Dissociations constants and Association thermodynamic functions of glycine acid in Dimethyl formaide mixtures from conductance measurements

Ahlam. M. Farhan** * Qhatan Adnan yousife**

Date of acceptance 14/2/2006

Abstract

The dissociation of glycine in Dimethyl formamide mixtures over the temperature range 293.15-308.15 K , has been studied by direct conductance measurements. The acid dissociation at each temperature was investigated at solvent composition (X2) involving 0.141.

The conductance measurements enabled the estimation of the degree of the acid dissociation, the molar conductivity of the acid at infinite dilution and the activation energy for the movement of cation and anion ions the solvent mixture at infinite dilution .

The resulting data have been used to determine the dissociation constant and the associated thermodynamic functions for the acid dissociation in the solvent Mixture. At any temperature in the range 293.15-308.15 K.

The pKa_1 and pKa_2 increased with increasing temperature.

Introduction:

The study of solutions is of great importance because most of the interesting and useful chemical and biological processes occur in liquid solutions. All biological and many chemical systems are aqueous solutions containing various ions. The stability of biomolecular and the rate of many biochemical reactions are very much dependent on the type and concentration of ions present. It is important to have at least qualitative understanding of the behaviour of ions in solutions (1,2) .

The study of the behaviour of the amino acids in aqueous solutions is useful models for understanding the thermodynamics behaviour of proteins(3,4) .The physical and chemical properties of proteins are determined by its constituent amino acids (5) .

The structure of an amino acid in solution various with the pH of the solution, amine and carboxylic acid have conjugate acid-base forms in water that are dependent upon the pH of solution in which find themselves (6)

The study of the dissociation constant and the associated thermodynamic properties of acid mean of investigating the change in the solute-solvent interaction patterns that are attributed to the variation of the solvent composition. We have accordingly undertaken the dissociation of glycine in Dimethyl formamide mixture at various temperatures from direct conductance measurements.

There is a lack of knowledge regarding the dissociation of glycine in Dimethyl fromamide mixtures despite numerous studies on the dissociation and thermodynamic properties of the acid in a number of other solutions (6) .

---

*Department of Chemistry, College of science for women, Baghdad University.

**Department of Chemistry, College of Education, Al-Qadissiya University.

Experimental:

(a) Materials :-

Glycine 99% pure (BDH) , was used after re-crystallzation from doubly distilled water . They were dried and stored in a glass desiccator over P_2O_5. Dimethyl formamide (DMF) of purity > 99% obtained from fluka was passed through a freshly prepared activated molecular seive without any further purification. The solvent containing 40% W/W DMF was prepared by mass ratio using doubly distilled water and then used for preparation of amino acid in the concentration of study .

(b) Measurements :-

Viscosities were determined using a suspended level ubbelohde viscometer. The flow times were recorded electronically with an electronic timer of precision ± 0.015 and the temperature of the both was controlled to be better than ± 0.018. The instrument was calibrated with distilled water. Flow times were reproducible to 0.015(7). Tacussel electronique conductimeter, type CD810, was used to measured the conductivity of the deionized water and of the(8) prepared solutions with an accuracy of 1 ± 10^{-9} S-cm^{-1} .

The dielectric constants were measured using Radelkis precision dielectrometer type OH-302 of maxium error on the dielectric constant scale of (2%)(8) . The density and the dielectric constant data of (DMF) at various temperatures have been used to estimate the appropriate values of the Debye-Huckel-Onsugar constants A and B using the relation ships :

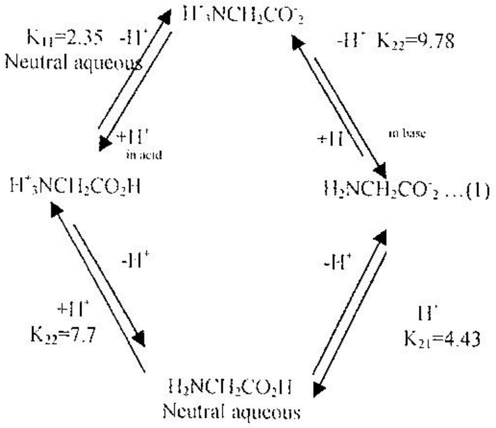
$$A = \frac{82.4}{\eta(DT)^{1/2}} \quad \text{and} \quad B = \frac{8.2 \times 10^5}{(DT)^{3/2}}$$

Where d , η and T represent respectively the Dielectric Constant , the viscosity and the temperature ; 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 (x) of Dimethyl formamide in the DMF + water mixture. The investigation covered one solvent compositions (x) which was 0.141 corresponding to 40% weight percentages of DMF in the mixtures.

Result and Discussion:

1. The degree of dissociation

The acid dissocation of amino acids offer interesting examples of the relations between the function K_a and the true or 'thermodynamic' constant Ka of glycine . In the dissociation of glycine (10)



The microscopic constants are K_{11}, K_{12}, K_{21}, K_{22} and so we define the first acid dissociation constant K_1, a macroscopic dissociation constant by

$$K_1 = \frac{(H+)[(+H_3NCH_2CO_2^-)+(H_2NCH_2CO_2H)]}{(+H_3NCH_2CO_2H)} \quad .(2)$$

And second acid-dissociation constant is given by

$$K_2 = \frac{(H+)(+H_2NCH_2CO_2^-)}{[(+H_3NCH_2CO_2^-)+(H_2NCH_2CO_2H)]} \quad ..(3)$$

An amino acid is a said to be isoelectric at the pH at which there are equal concentrations of the positively and negatively charged forms setting

$(H_3N^+ CH_2COO^-)$

And substituting from equations (2) and (3) yields

$$(H+)^2_{isoelectric} = K_1 K_2$$

Which may be written

$$pH_I = \frac{1}{2}(pK_1 + pK_2) \quad ....(4)$$

The onsager equation for incompletely dissociated electrolytes , can be written as(11,12)

$$\Lambda = \alpha[\Lambda_0 - (A+B\Lambda_0)(\alpha C)^{1/2}] \quad ..(5)$$

Where A and B are onsager constants and Λ_0 is the molar conductivity of the weak electrolyte at infinite dilution, Eqn.(5) may be written as:

$$\Lambda = \alpha\Lambda^- \quad ....(6)$$

Where

$$\Lambda^- = \Lambda_0 - (A+B\Lambda_0)(\alpha C)^{1/2} \quad ...(7)$$

$$\Lambda^- = \Lambda_0 - K(\Lambda c/\Lambda^-)^{1/2} \quad ...(8)$$

Λ^- is the molar conductivity of 1 mole of free ions, at the concentration C mole per liter, at the actual ionic concentration in the solution, where K , representing $A + B\Lambda_o$, is constant for a given solute in a particular solvent at a definite temperature.

In order to estimate the value of α in Eqn.(6), an approximate value of Λ_o for amino acid, for a given solvent composition and temperature, was first made by extrapolating the experimental data of Λ^- against $(c)^{1/2}$.

As a first approximation, Λ^- in the term. $(\Lambda c/\Lambda^-)^{1/2}$ of Eqn.(8) was then taken as equal to Λ_o and hence apreliminary value of Λ could be derived from Eqn.(8), by utilizing the experimental value of Λ at the concentration (c). The result for Λ^-, thereafter, inserted under the square root sign in Eqn.(8). thus obtaining a better value of Λ^- an here of α. Using such values of Λ^- and α in Eqn.(7), it was possible to derive the correct values of Λ_o from the plots of Λ^- values against the corresponding values of $(\alpha c)^{½}$.

Table 3 gives the resulting value of x_2 at a given temperature. The exact values of Λ_o could be derived, as mentioned earlier, from Λ^-, $(\alpha c)^{½}$ for solvent mixtures and temperatures and data obtained are presented in table 3.

The values of Λ_o (table 3) are then plotted aqainst the experimental temperature (T) as indicated in Fig. (1).

Fig. (1) shows that Λ_o at $x_2=0.141$ followed the sequence 308>303>298>293, implying an increase in Λ_o with increasing temperature.

The change in Λ_o with change of temperature in the range 293–308 K is seen in Fig. (1) to be almost linear suggesting a constant dependence of Λ_o values on temperature over the range refered to above . Thus, the increase of temperature invariably results in an increase of ion conductance. Since the conductance of an ion depends on its rate of movement, it seems reasonable to treat the conductance in a manner analogous to that employed for other processes taking at adefinite rate which increases with temperature, thus:

$$\Lambda_o = A\, e^{-E/RT} \quad .....(9)$$

where A is constant, which may be taken as being independent of temperature over relatively small range; E is the activation energy of the processes which determines the rate of movement of ions, R is the gas constant and T is the temperature in Kelvin , Eqn.(9) may be written as :

$$d\ln\Lambda_o/dt=(1/\Lambda_o)(d\Lambda_o/dt)=E/RT^2$$

and

$$E=\alpha RT^2 \qquad \ldots(10)$$

where $\alpha=(1/\Lambda_o)(d\Lambda_o/dt)$ is the temperature dependence of Λ_o.

From the slopes of the lines in Fig. (1) it was possible to evaluate the corresponding values of E, from Eqn.(10) , that cover the temperature range 293-308K. the such values of Λ_o have then been combined with the appropriate values of $d\Lambda_o/dt$ to calculate the values of α and E . Table 4 gives the values α and E glycine acid in Dimethyl form- amide at infinite dilutions.

2. The Dissociation constant for the acid

The relation between the function ka and the true or "thermodynamic" constant K of glycine may be written as :

$$K = Ka\, f^+ f^- \qquad \ldots\ldots..(11)$$

Where $Ka = \alpha^2 C / (1 - \alpha)$.

If the solution is sufficiently dilute for the Debye-Hukel law to applicable , it follows, for glycine type electrolyte, that

$$Log f+=Log f-=-A(\alpha C)^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

The ionic strength, $1/2\sum C_i Z_i^2$, being equal to $1/2[(\alpha C X_1^2)+(\alpha C X_1^2)]$. i.e; to αc .

Eqn.(12) may be expressed as :

$$LogK=LogKa-2A(\alpha C)^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

The plot Log ka , obtained at various concentrations C, against $(\alpha C)^{1/2}$ should be thus dive a straight line of intercept Log k .

Combining equations (6) and (13) , one may written :

$$\text{Log K} = \log\left[\frac{\Lambda^2 C}{\Lambda^{-}(\Lambda^{-}-\Lambda)}\right] - 2A(\Lambda C/\Lambda^{-})^{-2} \qquad \ldots\ldots(14)$$

Since Λ^{-} for various concentration can be obtained from conductance data (Table 2) and Onsager Eqn.(7). by method already described in the previous section, it would be possible to derive the values of the dissociation function ka for various acid concentration , and the ka_2 is obtained from the Eq.(13) :

$$Ka_2=4\alpha 2C2/1-\alpha \qquad \ldots..(15)$$

and , thereafter. calculate PI from Eqn.(4) .

Such results for the dissociation of glycine in Dimethyl formamide mixture at different temperature are given in (Table 5) .

The manner in which the pk values change with temperature as described in Fig. (3) .Suggests a relatively large dependence of pk on temperature;

The dissociation constants (k_1 and k_2) of glycine derived in the present work (Table5) are substantially less than those reported[8,14] for the acid in water and in a number of other solvents. This is likely to be due to greater basicity and lower dielectric constant of DMF mixture than water.

The dependence of pk values for glycine dissociation in DMF mixture an temperature could be expressed as:

$$PK=\frac{A_1}{T}-A_2+A_3T \qquad ...(16)$$

Where A_1,A_2 and A_3 are constants for a given solvent composition (x=0.141) over the temperature range 293-308k Inserting the appropriate values of pk and temperature from table (5) in Eqn.(16), the values of the constant (A_1.A_2.A_3) could be calculated and the results are given in table (6).

3. Thermodynamic of the acid Dissociation :

The standard thermodynamic function for glycine dissociation in DMF mixture may be calculated from equation [15]:

$$\Delta G^o=(R\ln 10)(A_1-A_2T+A_3T^2) \ldots\ldots(17)$$

$$\Delta H^o=(R\ln 10)(A_1-A_3T^2) \ldots(18)$$

$$\Delta S^o=(R\ln 10)(A_2-2A_3T) \ldots(19)$$

$$\Delta C^o_{Po}=(R\ln 10)(-2A_3T) \ldots(20)$$

Table (7) summarizes the values of the standard thermodynamic functions which have been derived by Eq.(17) to (20) for the dissociation of the glycine in DMF mixture at four temperature .

From the Table (7) could be obtained the information as following:

1. The value of ΔG° is negative values for pk is refer to spontaneous reaction and high positive values of ΔG for pka , at all temperature reflect the non spontaneous reaction .
2. The values of ΔH is high positive values at all temperature is reflect the large endothermic for pk_1 and negative value for pk_2 is reflect Exothermic step .
3. The values of ΔS° were generally positive which did not change significantly with the variation of temperature .
4. ΔC°_p values were negative for solvents with x_2=0.141, ΔC°_p reflects , the effect of temperature on H^o so that one can write

$$C^o_P=dH^o/dT \qquad ...(21)$$

It is shown in Table(7) that the negative sign of ΔC°_p, is due to decreasing tendency of ΔH° with the increase temperature .Thus the relatively more endothermic behavior and the greater increase in ΔS° .

The two sorts of interactions have to be considered ; the first the maximum interaction between the two components of thesolvent mixture and the second is the expected strong solute – solvent interaction due to the polarity and possibility of hydrogen bounds formation .

The values of ΔS for pka decrease because the decomposition of glycine is very order the reactant at path second stage pka_2 .

Moreover, the high positive ΔH values at this stage indicates that the undissociated acid molecules are highly stable so that the release of these molecules and subsequent dissociation stage should highly be endothermic.

Table 1: Dielectric Constants (D) , Viscosity , and the Onsager Constants (A and B) for Dimethyl Formamide at Four Temperature

X	T / K	Dielectric (D)	Viscosity	(A)	(B)
0.1410	293	63.01	2.338248	1.418005	0.3268574
	298	62.22	2.039288	1.24859	0.3497220
	303	60.32	1.810804	1.103171	0.3518375
	308	54.39	1.561893	0.904360	0.3781892

Table 2 : Values of Λ (S mol^{-1} cm^2) , Λ˚ (S mol^{-1} cm^2) , α and Ka (mol L^{-1}) For varsions concentrations C (mol L-1) Of Glycine in Dimethyl Formamide + Water Mixture at Different Temperature (293 - 308) K at $x_2 = 0.141$

T/K	Concentration	Λ	Λ•	α	Ka_1	Ka_2	PI
293	0.0179	1.769	1.931089	0.916063423	0.17895872	0.011737928	0.095348
	0.033826	0.9093	1.935254	0.469860804	0.014086372	0.000895528	0.014086
	0.05794	0.728	1.885942	0.386013992	0.014061321	0.001257962	0.014061
	0.0890987	0.6351	1.830806	0.346896394	0.016416813	0.002029645	0.016417
	0.194837	0.342	1.79544	0.190482556	0.008732843	0.00129641	0.008733
	0.327665	0.2738	1.667067	0.164240549	0.01057571	0.002276565	0.010576
298	0.0179	1.8033	2.039723	0.884090634	0.120705784	0.007640783	0.064173
	0.033826	1.0221	2.029986	0.503501009	0.017271616	0.001176641	0.017272
	0.05794	0.6448	2.018521	0.319441809	0.008687538	0.000643172	0.008688
	0.0890987	0.52	1.98381	0.262121877	0.008296469	0.000775047	0.008296
	0.194837	0.2997	1.941153	0.154392776	0.005492331	0.000660869	0.005492
	0.327665	0.2818	1.83601	0.153485003	0.009118582	0.001834355	0.009119
303	0.0179	1.9759	2.329072	0.84836364	0.084959857	0.0051610703	0.04506
	0.033826	1.069	2.326244	0.459539068	0.013216949	0.000821797	0.013217
	0.05794	0.6606	2.318815	0.284886893	0.006575801	0.00043417	0.006576
	0.0890987	0.54708	2.28441	0.239484156	0.006719186	0.000573489	0.006719
	0.194837	0.3505	2.227688	0.157338011	0.005723812	0.00070186	0.005724
	0.327665	0.28413	2.16428	0.131280535	0.006500673	0.001118541	0.006501
308	0.0179	2.1541	2.52732	0.852325784	0.088056133	0.00537376	0.046715
	0.033826	1.1621	2.524741	0.460284837	0.013278205	0.000826945	0.013278
	0.05794	0.7533	2.510253	0.300089274	0.007454814	0.000518473	0.007455
	0.0890987	0.6084	2.477396	0.24558044	0.007122722	0.000623406	0.007123
	0.194837	0.38828	2.418168	0.160567835	0.005984156	0.000748847	0.005984
	0.327665	0.3252	2.34815	0.138492004	0.007294913	0.001324143	0.007295

Table 3 : Values of the Molar Conductivity Dimethyl Formamide at Infinite Dilution (Λ° / S mol^{-1} cm^2) at $x_2 = 0.141$ And Different Temperature (293-308) K .

X_2	Temperature			
0.141	293	298	303	308
	Values of Λ°			
	1.96	2.05	2.33	2.53

Table 4 : The Temperature coefficients (α) and the energies of Activation (E) at Infinite Dilutions as a Function of the $X_2 = 0.141$

X_2	dΛo / dt	Λo	Slop	E(kJ/mole)	α
0.141	0.048	470.25605	0.08	2.5365914	3.3x10-3

Table 5 : Values of pK For the dissociation of Glycine in Dimethyl Formamide + Water Mixtures at Four temperature at $X_2 = 0.141$

X_2	T / K	pK1	pK2	PI
0.141	293	0.6	2.42	0.85
	298	0.82	2.64	1.06
	303	0.84	2.77	1.14
	308	0.92	2.78	1.16

Table 6 : Values of the Temperature Dependence Constants A_1 , A_2 , and A_3 at $X_2 = 0.141$ of DMF + Water

Values of P	A_1	A_2	A_1
pKa1	0.5119	0.002950057	9.03 x 10-6
pKa2	0.5119	0.00295	9.03 x 10-6
PI	0.6258	0.003682	5.119 x 10-6

Table 7 : The Standard thermodynamic Functions ForThe Dissociatation of Glycine in DMF + Water of Four Temperature (T / K)

Values of P	T/K	ΔG° J / mol	ΔH° J / mol	ΔS° J / mol	Δcp° J/K*mol
pKa_1	293	-312.38503	3.54117498	1.07892904	-0.084905
	298	-317.97605	3.11302709	1.07748015	-0.086354
	303	-323.35983	2.67763474	1.07603125	-0.087802
	308	-328.73637	2.23499793	1.07458236	-0.089251
pKa_2	293	7.930640631	-4.9445770	-0.0439427	-0.099195
	298	8.154586112	-5.4447839	-0.0456354	-0.100887
	303	8.386995331	-5.9534560	-0.0473281	-0.010258
	308	8.627868288	-6.4705889	-0.0490209	-0.104273
PI	293	-0.25341821	3.48934172	0.01277392	-0.056187
	298	-0.31489179	3.20600921	0.01181510	-0.057145
	303	-0.37156923	2.91788258	0.01085627	-0.058104
	308	-0.42345356	2.62496183	0.00989745	-0.059063

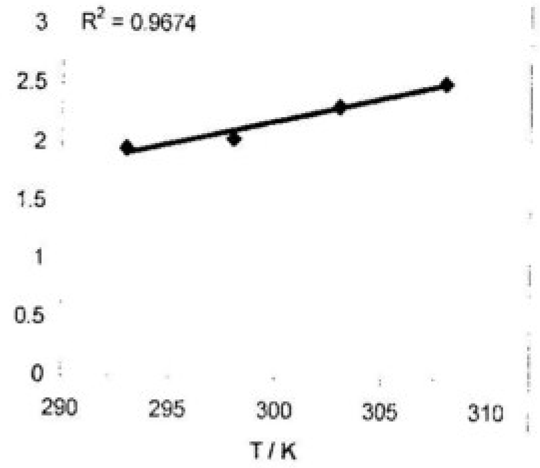


Fig 1 : Molar Conductivity (S mol^{-1} cm^{-2}) of Glycine in DMF + Water Mixture as a Function of the Temperature T

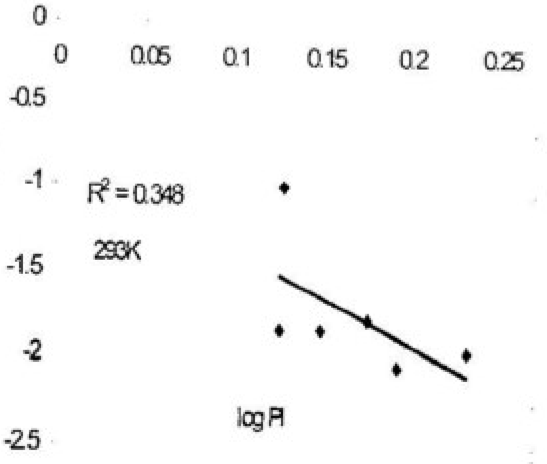


Fig 2 : Log PI Versus $(\alpha C)^{1/2}$ C expressed in Moles Per Liter

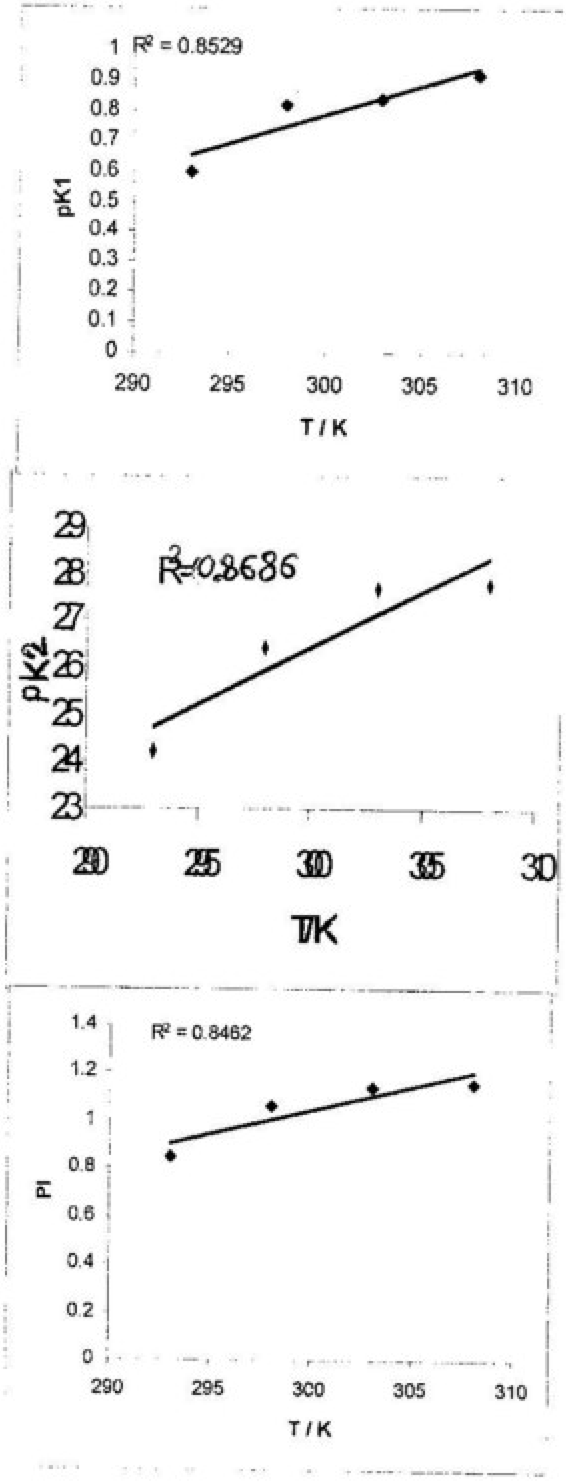


Fig 3 : pKa_1 pKa_2 and PI Value of Glycine as a Function of Temperature T

References:-

1. Raymond, C. 1981. Physical chemistry with application to biological system, NewYork,2nd ed.
2. Geoffery, L., William, W., and Dennis, E., 1993. Principle of Biochemistry, WCD Wm. C. Brown publishers Dubuque, 3rd ed.

3. Peter, A. M. 1993. Harpers Biochemistry, Drwael California, 26th ed.
4. Zena, M. S. 2005. A study of some physical properties for amino acid solutions in aqueous and acidic media over temperature range (293.15-308.15) k M. Sc, thesis, Naharin University .
5. Wade, L. G. 1999. Organic chemistry. Prentice Hall, Inc. New Jersey, 4th ed.
6. Philip, S. B. and Christina, A. B. 2000. Organic chemistry; A brief Survey of concepts and application. Prentice Hall Inc. London 6th ed.
7. Isa, S. A. and Farhan, A. M. 2000. Partial molal Volume and viscosity study of glycine, DL-Alanine and DL-Valine in aqueous dimethyl formamide solutions at 298k. Iraqi, J. Sci, 41A, (3):64-77.
8. Al-Namer, J. S. 1994. The Electrochemical behavior of hydrochloric acid glycine and DL-Alanine in glycerol – water and ethylene glycol-water mixtures – ph. D. thesis, Naharin University .
9. Al-Noori, M. K. , Al-Namer, T. S. and Isa, A. S. 2001. Partial molal Volume and viscosity study of glycine and DL-Alanine in ethylene glycol-water mixture at different temperatures, Iraqi, T. Sci, 42A, (2): 12.
10. Alberty A. R. and Daniel, F. 1984. Physical chemistry wiley eastern limited, 5th ed.
11. Robinson, R. A. and Stockes, R. H. 1970. Electrolytic solution. Butter Worths, 2nd ed, P.94.
12. Hrned, H. S. and Owen, B. B. 1950. The physical chemistry of Electrolytic solution, Reinhold, New York.
13. Azzouz, A. S.P and Othman, S. S.1997. The dissociation constants of benzo aldoximex, J. Edu. Sci. 26, 86.
14. Salah, R. A. 1985. Electrochemical studies of the thermodynamics of dissociation and transfer of glycine. M. Sc. thesis, Baghdad University.
15. Jalal, M. S. Nasrin, M. and Naema, A. H., 1990, Dissociation constants and Association thermodynamic functions of acetic in urea water mixtures from conductance measurement, Iraqi, J. Sci, 31,1,1.

الدول الثرموديناميكية وثوابت التفكك لحامض الكلايسين في مزيج من داي مثيل فورمايد من قياسات التوصيلية

احلام محمد فرحان* قحطان عدنان يوسف**

* أ.م.د./ جامعة بغداد/ كلية العلوم للبنات/ قسم الكيمياء.

** م.م./ جامعة القادسية/ كلية التربية.

الخلاصة :

تمت دراسة تفكك حامض الكلايسين من مزيج من داي مثيل فورمايد بنسبة وزنية 40% w/w في درجات الحرارة التي تراوحت بين 293.15 – 308.5 K وذلك من القياسات المباشرة للتوصيل الكهربائي للمحاليل واشتملت الدراسة في كل درجة حرارية على كسر مولي وهو 0.141 ساعدت قياسات التوصيلية على تقدير درجة التفكك وعلى ايجاد التوصيلية المولارية للحامض عند التخفيف النهائي للمحلول بالاضافة الى ايجاد طاقة التنشيط لحركة الكاتيون والانيون عند التخفيف النهائي.

واستخدمت النتائج المستحصلة في ايجاد ثابت تفكك والدوال الثرموديناميكية للحامض في مزيج المذيب وفي كل درجة من الدرجات الحرارية في المدى 293.15 –308.15 كلفن وكانت قيم pKa_1 , pKa_2 تزداد مع ازدياد درجة الحرارة .