) of monochloroacetic acid electrolyte in ethanol + water mixtures .

## References

- 1- A.K.Covington and T.Dickinson , " physical chemistry of organic solvent systems " , second Edition , Plenum press , New York , (1973) .
- 2- J.S.Al-namer , Ph.D ,Thesis, college of science, university of Al-nahrian , June 1994 .
- 3- Y.Aihara , K.Sugimoto and S.P.william , *Journal of chemical physics* , **13** , 1981-1990 , 2000.
- 4- A.K.Shames M.Sc., Thesis, college of science , university of Al-nahrian , January 1996
- 5- Y.Marcus , " Ion solvation " , second Edition , Wiley Interscience , New York , (1985).
- 6- J.I.Bhat and T.N.Sreelatha , *Journal on Molecular Liquids* , 2005, **116**, 175 .

- 7- <http://www.weblakes.com/toxic/chloroacetic.HTML>.
- 8- R.Ghorbani, J.Ghasemi and B.Abdollahi, *Journal of hazardous Materials*, 2006, **131**, 13.
- 9- M.S.Niazi and M.I.Khan, *Journal of solution chemistry*, 1993, **22**, 437.
- 10- L.R.Dawson, R.A.Hagstrom and P.G.Sears, *Journal Electrochem. Soc.*, 1955, **102**, 341.
- 11- A.D.Penthybridge and S.S.Taba, *J.Chem.Soc. Faraday Trans.*, 1982, **78**, 1331.
- 12- M.S.Niazi and M.Hussain, *J. Chem. Eng. Data*, 1994, **39**, 48.
- 13- D.Nandi, D.K.Hazra, *J. Chem. Eng. Data*, 1998, **43**, 523.
- 14- J. Barthel and R.Neueder, *J. Electroanal. Chem.*, 1999, **47**, 78.
- 15- T. Zamir and T.Neueder, *J. Solution Chem.*, 2003, **32**, 463.
- 16- P. Halder and B.Das, *J. Chem. Eng. Data*, 2005, **50**, 1768.
- 17- N. G. Tsierkezos and I.E. Molinou, *J.Chem. Thermodynamics*, 2006, **38**, 1422.
- 18- I. E. Molinov and N. G. Tsierkezos, *J. Chem. Eng. Data*, 2001, **45**, 1399.
- 19- I. E. Molinov and N. G. Tsierkezos, *J. Chem. Eng. Data*, 2001, **46**, 1399.
- 20- M. M. Palaiologous, I. E. Molinou and N.G.Tsierkezos, *J. Chem. Eng. Data*, 2002, **47**, 1285.
- 21- N. G. Tsierkezos and I. E. Molinou, *Z. phys.Chem.*, 2002, **216**, 961.
- 22- TKA Company, manual's user, machine type " TKA DI 425 ", NIEDERLBERT, 05 MAY 2000.
- 23- N. H. Abood, M.Sc., Thesis, college of Education Ibn Al-Haithem, university of Baghdad, 2002.
- 24- M. S. Niazi, O.Fischer and E. Fischerova, *J. Solution Chem.*, 1986, **15**, 957.
- 25- D.R.Lide, "handbook of chemistry and physics" 84<sup>th</sup> Edition, CRC press, (2003-2004).
- 26- Brookhaven Corporate park, Instruction Manual for BI-870 Dielectric Constant Meter, Holtsville, New York, USA, First printer: January 2001.

- 27- A. M. Frahan and Q. A. Yousif, *journal of Um-Salama for Science* , 2006, **3**, 301.
- 28- K. Izutsu , " Electrochemistry in Nonaqueous Solution" first Edition , Wiley-VCH GmbH & KGaA , (2002) .
- 29- Z. Orekhova , M. BenHamo and A. Apelblat , *J. Solution Chem.*, 2005, **34**, 687.
- 30- C.P. Melanie , L.B. Sanford and P.M. David " Levine's Guide to SPSS for analysis of variance " Second Edition, L.E. Associates , Inc. publishers , New Jersey , (2003).
- 31- M.R. Wright, " An introduction to aqueous electrolyte solutions " , first Edition , John Wiley & sons ; Ltd , England , (2007) .
- 32- S. Glasston , " An introduction to Electrochemistry " , Tenth Edition , Affiliated East-West press ,PVT . LTD , New DELHI , (1942) .
- 33- J.O.M. Bockris , A.K.N. Reddy , " Modern Electrochemistry " vol. 1 , second Edition , Plenum press , New York , (1998) .
- 34- J.M. Saleh , N. Mohammed and N.A. Hakamet , *Iraqi J. Soc.*, 1990, **31**, 1.
- 35- A.N. Martin, "Physical chemistry" second edition , Philadelphia ; Lea and Febiger press , (1969) .
- 36- E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, 1951, **73**, 4939.