Medium Effects On the Dissociation Reactions Of Adipic Acid In Ethanol - Water Mixtures.

G.A.El-Naggar[a], M. El- Batouti[b], and A.A. Zaghloul[b].

a) Chemistry Department, Faculty of Education, Damanhour Branch, Alexandria University, Alexandria, Egypt.

b) Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

Abstract

The first and second dissociation constants of adipic acid have been determined by a precise emf method in water and in aqueous binary mixtures of ethanol, over a wide range of solvent composition (0-70%(w/w) ethanol). Measurements were conducted at different temperatures ranging from 30 °C to 60 °C at intervals of 10 °C, by emp measurements. The thermodynamic parameters ($\Delta H°$, $\Delta G°$ and $\Delta S°$) for the first and second dissociation reactions have been computed, analyzed and discussed in terms of solute-solvent interactions. The pK values have been correlated with the mole fraction of the organic solvent and the effect of dielectric constant on the dissociation processes was then discussed.

Introduction

The effect of solvent composition on the dissociation of weak acids is of great interest in chemical analysis. A number of papers [1-10] deal with solvation of ions and its effect on dissociation of weak acids. Nevertheless, this problem still attracts attention[11-20]. Therefore, the present article is devoted to the study of medium effects on the pK_a values of adipic acid in aqueous solutions containing varying mole fractions of ethanol which is amphiprotic solvent. Water is very structured solvent and although it interacts strongly with acids and dissociated ions, the energy needed for

formation of a cavity is very high. Ethanol is a solvent with lower polarity and hydrogen bonding abilities, and therefore it interacts less with the solute but it is also a less structured solvent and the energy needed for formation of a cavity is much lower than in water. The ethanol - water mixed solvent is the solvent preferred by acids and they are preferentially solvated by it. It has polarity and hydrogen bonding abilities comparable to those of water but it is constituted by two different kinds of molecules, water and ethanol it is unlikely that it can form a very compact structure. Thus, the solvation of the acid by this mixed solvent is reference to ethanol in favored by its stronger polarity and hydrogen bonding abilities. Solvation of the acid by the mixed solvent in reference to water is unfavored by its weak polarity and hydrogen bonding abilities, but this is overwhelmed by its much less compact structure.

The thermodynamic acidity constants of adipic acid were evaluated from the results of emf measurements. This method[12,23] has been proved to be the most precise and direct method for the evaluation of dissociation constants at zero ionic strength of the acid in water and organic solvent.

Experimental

Materials

Adipic acid (B.D.H) was recrystallized and dried. Ethanol (Prolabo) was purified as described previously[22]. Stock solutions of HCl [= 0.2 m (mol kg^{-1})] were analysed by AgCl weighings, and Na$_2$CO$_3$ (dried at 300 °C for 3 hr) were made up, by weight from (B.D.H.) Analar samples.

Methods and Measurements

K_1 and K_2 determinations were based on the emf measurements of the cell ; Glass electrode/HCl (m$_1$), H$_2$ L (m$_2$), Na$_2$CO$_3$ (m$_3$)/AgCl$_{(s)}$/Ag, where H$_2$L = adipic acid; m$_1$, m$_2$ and m$_3$ are the molal concentrations of HCl, H$_2$L and Na$_2$CO$_3$ respectively. The practical work has been simplified by adopting a practice[12,23] which prevents movements of the electrode between its calibration and usage. This is preferable to the technique[24,25] of transfering the glass electrode from an HCl solution to an acid ligand solution followed by extrapolation of timed reading to compensate for any emf drifts. This procedure is considerably faster than that required with a

Pt/H$_2$ electrode where each measurement necessitates refilling with a fresh buffer solution. Moreover several values of K_1 and K_2 could be computed from a single run. The buffer compositions were taken as [H$_2$L]: [Na$_2$CO$_3$] $\cong$ 3:1 for K_1 and 1.2:1 for K_2 work. About 230 g of the required wt% ethanol (to ± 0.01 g) was weighed into the cell together with sufficient dilute HCl containing the required wt% ethanol ($\cong$ 0.035 m) to make $\cong$ 0.0015 to 0.0025 m (addition by weight pipette to ± 0.1 mg) with the electrodes in positions, the cell was equilibrated at the desired temperature. The temperature was controlled to ± 0.01°C, this could take up to three hours, the HCl solution was then given a short stir (5 seconds) by a fitted microstirrer and left to settle until emf (E$_o$) was constant (30 min). Up to six additions to stock buffer were then added by weight pipette. In the first addition about 15 g of stock buffer solution were added while in the latter additions, about 8g of this solution were added in each case. After each addition the solution was stirred and emf of the cell then monitored to constancy. The time needed could vary from 1 hour for the first addition for a K_2 series (the point of the greatest emf change) down to $\cong$ 15 minutes for the latter additions and also for all K_1 series. The constancy of the emf values was checked by the difference between the first and the last readings which was never more than ± 0.1 mV. Measurements to ± 0.1 mV were made with a digital pH meter (Beckman type). The AgCl electrode was made by plating a thin spiral Pt wire with Ag in 0.5% KAg(CN)$_2$ for $\cong$ 1 hour with a 9-V battery followed by electrolysis for AgCl in 0.05 M HCl with a 9-V battery for 20 seconds.

Results And Discussion

Treatment of Data for the Determination of pK Values

The first and second dissociation constants (K_1 and K_2) of adipic acid have been determined in ethanol-water media of varying compositions (0-70 % (w/w) ethanol) within the temperature range (30 °C -60 °C). The expressions used for calculating pK$_1$ and pK$_2$ are,

$$K_1 = [H^+][HL^-] \gamma_H \gamma_{HL} / [H_2L] \tag{1}$$

$$K_2 = [H^+][L^{2-}] \gamma_L / [HL^-] \tag{2}$$

$$K_{NaL} = [Na^+][L^{2-}] \gamma_L / [NaL^-] \tag{3}$$

$$-\log\gamma_i = AZ_i^2\left[I^{\frac{1}{2}} / (1 + BI^{\frac{1}{2}}) - QI \right] \tag{4}$$

$$E_{cell} = E^o_{cell} - k^{'} \log([H^+][Cl^-]\gamma_H \gamma_{Cl}) \tag{5}$$

$$k^{'} = 2.3026 \ RT / F$$

where I and γ represent ionic strength and activity coefficient respectively (γ_{H_2L} was negligible i.e. close to 1). The Debye-Huckel constant "A" was calculated for each temperature and each solvent composition while values of the constants B and Q, were taken as 1.3 and 0.3 respectively[12]. The E^o_{cell} was calculated from Eqns. (4) and (5) by knowing E^o_{cell} of the diluted HCl solution (I = [HCl]). If the stoichiometric molal concentrations of HCL, H_2L and Na_2CO_3 are m_1, m_2 and m_3, respectively, the following equations are used together with Eqns. 1-5 for calculating K_1.

$$[H_2L] = m_1 + m_2 - 2m_3 - [H^+] + [L^{2-}] + [NaL^-] \tag{6}$$

$$[HL^-] = m_2 - [H_2L] - [L^{2-}] - [NaL^-] \tag{7}$$

Approximate values of $[H^+]$ on the addition of buffer solution were calculated from Eqns. (4) and (5) with $I = m_1$ followed by the use of Eqns. (6) and (7) with $[L^{2-}] = 0$ and $[NaL^-] = 0$ in the first cycle. The subsequent value of I was used to recalculate $[H^+]$ followed by determining of $[L^{2-}]$ via Eqn. (2) with published or estimated values of K_2. $[NaL^-]$ was calculated from Eqn. (3) using $K_{NaL} = 0.2$. If the present estimates of K_2 were significantly different, the calculations were repeated until the difference between successive values of $[H^+]$ agreed to $\Delta[H^+] \leq 1 \times 10^{-9}$ m, K_1 was then obtained from Eqns. (1) and (4). For K_2, $[H^+]$ was calculated as described above and then by applying Eqns. (8) and (9).

$$[HL^-] = m_1 + 2 m_2 - 2 m_3 - [H^+] - 2[H_2L] \tag{8}$$

$$[L^{2-}] = m_2 - [H_2L] - [HL^-] - [NaL^-] \tag{9}$$

with $[H_2L] = 0$ and $[NaL^-] = 0$ in the first cycle followed by the use of Eqns. (1) and (3) for calculating $[H_2L]$ and $[NaL^-]$, respectively. K_2 was calculated from Eqns. (2) and (4) when the difference between two successive values of $[H^+]$ agreed to $\Delta[H^+] \leq 1 \times 10^{-9}$ m . All computations were performed by means of Basic computer programmes.

Some of the obtained K_1 and K_2 values for the different ionic strengths and temperatures are presented in Table (1). It is obvious that most of the K_1 and K_2 values of a single run varied with ionic strength. Accordingly, the extrapolated K_1 and K_2 at zero ionic strength were computed by the least squares method. This method was also used earlier[12,23], and was found to be valid and efficient under different experimental conditions. The computed pK_1 and pK_2 values at zero ionic strength for different solvent compositions and temperatures are shown in Table (2) together with their respective estimates of errors. These values readily reflect the influence of medium composition medium on the first and second ionization constants. The effect of changing the solvent on the dissociation constant of a weak acid is an interesting means of inferring changes in the pattern of solute-solvent interactions in binary mixed solvents such as ethanol - water mixtures. The dissociation constant of a weak uncharged acid (e.g. adipic) expressed by a process involving a net increase in solvated ions, is sensetive to changes in the dielectric constant (D) of the medium. Hence, a decrease in D, by increasing the organic solvent composition in the medium, would increase the pK values as can be observed from Table (2). So far as the effect of solvent change on the dissociation constant is concerned , the second dissociation constant is more depressed by changing solvent composition than the first dissociation constant since the electrostatic effect due to the negative charge on the first carboxylate ion is more readily transmitted to the seat of the second dissociation as the solvent composition increases. The stabilization of the intramolecular hydrogen bond with increasing solvent composition increases the dissociation constant K_1 of the uncharged acid at the expense of K_2 for the acid anion, so that K_1/K_2 ratios increases. The presence of such intramolecular hydrogen bonding was observed in many dicarboxylic acids[26] and it was stated that the strain as a result of steric crowding of carboxyl groups is relieved to some extent by the formation of intramolecularly hydrogen bonded mono-anion. In aqueous medium[27] there is a strong hydrogen bonding of the carboxylate ion and to a much smaller extent of the carboxyl to the solvent. The addition of ethanol to water causes the hydrogen bond donating capacity of the medium to be changed gradualy so that hydrogen bonding of the carboxylate

Table (1): Some values of K_1 and K_2 at different compositions and different temperatures for adipic acid.

30% — K_1

	50°C ($-E_0$ (mV) = 545.7, $-E_1$(mV) = 2.54, 10^3 m_1 = 6.022)				40°C ($-E_0$ (mV) = 483.2, $-E_{11}$(mV) = 189.5, 10^3 m_1 = 5.064)			
10^3 m_2	10^3 m_3	$-E$(mV)	10^3 I	10^3 K_1	10^3 m_3	$-E$(mV)	10^3 I	10^3 K_1
20.644	5.174	157.1	10.611	5.245	5.269	65.8	10.614	1.659
31.695	7.944	142.9	16.181	5.254	7.850	56.9	15.782	1.796
40.134	10.059	138.1	20.489	5.458	10.143	54.5	20.386	2.022
50.149	12.569	135.7	25.608	6.012	12.741	52.6	25.602	2.236
60.011	15.040	132.2	30.665	6.106	15.249	52.6	30.637	2.564
67.744	16.979	131.8	34.608	6.674	17.227	52.6	34.607	2.829

50% — K_2 / 70%

	60°C ($-E_0$ (mV) = 601.9, $-E_1$(mV) = 280.3, 10^3 m_1 = 4.317)				60°C ($-E_0$ (mV) = 590.3, $-E_{11}$(mV) = 278.8, 10^3 m_1 = 5.221)			
10^3 m_2	10^3 m_3	$-E$(mV)	10^3 I	10^3 K_1	10^3 m_3	$-E$(mV)	10^3 I	10^3 K_1
9.926	7.940	62.5	18.792	4.943	9.076	22.5	20.688	9.531
14.855	11.884	52.8	29.619	5.188	12.883	14.3	31.174	1.214
19.868	15.894	49.1	40.727	5.679	16.303	11.8	40.699	1.422
24.845	19.876	46.9	51.761	6.107	20.624	10.5	52.582	1.676
28.777	23.022	46.0	60.489	6.544	23.316	9.9	60.016	1.816
32.736	26.189	45.3	69.278	7.004	25.094	9.7	64.926	1.916

Table (2). pK_1 and pK_2 values of Adipic acid in ethanol-water mixture, and dielectric constant (D) at different temperatures.

wt %	T°C	30	40	50	60
0	pK_1	441 ± 003	4.31 ± 0.01	4.28 ± 0.01	4.19 ± 0.01
	pK_2	5.11 ± 0.02	5.27 ± 0.02	5.33 ± 0.03	5.40 ± 0.01
	D	78.73	73.12	69.85	66.63
10	pK_1	4.28 ± 0.12	4.11 ± 0.01	4.08 ± 0.15	3.85 ± 0.18
	pK_2	5.23 ± 0.04	5.25 ± 0.05	5.29 ± 0.09	5.34 ± 0.05
	D	70.79	67.86	64.42	61.38
30	pK_1	4.52 ± 0.18	4.44 ± 0.04	4.43 ± 0.04	4.29 ± 0.05
	pK_2	5.85 ± 0.03	5.99 ± 0.02	6.01 ± 0.02	6.31 ± 0.04
	D	58.88	56.73	53.70	50.93
50	pK_1	5.07 ± 0.16	5.04 ± 0.04	5.03 ± 0.09	4.97 ± 0.06
	pK_2	5.91 ± 0.07	6.10 ± 0.22	6.37 ± 0.05	6.49 ± 0.02
	D	47.86	45.29	42.86	40.64
70	pK_1	5.11 ± 0.06	5.09 ± 0.03	5.08 ± 0.05	5.04 ± 0.04
	pK_2	7.18 ± 0.01	7.31 ± 0.01	7.38 ± 0.08	7.40 ± 0.02
	D	37.15	34.87	32.81	30.83

ion with solvent appears to decrease gradually[27] giving the chance to such intramolecular hydrogen bonding to increase. This finding is confirmed from Table (2) and the largest value of K_1/K_2 has been obtained for 70 % (w/w) ethanol and was found to be 165.3. Comparing this value with that obtained in 70 % (w/w) methanol for the same acid[28], it was found that the latter value is higher and equal to 307.9 indicating greater stabilization of the intramolecular hydrogen bonding in methanol-water binary mixture and reflecting a difference in hydrogen bond donating capacity between the two media.

The pK_1 and pK_2 values of adipic acid in a ethanol - water mixture were found to be linearly correlated with the mole fraction of ethanol (X).

The correlations take the forms:

$$pK_1 = pK^w_1 + 4.239 \; X_{EtoH} \qquad (10)$$
$$r_1 = 0.92$$
$$pK_2 = pK^w_2 + 8.181 \; X_{EtoH} \qquad (10)$$
$$r_2 = 0.948$$

where $pK_{1 \; or \; 2}$ is the pK value in each mixed solvent, $pK^w_{1 \; or \; 2}$ is its pK value in water. These Eqns. are represented graphically in Fig. (1) at 40°C, and from such plots the pK at any particular composition of the organic solvent can be predicted.
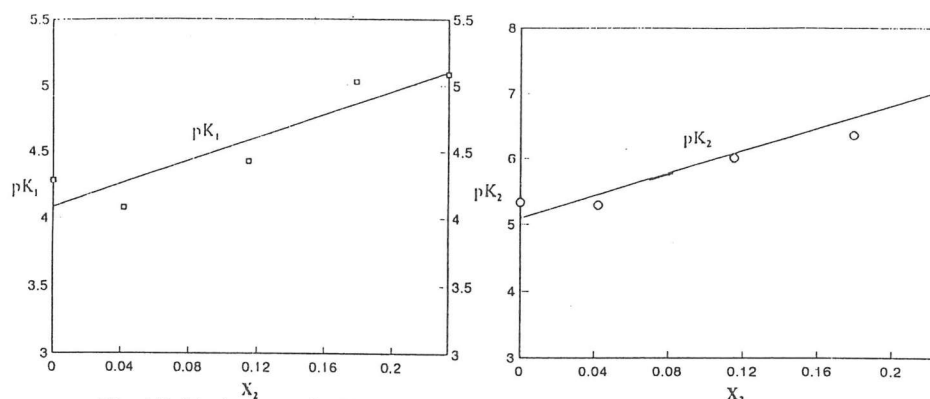

Fig.(1) Variation of pK1 and pK2 with mole fraction ethyl-alcohol at 40°C

The strength of an acid in a particular mixed solvent depends on many factors. However, assuming that both the Bronsted theory[29] and Dension - Ramsay - Gilkerson theory[30] can be applied to an H_2L system, if an acid H_2L is transferred from water into non-aqueous solvent it will be weakened or strengthened by a constant amount, that is $\Delta pK_{1 \; or \; 2} = pK^s_{1 \; or \; 2} - pK^w_{1 \; or \; 2}$. It is significant for a certain purpose to correlate the $pK_{1 \; or \; 2}$ values for different H_2L acid type in ethanol - water mixtures. Table (3) shows the ΔpK_a values for some dicarboxylic acid in the ethanol-water mixed solvent and water[9,10]. The similarity of $\Delta pK_{1 \; or \; 2}$, with an approximate error of $\pm$ 0.2, for these acids at each composition of solvent means that the dicarboxylic acids are weakened by an approximately constant amount regardless of acid strength. If this finding is extrapolated to other dicarboxylic acids, it can be deduced from Eqns. (10) and (11) that $pK_{1 \; or \; 2}$ values for a dicarboxylic acid in ethanol - water mixtures can be

Table (3): ΔpK_a values in different solvent composition for some dicarboxylic acids at 40°C.

Wt%	10	30	40	50	60	Wt%	10	30	40	50	60
acids		ΔpK_2				acids		ΔpK_1			
succinic	0.2	0.7	0.9	1.4	1.9	Succinic	0.2	0.6	0.8	0.9	1.3
Malic	0.1	0.7	0.9	1.1	1.5	Malic	0.1	0.5	0.8	0.8	1.1
Tartaric	0.2	0.5	0.9	1.3	3.8	Tartaric	-	0.5	0.8	1.1	1.4
Malonic	0.2	0.6	0.8	1.7	2.4	Malonic	0.1	0.4	-	0.6	0.9

predicted provided that its pK^w is known. This approximate rule for the calculation of $pK_{1 \; or \; 2}$ values is very useful in non - aqueous titrimetry because once the $pK_{1 \; or \; 2}$ values of a dicarboxylic acid are known, valuable information concerning titration can be obtained [31].

Effect Of Dielectric Constant

A more detailed understanding of the effects of solvent and solvation of particles on pK can be gained in terms of Gibbs energy of transfer of the dissociation process of adipic acid (ΔG^o_t) which can be defined for the first dissociation process by Eqn. (12)

$$H_2L = H^+ + HL^-$$

$$\Delta G_t^O = \Delta G_{H^+}^O + \Delta G_{HL^-}^O - \Delta G_{H_2L}^O \qquad (12)$$
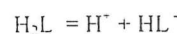
ΔG_t^O can be considered to consist of an electrostatic part, $\delta\Delta G_{ele}^O$ and a non-electrostatic part, $\delta\Delta G_{non}^O$, reflecting the contributions of solvations and other specific solute-solvent interactions

$$\Delta G_t^O = \delta\Delta G_{ele}^O + \delta\Delta G_{non}^O \qquad (13)$$

To a first approximation, the change in free energy due to because of electrostatic interactions[32] is

$$d\Delta G_{ele}^o = (Ne^2 \quad 2)(1 \quad r_{H^+} + z_{HL^-}^2 \, / \, r_{HL^-} - z_{H_2L}^2 \, / \, r_{H_2L})(1 \, / \, D_s - 1 \, / \, D_w) \quad (14)$$

where r denotes the solvated radius of the species considered, z_{H_2L} and z_{HL^-} are the the charge of the acid and its conjugate base respectively, S and W refer to the solvent and water, respectively.

Assuming that $r_H \cong r_{H_2L}, r_{HL^-} = r^-$ one can write

$$d\Delta G_{ele}^o = (Ne^- \quad 2)[(1 + z_{HL^-}^2 - z_{H_2L}^2) \, / \, r^- \,](1 \, / \, D_s - 1 \quad D_w) \quad (15)$$

Further as $\Delta G_t^o = 2.303 \, RT(pK^s - pK^w)$ and with $Q(z,r) = (1 + z_{HL^-}^2 - z_{H_2L}^2) \, / \, r^-$

$$pK = pK^w + d\Delta G_{non}^o \quad 2.303 \, RT + (Ne^2 \quad 2)Q(z,r)(1 \quad D_s - 1 \quad D_w) \quad 2.303 \, RT (16)$$

when pK for the first or second ionization process is plotted against $1/D_s$ (D_s values for ethanol - water mixtures are taken from reference (33), the plots are linear Fig (2). Hence Eqn. (3) holds well, i.e the change in pK after changing the medium can be attributed to electrostatic phenomena. In such a case, it is assumed that all non-electrostatic solute-solvent interactions such as hydrogen bonding and solvent basicity as well as dispersion forces remain constant regardless of the solvent composition in the medium (i.e. the non-electrostatic part of the free energy of transfer is constant) $\Delta G_t^O \cong \delta\Delta G_{ele}^O$ according to the sign of the medium effect on the dissociation constant for first and second ionization processes, the studied acid is characterized by a positive value of ΔG_t^O Table (4) which therefore points to the vlaue of $\delta\Delta G_{ele}^O$.
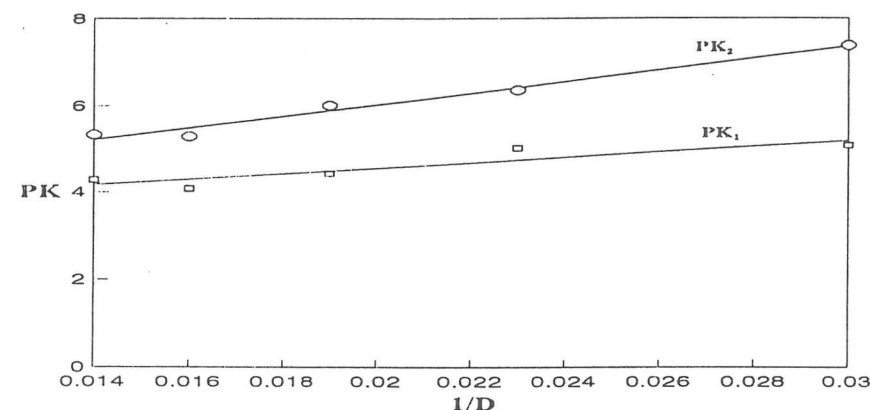
Fig. (2): Variation of pK_1 and pK_2 with D^{-1} at 50°C

Table (4). ΔG_t^o values of adipic acid in different solvent composition and at different temperatures [$\Delta G_{1,2}^o$ (kj mol^{-1})].

wt%	T°C	30	40	50	60
10	ΔG_1^o	-731.36	-1199.2	-1256.04	-2207.1
	ΔG_2^o	708.14	-83.94	-247.49	-402.51
30	ΔG_1^o	653.58	773.48	897.17	593.23
	ΔG_2^o	4227.88	4333.86	4195.06	5772.88
50	ΔG_1^o	3819.33	4401.01	4621.99	4962.76
	ΔG_2^o	4666.78	5000.60	6391.58	6901.94
70	ΔG_1^o	4097.95	4676.82	4968.48	5377.39
	ΔG_2^o	120 09.4	12219.7	12647.0	12744.9

Thermodynamics Of Acid Dissociation.

The thermodynamic parameters for the first and second ionization processes were evaluated from the well - known thermodynamic relations. The plot of pK_1 or pK_2 versus $1/T$ gave a straight line, Fig. (3), which shows that ΔH_1^o and ΔH_2^o may be treated as sensibly constant over the temperature range studied. The values of these thermodynamic functions for both ionization processes at 40°C are shown in Table (5) together with the respective estimates of the errors while their variation with the mole fraction of ethanol is shown in Fig. (4). The profile of ΔH^o and ΔS^o versus mole

fraction curves predicts that a compensation effect may exist between ΔH° and ΔS° for both ionization reactions. The true explanation of this compensation effect must lie in terms of solute-solvent interactions. Any effect that leads to a stronger binding between the solute species and solvent molecules will lower the entropy. It will also lower the entropy by restricting the freedom of vibration and rotation of the solvent. Application of more exact theories to those effects leads to the result that they generally will give rise to a fairly exact compensation[28]. It can be seen from Table (5) that ΔG°_1 and ΔG°_2 have positive values which indicate the preferential stabilization of H_2L in the first dissociation process and of the species HL^- in the second dissociation process by the mixed solvent. These positive values of ΔG° for both dissociation processes increase with increasing the organic content of the mixed solvent. This trend is consistent with the effect of the lowered dielectric constant of the mixed solvent and it is caused by the increase of the electrostatic free energies of the ions produced in the dissociation process. The standard entropy of dissociation of adipic acid has large negative values for both ionization reactions which can be explained on the basis of electrostatic action of the carboxylic groups transmitted through CH_2 - groups and through solvent molecules.
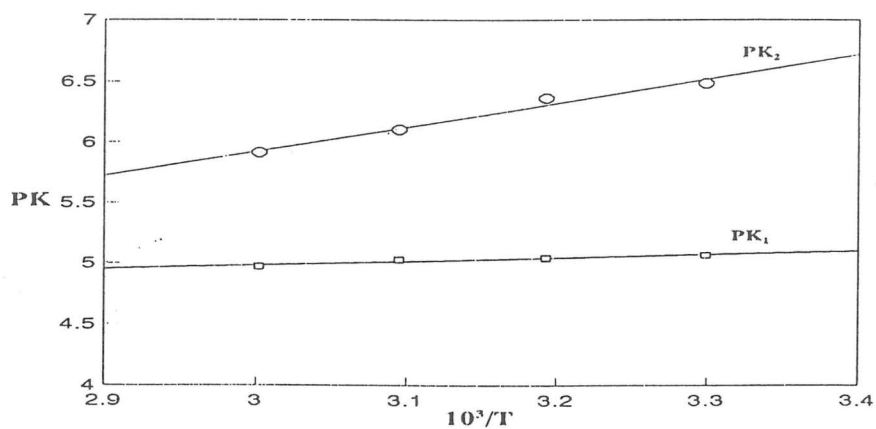

Fig. (3): Van't Hoff plots of the first and second dissociation reactions in 50wt% ethanol.

Table (5). Thermodynamic parameters ΔH°, ΔG° and ΔS° for the first and second Ionization constants in different solvent compositions and at different tempratures. (ΔH°, ΔG° in k. j. mol^{-1} and ΔS° in j. mol^{-1} K^{-1}).

| wt/ %	T°C	30	40	50	60
0	$-\Delta H^\circ_1$	12.91±0.08	12.91±0.08	12.91±0.08	12.91±0.08
	ΔG°_1	25.58±0.15	25.84±0.07	26.49±0.08	26.75±0.12
	$-\Delta S^\circ_1$	41.80±0.60	41.29±0.30	42.02±0.34	41.55±0.40
10	$-\Delta H^\circ_1$	15.45±0.15	15.45±0.15	15.45±0.15	15.45±0.15
	ΔG°_1	24.85±0.07	24.64±0.66	25.23±0.40	24.55±0.49
	$-\Delta S^\circ_1$	31.02±2.4	29.36±2.2	30.28±0.30	27.32±1.6
30	$-\Delta H^\circ_1$	13.54±0.08	13.54±0.08	13.54±0.08	13.54±0.08
	ΔG°_1	26.23±1.0	26.61±0.23	27.39±0.23	27.35±0.34
	$-\Delta S^\circ_1$	41.88±3.4	41.74±0.80	42.85±0.80	41.44±0.40
50	$-\Delta H^\circ_1$	5.68±0.03	5.68±0.03	5.68±0.03	5.68±0.03
	ΔG°_1	29.39±0.94	30.24±0.30	31.11±0.59	31.71±0.38
	$-\Delta S^\circ_1$	78.25±3.1	78.43±0.80	78.70±1.8	78.15±1.2
70	$-\Delta H^\circ_1$	4.52±0.03	4.52±0.03	4.52±0.03	4.52±0.03
	ΔG°_1	29.68±0.34	30.51±0.60	31.46±0.34	32.13±0.26
	$-\Delta S^\circ_1$	82.99±1.1	83.01±0.60	83.37±1.1	82.88±0.80
0	$-\Delta H^\circ_2$	18.34±0.10	18.34±0.11	18.34±0.11	18.34±0.11
	ΔG°_2	29.65±0.12	31.59±0.11	32.99±0.15	34.46±0.25
	$-\Delta S^\circ_2$	158.29±0.50	159.42±0.5	158.82±0.70	158.48±0.50
10	$-\Delta H^\circ_2$	6.92±0.04	6.92±0.04	6.92±0.04	6.92±0.04
	ΔG°_2	30.36±0.24	34.51±0.30	32.74±0.55	34.06±0.31
	$-\Delta S^\circ_2$	122.99±0.80	122.69±0.90	122.74±1.7	123.01±0.9
30	$-\Delta H^\circ_2$	2.68±0.17	2.68±0.17	2.68±0.17	2.68±0.17
	ΔG°_2	33.93±0.19	35.92±0.09	37.19±0.12	40.24±0.24
	$-\Delta S^\circ_2$	120.77±0.90	123.26±0.60	123.37±0.60	128.82±0.90
50	$-\Delta H^\circ_2$	3.79±0.08	3.79±0.08	3.79±0.08	3.79±0.08
	ΔG°_2	34.23±0.39	36.59±1.33	39.38±0.32	41.37±0.13
	$-\Delta S^\circ_2$	128.70±1.3	128.93±4.2	133.58±1.00	135.53±0.80
70	$-\Delta H^\circ_2$	14.03±0.12	14.03±0.12	14.03±0.12	14.03±0.12
	ΔG°_2	41.67±0.08	43.81±0.09	45.64±0.52	47.21±0.12
	$-\Delta S^\circ_2$	183.71±0.40	184.68±0.04	184.64±1.6	183.80±0.50
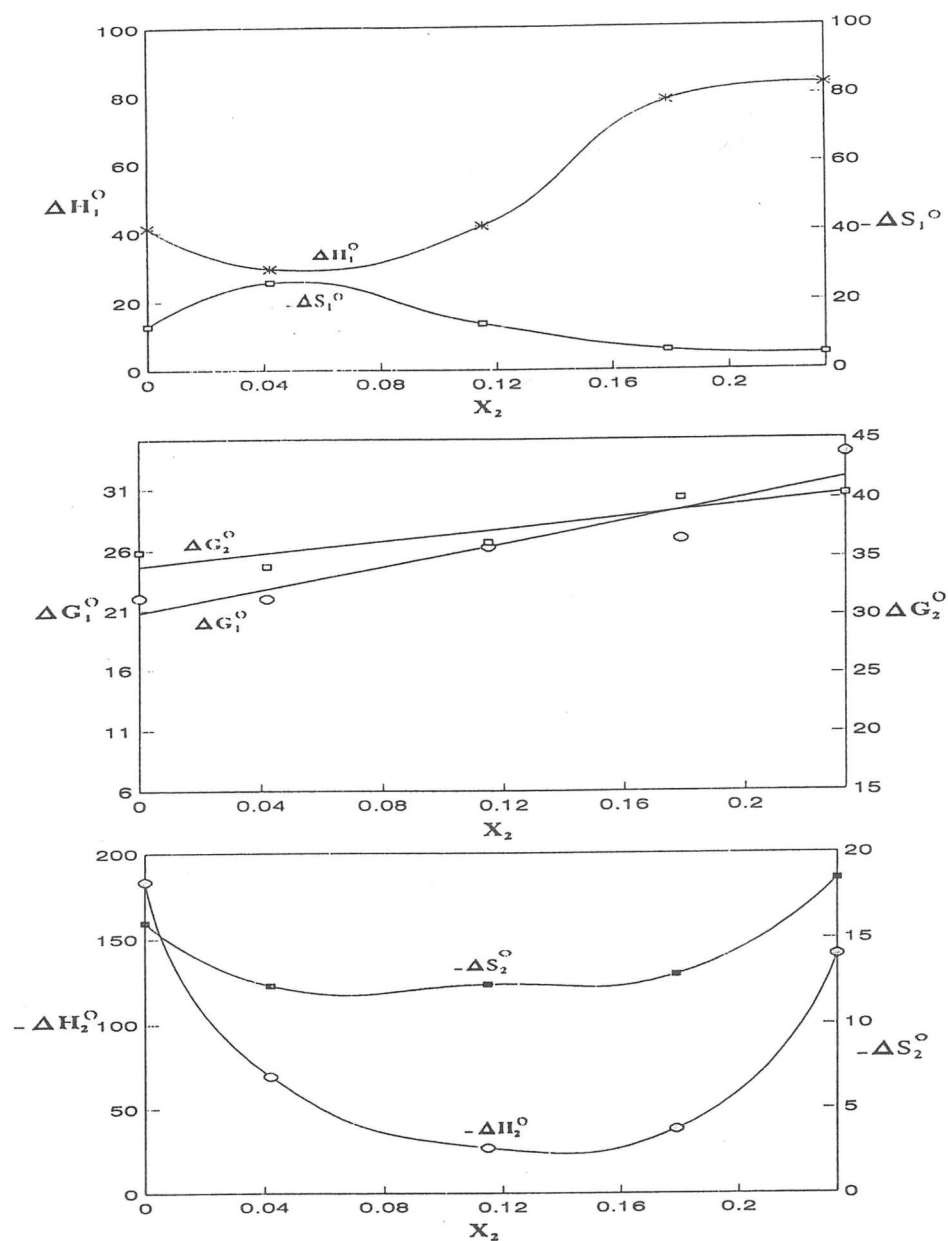
Fig. (4): Variation of ΔH^o, ΔG^o and ΔS^o with the mole fraction of ethyl-alcohol at 40°C.

The charged anions of this acid impose order on the surrounding solvent molecules, which in turn interfere with the internal rotation of the alkyl chain of the acid. Adipic acid has the formula $(CH_2)_4 (COOH)_2$ and has a long chain length and hence the partial molal entropies of its anion decreases noticeably (relative to the neutral acid). ΔS^o_2 values are more negative than ΔS^o_1 values, since solvent interactions in adipate anion (L^{2-}) is properly higher than that in adipate mono anion (HL^-). Accordingly, we expect ΔH^o_2 for the second ionization reaction to be more negative (exothermic) than ΔH^o_1 for the first dissociation reaction. The variation of $DS^o_{1,2}$ with the mole fraction of ethyl alcohol (X_2) is non – linear which is a criterion of specific solvation of the species produced through the dissociation processes .

An extrathermodynamic analysis for the first and second dissociation reactions of adipic acid have been examined in the light of ΔH^o - ΔS^o relationship. It was found that both ΔH^o - ΔS^o correlations for the two ionization reactions were non-linear. This behaviour was attributed to the complexity of ΔH^o and ΔS^o variations with the mole fractions of organic solvent[35].

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