



First and Second Dissociation Constants of Some Dicarboxylic Acids and Related Thermodynamic Functions in Water-1,4-Dioxane Medium

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First and second dissociation constants (K_1 and K_2) of succinic acid, tartaric acid, malonic acid, maleic acid, malic acid and phthalic acid in 20 wt % 1,4-dioxane have been determined at different temperatures (30-60 °C) by using a precise electromotive force method. The thermodynamic functions of dissociation of the acids viz., ΔG° , ΔH° and ΔS° for the first and the second dissociation reactions of these acids have been computed, analyzed and discussed in terms of solute-solvent interactions. An extra thermodynamic analysis has been done in the light of the isoequilibrium temperature values for both reactions indicating that these reactions are entropy controlled reactions.

Keywords: Dissociation constant, Dicarboxylic acids, Water-1,4-Dioxane medium.

INTRODUCTION

This paper is a part of our research on first and second dissociation constants of dicarboxylic acids [1-8]. Saturated dicarboxylic acids and their derivatives were used in different fields such as production of polymers, synthetic fibers and medicinal drugs, in dyeing of fabrics, as corrosion inhibitors and in organic synthesis. Many of them were found in plant, blood, urine and animal tissues [9]. Recently, there were a significant achievements in the theoretical and practical studies of dissociation, bonding, thermodynamics of solvation and the determination of carboxylic acids in its different forms (mono, di, or poly) [1]. However, extra fundamental thermodynamic data is still required to understand various forms of molecular recognition and leads to useful information about the interactions between solutes and solvents. The dicarboxylic acids being studied in the present investigation (succinic acid, malic acid, tartaric acid, malonic acid, maleic acid and phthalic acid) are chosen because of their sensitivity toward ion-solvation as well as to ion-association.

Dissociation constants (pK_a values) are of particular importance in pharmaceutical industries especially in understanding the pharmacokinetic and pharmacodynamics properties of certain drug substance [10]. This is because of the fact that pK_a values could accurately describe the degree of dissociation of functional groups with respect to pH. This could be helpful for choosing appropriate acidic or basic reagents through the course of drug discovery and development.

In this paper, the results obtained in 1,4-dioxane-water mixture of 20 wt % 1,4-dioxane composition are compared with other isodielectric solvent-water mixtures ($D = 56$) of the compositions: 25 wt % *n*-propanol [10,11], 30 wt % ethanol [6,7] and 50 wt % ethylene glycol [4]. The non-polar aprotic class of solvents (like dioxane) has no ability to form hydrogen bonding. Despite so, dioxane can associate by hydrogen bonding because it contains ethereal oxygen. Dioxane is widely used in the pharmaceutical sciences as a versatile model for studying drug solubility and some other relevant physico-chemical properties in the design of homogeneous dosage forms [12]. Water forms hydrogen bonds with the clusters of pure 1,4-dioxane without altering its bulk structure [13]. This leads to the formation of small binary clusters that consist of one or two dioxane molecules and several H_2O molecules through the solvent mole fraction range $0.1 \leq x_{\text{dioxane}} \leq 0.2$. Increasing the concentration of dioxane after this range breaks down the hydrogen bonded network of water [14]. 1,4-dioxane- H_2O mixture was found also to be more basic than the pure solvent (either for pure water or pure dioxane).

EXPERIMENTAL

Solutions for EMF measurements: The acids under investigation (B.D.H., AnalaR) were recrystallized and dried. 1,4-Dioxane was purified by a standard procedure [15]. The required stock solutions of HCl were analyzed. Stock dicarboxylate buffer solutions were made up, by weight, from B.D.H. AnalaR samples of dicarboxylic acid and sodium carbonate.

Apparatus: Crison pH-meter MM 41 type read to ± 0.1 mv was used. The Crison electrode version T has a built-in temperature sensor, type pt 1000 class B, inside the membrane. In this way the EMF and the temperature are measured exactly at the same point. The sensor pt 1000 contacts directly with sample, patented "contact" system. It avoids the imbalance between the EMF and T typical for the classical electrodes with built-in T sensor. The T sensor closeness to the sample during measurement makes the Crison pH electrodes version "T" suitable for use as a precise thermometer.

EMF measurements: The practical work for K_1 and K_2 determinations was described earlier [16,17] by equilibrating the cell and the electrode in dilute HCl solution in the desired 1,4-dioxane-water mixture for determining E°_{cell} followed by additions of stock dicarboxylate buffer solutions. The details of measurements were reported earlier [18].

RESULTS AND DISCUSSION

Data analysis and calculation of pK values: In this work, K_1 and K_2 values were determined for different dicarboxylic acids in 20 wt % 1,4-dioxane mixture within the temperature range (30–60 °C). According to Monk and Amira method [17], the values of K_1 and K_2 were calculated with the help of eqns. 1–8. Taking into consideration the possible formation of NaL^- ion-pair we get:

$$K_1 = [\text{H}^+][\text{HL}^-]\gamma_{\text{H}}\gamma_{\text{HL}}/[\text{H}_2\text{L}] \quad (1)$$

$$K_2 = [\text{H}^+][\text{L}^{2-}]\gamma_{\text{L}}/[\text{HL}^-] \quad (2)$$

$$K_{\text{NaL}} = [\text{Na}^+][\text{L}^{2-}]\gamma_{\text{L}}/[\text{NaL}^-] \quad (3)$$

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

$$E_{\text{cell}} = E^\circ_{\text{cell}} - K' \log [\text{H}^+][\text{Cl}^-]\gamma_{\text{H}}\gamma_{\text{Cl}} \quad (K' = 2.3026 \text{ RT/F}) \quad (5)$$

where I and γ are the ionic strength and the activity coefficient respectively ($\gamma_{\text{H}_2\text{L}} = 1$). For each temperature, the Debye Hückel constant (A) was also calculated. The constants (B) and (Q) values were considered to be 1.3 and 0.3, respectively based on data from Monk and Amira [17]. As a first step, eqns. 4 and 5 were used to calculate E°_{cell} in terms of E°_{cell} of the diluted HCl solution ($I = [\text{HCl}]$). Then, the following equations were used (with eqns. 1–5) for calculating K_1 :

$$[\text{H}_2\text{L}] = m_1 + m_2 - 2m_3 - [\text{H}^+] + [\text{L}^{2-}] + [\text{NaL}^-] \quad (6)$$

$$[\text{HL}^-] = m_2 - [\text{H}_2\text{L}] - [\text{L}^{2-}] - [\text{NaL}^-] \quad (7)$$

where m_1 , m_2 and m_3 are the stoichiometric molal concentrations of HCl, H_2L and Na_2CO_3 respectively.

For approximate calculation of $[\text{H}^+]$ values upon addition of buffer solution, eqns. 4 and 5 were used considering $I = m_1$ followed by use of eqns. 6 and 7 where $[\text{L}^{2-}] = 0$ and $[\text{NaL}^-] = 0$ in the first cycle. The details of the method of calculations were described earlier [6,16,17]. All computations were performed using a computer program that is based on the successive approximation method. Table-1 shows some examples for these calculations, together with the corresponding EMF values of different dicarboxylic acids at different temperatures. It was noticed that most of the K_1 and K_2 values for the acids under study depend on the ionic strength. Table-2 shows the computed pK_1 and pK_2 values at zero ionic strength at different

TABLE-1
 K_1 AND K_2 VALUES OF DICARBOXYLIC
ACIDS AT DIFFERENT TEMPERATURES

Malonic acid 60 °C			
$10^3 m_1 = 3.436 - E_1 \text{ (mv)} = 279.2 - E^\circ \text{ (mv)} = 609.2$			
$10^3 m_2$	$10^3 m_3$	-E (mv)	$10^3 k_1$
28.443	9.497	232.1	0.8824
40.876	13.649	229.3	0.9461
50.981	17.023	228.2	1.003
62.114	20.741	227.6	1.071
73.234	24.454	2227	1.126
$K_1 = 1.01 \times 10^3$			
Succinic acid 35 °C			
$10^3 m_1 = 3.265 - E_1 \text{ (mv)} = -259.2 - E^\circ \text{ (mv)} = -568.2$			
$10^3 m_2$	$10^3 m_3$	-E (mv)	$10^5 k_1$
14.641	4.891	-141.2	2.709
24.668	8.241	-132.9	2.839
32.779	10.951	-130.2	2.995
40.293	13.461	-128.9	3.182
47.228	15.778	-128.3	3.398
53.069	17.729	-127.8	3.568
$K_1 = 3.115 \times 10^{-5}$			
Tartaric acid 30 °C			
$10^3 m_1 = 3.460 - E_1 \text{ (mv)} = 252.2 - E^\circ \text{ (mv)} = 553.2$			
$10^3 m_2$	$10^3 m_3$	-E (mv)	$10^5 k_2$
8.067	6.698	146.6	2.081
12.564	10.432	135.2	2.093
16.147	13.407	131.2	2.172
19.714	16.369	128.4	2.243
23.227	19.285	127	2.366
$K_2 = 2.191 \times 10^{-5}$			
Malic acid 60 °C			
$10^3 m_1 = 3.322 - E_1 \text{ (mv)} = 277.3 - E^\circ \text{ (mv)} = 610.8$			
$10^3 m_2$	$10^3 m_3$	-E (mv)	$10^6 K_2$
7.776	6.471	123.8	4.500
12.111	10.079	103.6	3.574
16.013	13.326	95.8	3.402
19.691	16.387	92.3	3.471
23.108	19.231	90.2	3.572
26.651	22.179	88.5	3.678
$K_2 = 3.700 \times 10^{-6}$			

experimental conditions together with their respective estimates of errors. It was noticed that the dissociation constant values are smaller (pK values are higher) in case of 20 wt % 1,4-dioxane compared to those obtained in H_2O [1–8].

Generally speaking, it agreed that the solvent properties like relative permittivity, acidic or basic strength, play an important but not exclusive role affecting the ionization of weak acids. Other factors might also play an important role in the ionization process. Some examples are the stabilization of the different species existing in equilibrium through hydrogen bonding, ion-solvent interactions and the dispersion forces [19]. Water has strong polarity and hydrogen bonding abilities and therefore, acids under investigation show low pK values in water medium. Dioxane is a non-polar aprotic solvent, acts as a Lewis base in aqueous medium, able to form hydrogen bond because of its ethereal oxygen. It is well known [12,13] that at small fractions of dioxane, the hydrogen bonded network structure of water breaks down accompanied by a decrease in the number of hydrogen bonds estimated for the mixture. Thus,

TABLE-2
pK₁ AND pK₂ VALUES OF DICARBOXYLIC ACIDS IN 20 wt % 1,4-DIOXANE-WATER MIXTURE AT DIFFERENT TEMPERATURES

Temp. (°C)		Malonic acid	Succinic acid	Malic acid	Maleic acid	Phthalic acid	Tartaric acid
30	pK ₁	2.93 ± 0.04	4.51 ± 0.04	3.72 ± 0.03	1.80 ± 0.06	3.21 ± 0.03	3.28 ± 0.05
	pK ₂	6.07 ± 0.02	6.03 ± 0.03	5.38 ± 0.01	6.74 ± 0.03	5.90 ± 0.06	4.66 ± 0.02
35	pK ₁	2.95 ± 0.04	4.51 ± 0.05	3.70 ± 0.04	1.83 ± 0.05	3.21 ± 0.03	3.27 ± 0.04
	pK ₂	6.07 ± 0.09	6.05 ± 0.03	5.39 ± 0.04	6.81 ± 0.03	5.96 ± 0.05	4.69 ± 0.03
40	pK ₁	2.95 ± 0.04	4.49 ± 0.05	3.69 ± 0.04	1.86 ± 0.05	3.20 ± 0.04	3.27 ± 0.05
	pK ₂	6.13 ± 0.01	6.07 ± 0.03	5.39 ± 0.04	6.86 ± 0.03	5.99 ± 0.01	4.70 ± 0.03
50	pK ₁	2.99 ± 0.04	4.46 ± 0.05	3.67 ± 0.04	1.88 ± 0.05	3.19 ± 0.04	3.27 ± 0.06
	pK ₂	6.16 ± 0.04	6.10 ± 0.03	5.41 ± 0.06	6.97 ± 0.03	6.03 ± 0.03	4.73 ± 0.04
60	pK ₁	3.00 ± 0.04	4.46 ± 0.05	3.66 ± 0.04	1.92 ± 0.06	3.17 ± 0.05	3.26 ± 0.05
	pK ₂	6.19 ± 0.01	6.14 ± 0.03	5.43 ± 0.04	7.03 ± 0.04	6.09 ± 0.04	4.77 ± 0.01

at 20 wt % 1,4-dioxane, the number of hydrogen bonds is lower than in pure water. So, pK values are higher in 20 wt % 1,4-dioxane than in pure water.

The reported increase in pK₁ and pK₂ values on addition of 1,4-dioxane could be explained in terms of two competing factors:

(1) The stabilization of the conjugate bases by a donor hydrogen bond which is relatively higher in the pure aqueous medium compared to that in mixed solvent. This is attributed to the greater tendency of water molecules to donate hydrogen compared to other solvent molecules [20]. Therefore, the addition of 1,4-dioxane to water will raise the activity coefficient of conjugate base, causing an increase in pK value.

(2) Ion-solvent interactions that provide greater stabilization of the proton in case of 1,4-dioxane-water mixture relative to that in pure water [21,22]. This will cause a decrease in the coefficient activity of the proton in the 1,4-dioxane-water mixture compared to that in pure water therefore, causing a slight decrease in pK_a. The first factor is the predominate one and resulting with an increase in pK_(1 or 2) by the addition of 1,4-dioxane to water. The second dissociation constant is depressed more than the first one by the addition of 1,4-dioxane to water. This behaviour is reflected by the observed high K₁/K₂

ratio obtained for the different acids (Table-3). The electrostatic effect caused by the negative charge on the first carboxylate anion is more readily transmitted to the seat of second dissociation. The stable intramolecular hydrogen-bonding causes an increase in the dissociation constant K₁ of the uncharged acid at the expense of the second one of the carboxylate anion. As can be seen from Table-3 the greatest stability of hydrogen bonding is observed for maleic acid while the weakest is for tartaric acid as the geometrical structure plays an important role in the intramolecular hydrogen-bond formation.

It is useful to compare pK values of the present work with those reported in other isodielectric media having co-organic solvents of different properties and structures like 25 wt % *n*-propanol [11], 30 wt % acetone [1,2], 30 wt % ethanol [6,7] and 50 wt % ethylene glycol [4] (Table-4). These chosen media are isodielectric with the studied medium and all of relative permittivities nearly equal to 56. This indicates [23] that the electrostatic effects play only a limited role on acid dissociation equilibria while other solvent effects dominate.

It is found that pK₁ values at 40 °C Table-4 for phthalic acid, tartaric acid, malonic acid, succinic acid, malic acid and maleic acid in ethanol [6,7] and ethylene glycol [4], are higher than those observed in 1,4-dioxane (present work) and *n*-

TABLE-3
VALUES OF (K₁/K₂) OF DICARBOXYLIC ACIDS IN 20 wt % 1,4-DIOXANE-WATER MIXTURE AT DIFFERENT TEMPERATURES

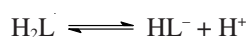
Temp. (°C)	Malonic acid	Succinic acid	Malic acid	Maleic acid	Phthalic acid	Tartaric acid
30	1386.44	33.097	45.73	86601.31	486.26	23.990
35	1336.65	34.950	49.19	95499.03	571.35	25.996
40	1508.15	37.844	50.94	100584.54	612.11	26.990
50	1505.85	42.690	54.06	122367.69	697.09	28.660
60	1573.21	44.070	59.19	12776.02	823.60	31.660

TABLE-4
VALUES OF pK₁ AND pK₂ OF DICARBOXYLIC ACIDS IN DIFFERENT SOLVENTS AT 40 °C

		Succinic acid	Malonic acid	Malic acid	Maleic acid	Phthalic acid	Tartaric acid
20 wt % 1,4-dioxane	pK ₁	4.490	2.950	3.690	1.890	3.20	3.27
	pK ₂	6.070	6.130	5.390	6.860	5.99	4.70
30 wt % ethanol	pK ₁	4.708	3.232	3.921	1.978	3.275	4.521
	pK ₂	6.303	6.365	5.899	7.235	6.663	4.892
25 wt % <i>n</i> -propanol	pK ₁	4.460	3.020	3.66	1.740	3.180	3.240
	pK ₂	6.100	6.480	5.480	6.980	6.250	4.64
30 wt % acetone	pK ₁	—	3.452	4.240	2.198	—	—
	pK ₂	—	7.127	6.049	7.622	—	—
50 wt % ethylene glycol	pK ₁	4.740	3.370	3.950	2.350	3.530	3.620
	pK ₂	6.240	6.530	5.760	7.350	6.270	4.740

peropropanol-water medium [11]. Ethanol and ethylene glycol are both amphiprotic solvents, hydrogen-bond donor-acceptor solvents. The hydrogen-bond abilities in such solvents are higher than those in 1,4-dioxane and *n*-propanol. This gives higher stability of the conjugate bases in the former media, but it seems that the greater stabilization of proton in 1,4-dioxane-water and *n*-propanol-water mixed solvents will bring a reversed action on pK_1 . This factor will generate a low activity coefficient of the proton resulting of lower pK_1 values in *n*-propanol and 1,4-dioxane. Moreover, reported pK_1 values for malonic acid, malic acid and maleic acid at 40 °C in acetone-water medium [1,2] are higher than those of the present work. Acetone is a weakly basic solvent [23]. It could be predicted for the basicity of acetone-water mixture to be lower than that for 1,4-dioxane-water and *n*-propanol-water medium. Therefore, this leads to lower interaction of acids in the former medium. *i.e.* higher pK_1 values are resulted.

The effect of coorganic solvent on the acid dissociation equilibria of the acids under investigation may also interpreted using the standard free energies of transfer of the proton from H_2O to the mixed solvent [24] according to the following equations:



$$\Delta G_t^\circ(H_2L) = \Delta G_t^\circ(H^+) + \Delta G_t^\circ(HL^-) - \Delta G_t^\circ(H_2L) \quad (8)$$

$$\begin{aligned} \Delta G_t^\circ(H_2L) &= \partial[\Delta G_t^\circ(H_2L)] = \Delta G_s^\circ(H_2L) - \Delta G_{H_2O}^\circ(H_2L) \\ &= 2.303 RT[(pK_1)_s - (pK_1)_{H_2O}] + RT \ln M_s/M_{H_2O} \quad (9) \end{aligned}$$

and



$$\Delta G_t^\circ(H_2L) = \Delta G_t^\circ(H^+) + \Delta G_t^\circ(HL^-) - \Delta G_t^\circ(H_2L) \quad (10)$$

$$\begin{aligned} \Delta G_t^\circ(HL^-) &= \partial[\Delta G_t^\circ(HL^-)] = \Delta G_s^\circ(HL^-) - \Delta G_{H_2O}^\circ(HL^-) \\ &= 2.303 RT[(pK_2)_s - (pK_2)_{H_2O}] + RT \ln M_s/M_{H_2O} \quad (11) \end{aligned}$$

where, M_s and M_{H_2O} are the mean molar mass of the mixed solvent (s) and the reference solvent (H_2O) respectively. The standard free energies of transfer values for the first and the second dissociation processes $\Delta G_t^\circ(H_2L)$ and $\Delta G_t^\circ(HL^-)$ are listed in Table-5. These values illustrates the solvent effect on the deprotonation equilibria of the studied acids which are of similar charge type but of different structures and reflects a monotonous increase of resistance to the extent of the

deprotonation equilibria for H_2L and HL^- acids. This behaviour is also guided by the combined effects of the individual species involved. As a general trend, the positive ΔG_{1t}° or $2t$ values increases gradually as the hydrophobic acid carbon chain length increases indicating decreased stabilization of the corresponding conjugate bases as the number of carbon atoms increases in the acid chain, this factor can be followed by comparing ΔG_{1t}° values of malonic and succinic acids. ΔG_{1t}° is also affected by substitution on central carbon atoms, which is clearly seen in malic acid and tartaric acid. Also ΔG_{1t}° is clearly affected by hyper conjugation effects as can be seen by the values of ΔG_{1t}° of maleic acid and phthalic acid. On examining ΔG_{1t}° for succinic acid (Table-6), in different iso-dielectric media [1,2,4-6,11], the following trend for increasing ΔG_{1t}° was observed,

$$\Delta G_{1t}^\circ (25 \text{ wt } \% n\text{-propanol}) < \Delta G_{1t}^\circ (20 \text{ wt } \% 1,4\text{-dioxane}) < \Delta G_{1t}^\circ (30 \text{ wt } \% \text{ ethanol}) < \Delta G_{1t}^\circ (50 \text{ wt } \% \text{ ethylene glycol})$$

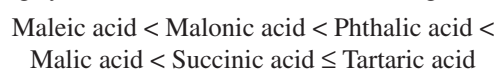
This trend is in accordance with the decreasing of the stabilization of the dissociation products in such media.

The distance r (in Å) between the two carboxylic groups of the studied acids was calculated at different temperatures according to Bjerrum's equation [23] in the form:

$$\ln(K_1 / 4K_2) = Ne^2 / RT\epsilon_r r \quad (12)$$

Table-7 shows the obtained r values. The distance “ r ” was found to be a function of some parameters like: (i) The chain length separating the two carboxyl groups. It was observed that for a series of symmetrical acids of the formula $(HOOC-(CH_2)_n-COOH)$, “ r ” values increases as “ n ” increases [25] (this appears in malonic acid and succinic acid). (ii) The substituent effect [26], where the substitution on the central carbon atom of the acids can affect the values of “ r ”. (iii) Internal inductive effect [27] which can cause chain shorting or chain stretching. (iv) Ion-solvent [28] effects.

All the above factors affect the r 's values of the studied acids. It can be concluded from Table-7 that r values of the following symmetrical acids increase according to the order:



The smaller “ r ” values of maleic acid and malonic acid in this trend are attributed to the geometrical structure of maleic acid that allows the two carboxyl groups to be closer to each other while in malonic acid, the separation distance between

TABLE-5
VALUES OF STANDARD FREE ENERGY OF TRANSFER (KJ mol⁻¹) OF
DICARBOXYLIC ACIDS IN 20 wt % 1,4-DIOXANE-WATER AT 40 °C

	Malonic acid	Succinic acid	Malic acid	Maleic acid	Phthalic acid	Tartaric acid
ΔG_{1t}°	1.60	2.15	1.670	-0.430	-0.470	0.480
ΔG_{2t}°	1.94	2.80	0.840	3.410	4.390	1.950

TABLE-6
VALUES OF STANDARD FREE ENERGY OF TRANSFER (KJ mol⁻¹) OF
SUCCINIC ACID IN DIFFERENT SOLVENT COMPOSITION AT 40 °C

	20 wt % dioxane	25 wt % <i>n</i> -propanol	30 wt % ethanol	50 wt % ethylene glycol
ΔG_{1t}°	2.15	1.96	3.46	3.75
ΔG_{2t}°	2.80	3.04	4.25	4.06

TABLE-7
VALUES OF DISTANCE $r/\text{\AA}$ BETWEEN THE DICARBOXYLIC GROUPS OF DICARBOXYLIC ACIDS IN 20 wt % 1,4-DIOXANE-WATER MIXTURE AT DIFFERENT TEMPERATURES

Temp. (°C)	Malonic acid	Succinic acid	Malic acid	Maleic acid	Phthalic acid	Tartaric acid
30	1.589	4.397	3.814	0.9308	1.936	5.187
35	1.616	4.333	3.743	0.9316	1.893	5.018
50	1.631	4.085	3.714	0.9363	1.874	4.911
60	1.656	4.124	3.673	1.2260	1.857	4.783

the two carboxyl groups is the smallest in all acids studied, as $n = 1$. The steric hindrance of OH groups in malic acid and tartaric acid induces rigidity in the acid structure, making it favourable for the carboxylic groups to be away from each other (higher values of “ r ”). The order of increase of r can be interpreted with the gradual increase of chain length from malonic acid to tartaric acid. Moreover, the hyper conjugation effect on “ r ” can be readily seen from the similarities of “ r ” values in phthalic acid and maleic acid.

The solvent effects on “ r ” such as: polar, interionic, hydrogen bond and dispersion forces effects can be investigated by comparing “ r ” values in 20 wt % 1,4-dioxane mixture with those of other isodielectric media of 25 wt % *n*-propanol–water [11], 30 wt % acetone–water [1,2], 50 wt % ethylene glycol–water [4] and 30 wt % ethanol–water [5,6] mixed solvents which are represented in Table-8. From this Table-8, it can be readily seen the constancy of “ r ” values among the different systems indicating the poor chemical effects of organic solvent components on the value of “ r ”.

Thermodynamics of acid dissociation: The linear least square van’t Hoff plots of $\text{p}K_1$ and $\text{p}K_2$ versus $1/T$, for the studied dicarboxylic acids (Figs. 1 and 2), indicates that the enthalpy of dissociation may be treated as sensibly constant over the temperature range covered. From the slopes of these plots, the values of ΔH_1° , ΔH_2° have been calculated. The other thermodynamic parameters, for both ionization reactions, were computed from the well-known thermodynamic relations. The values of these parameters at 40 °C as an example are collected in Table-9 with their respective estimates of errors.

TABLE-8
VALUES OF DISTANCE $r/\text{\AA}$ BETWEEN THE DICARBOXYLIC GROUPS OF DICARBOXYLIC ACIDS IN ISODIELECTRIC MEDIA AT 35 °C

	Malonic acid	Succinic acid	Malic acid	Maleic acid	Phthalic acid	Tartaric acid
20 wt % 1,4-dioxane	1.616	4.333	3.743	0.9316	1.893	5.018
25 wt % <i>n</i> -propanol	1.530	4.035	3.385	0.882	1.656	5.166
30 wt % ethanol	1.634	4.184	3.077	0.865	1.458	6.135
50 wt % ethylene glycol	1.549	4.498	3.422	0.886	1.818	8.338
30 wt % acetone	1.346	–	3.280	0.847	–	6.070

TABLE-9
THERMODYNAMIC PARAMETERS (ΔH° , ΔG° , ΔS°) FOR THE FIRST DISSOCIATION CONSTANT (K_1) AND THERMODYNAMIC PARAMETERS (ΔH° , ΔG° , ΔS°) FOR THE SECOND DISSOCIATION CONSTANT (K_2) IN 20 WT % DIOXANE-WATER AT 40 °C (ΔH°_1 , ΔG°_1 , ΔH°_2 , ΔG°_2 in KJ mol^{-1} and ΔS°_1 , ΔS°_2 in $\text{J mol}^{-1} \text{K}^{-1}$)

	Malonic acid	Succinic acid	Malic acid	Maleic acid	Phthalic acid	Tartaric acid
ΔH°_1	-4.70 ± 0.40	3.92 ± 0.46	3.43 ± 0.49	-7.29 ± 0.72	2.45 ± 0.28	0.82 ± 0.14
ΔG°_1	17.71 ± 0.24	26.92 ± 0.28	22.10 ± 0.23	11.15 ± 0.30	19.18 ± 0.22	19.62 ± 0.29
$-\Delta S^\circ_1$	71.58 ± 1.48	73.44 ± 1.71	59.60 ± 1.72	58.90 ± 2.49	53.42 ± 1.14	60.03 ± 1.02
$-\Delta H^\circ_2$	8.48 ± 1.30	6.40 ± 0.33	3.31 ± 0.39	18.82 ± 1.21	11.28 ± 1.33	6.40 ± 0.46
ΔG°_2	36.77 ± 0.06	36.39 ± 0.18	32.33 ± 0.25	41.13 ± 0.18	35.89 ± 0.58	28.20 ± 0.19
$-\Delta S^\circ_2$	144.48 ± 4.15	136.66 ± 1.20	113.80 ± 1.49	191.44 ± 3.92	150.66 ± 4.62	110.46 ± 1.60

It can be seen from Table-9 that $\Delta G^\circ_{1(\text{or } 2)}$ values for the studied acids are positive indicating that H_2L and HL^- species are preferentially stabilized in the first and second dissociation processes respectively in case of mixed solvents. The values of ΔS°_1 and ΔS°_2 are always negative in 1,4-dioxane–water mixture. Regarding $\Delta S^\circ_{1(\text{or } 2)}$, they possess negative values owing to the fact that the H^+ , HL^- and L^{2-} species will tend to orient solvent molecules to a greater extent [29]. The trend ΔS°_1 of values among the studied acids is: phthalic acid < maleic acid < malic acid < tartaric acid < malonic acid < succinic acid. This trend is primarily attributed to the electrostatic action on the carboxylic groups transmitted through CH_2^- groups (malonic acid, succinic acid) and its hydroxy substituents (malic acid and tartaric acid) and is also because of the conjugation effects of maleic acid and phthalic acid. Moreover, the electrostatic action transmitted through solvent molecules (field effect) also affects these types of interactions and the charged anions of these acids impose order on the surrounding solvent molecules, which in turn interfere with the internal rotation of the alkyl chain of the acid and hence the partial molal entropies of the anions decrease (relative to the neutral acid), thus ΔS°_1 should be more negative as the length of the alkyl chain increases. Everett and Pinsent [30] have pointed out; it is a general principal of electrostatics that a region of low dielectric constant immersed in a medium of higher dielectric constant is repelled from an electrostatic charge. The alkyl chains attached to ions therefore repelled from the charged part of the ion and are stiffer than in the corresponding uncharged molecule. King and King [31] have discussed these

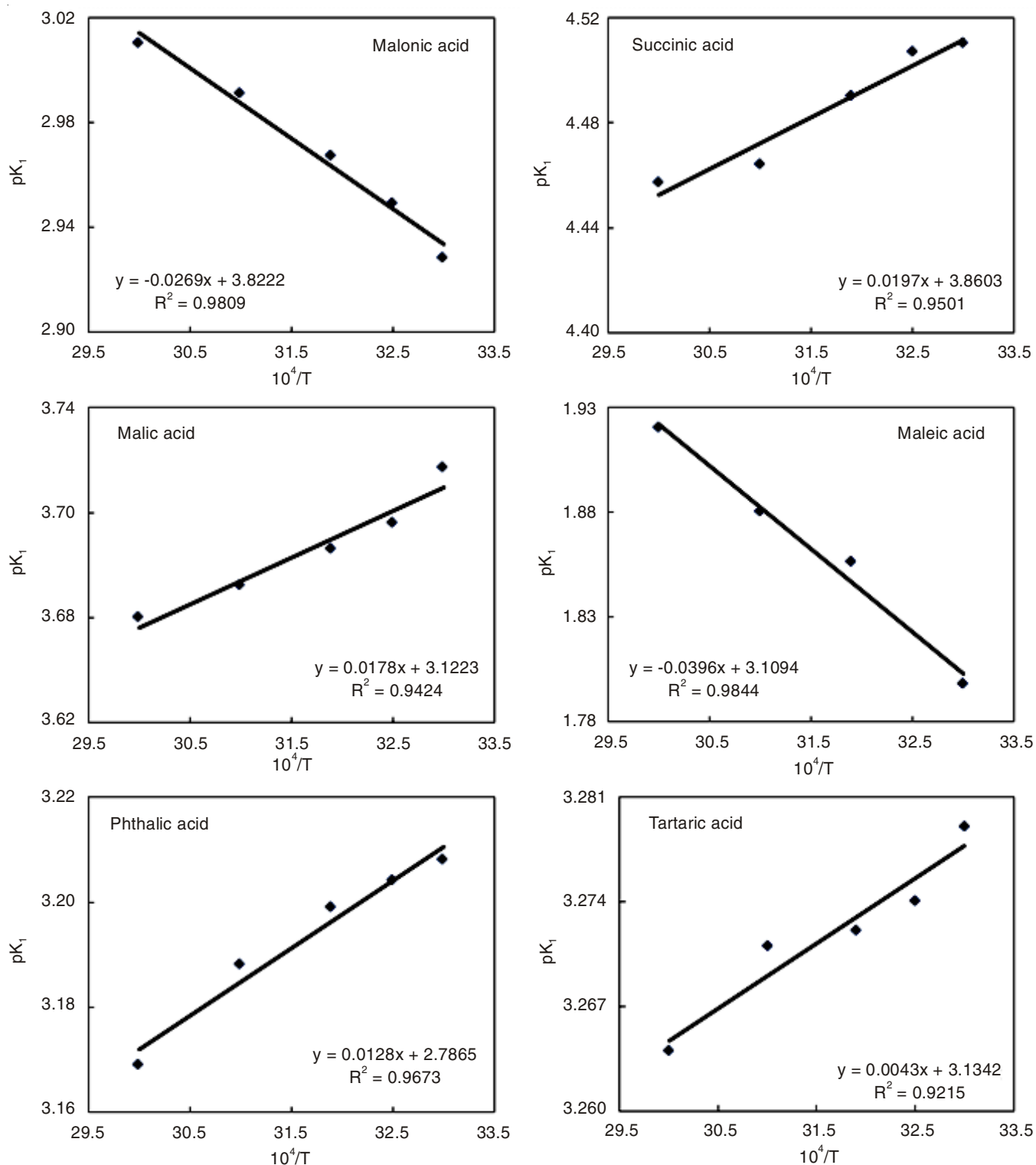


Fig. 1. van't Hoff plots for the first dissociation reaction of different dicarboxylic acids

related ideas in great details, with particular attention to various amino-acids. The present investigation concerned with dicarboxylic acids of general formula $R-COOH$ where R represents $-CH_2-COOH$ in malonic acid, CH_2-CH_2-COOH in succinic acid, $-CH_2-CH(OH)COOH$ in malic acid, $-HC(OH)-CH(OH)-COOH$ in tartaric acid, $CH=CHCOOH$ in maleic acid and $Ph-COOH$ in phthalic acid. In the light of the above discussions the effect of alkyl chain length for the order imposed on the solvent about the succinate, monoanion (higher chain length)

should restrict internal rotation more than that of the malonate monoanion. This restriction of internal rotation lowers the partial molal entropy of succinate monoanion more than that of malonate monoanion (relative to their neutral acids) and ΔS° of succinate mono anion becomes more negative. The higher negative ΔS° value of succinic acid than that of malic acid and tartaric acid (possessing the same alkyl chain length) is strongly related to the hydrogen bonding which exists only in malic acid and tartaric acid. The existence of such type of

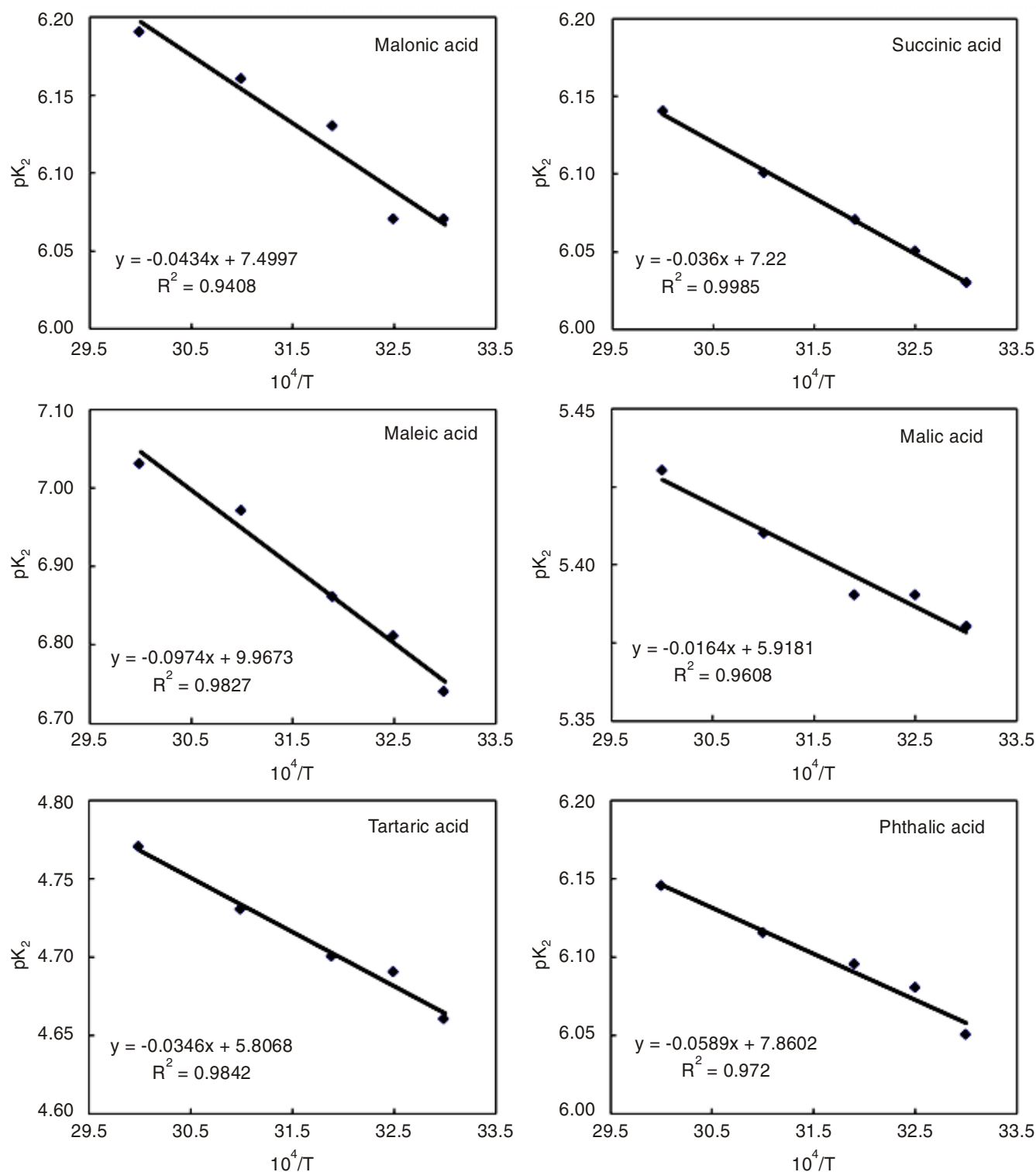


Fig. 2. van't Hoff plots for the second dissociation reaction of different dicarboxylic acids

bonding will decrease the basicity of both malate and tartrate mono anions causing a decrease in solvation and correspondingly less negative ΔS_1° values compared to that for succinic acid. ΔS_2° values are more negative (Table-9) than the corresponding ΔS_1° values, since solvent interactions in acid anion (L^{2-}) is properly higher than that in acid mono anion (HL^-). Accordingly, we expect ΔH_2° for the second ionization reaction to be more negative (exothermic) than ΔH_1° for the first dissociation reaction.

Extra thermodynamic analysis (isoequilibrium relationship): An extra thermodynamic analysis of the obtained results has been examined in the light of $(\Delta H^\circ - \Delta S^\circ)$ relationship, which was applied for the first and second dissociation reactions of the different studied acids. The $(\Delta H^\circ - \Delta S^\circ)$ correlation for the second dissociation reactions of the studied acids are linear with positive slopes (Fig. 3). For a series of acids of common type, such a linear correlation might be explained on the basis that small changes in the dissociation constants

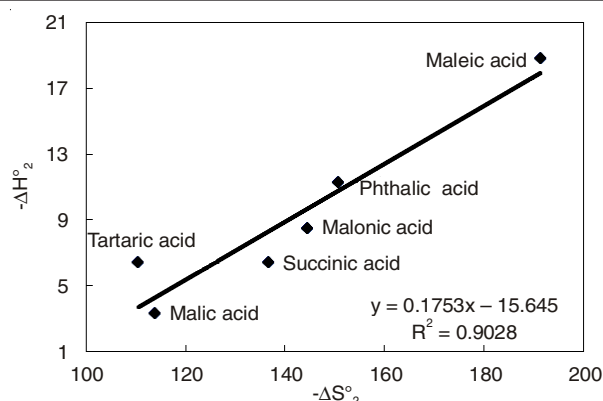


Fig. 3. Represented data for isoequilibrium for the second dissociation reaction of dicarboxylic acids in 20 wt % 1,4-dioxane-water medium at 40 °C

arise probably from parallel changes in ΔH° and ΔS° . Such parallel correlation between $\partial(\Delta H^\circ)$ and $\partial(\Delta S^\circ)$ among the investigated acids supports the suggestion that the second dissociation reactions of these acids are similar. The slope of this plot represents the isoequilibrium temperature (β) which is 175 K. This temperature is lower than the experimental ($T = 313$ K) indicating that this dissociation reaction is of entropy controlled type in which the solute-solvent interaction play an important role [32].

For the first dissociation reaction, the relation between ΔH° and ΔS° is not linear. It is not necessarily for the functional relationship between ΔH° and ΔS° in a series of homologous reaction series to be linear [33], when such relationship does exist, it is very important, yet also very difficult, to conclude the actual relationship between the two variables that is affected

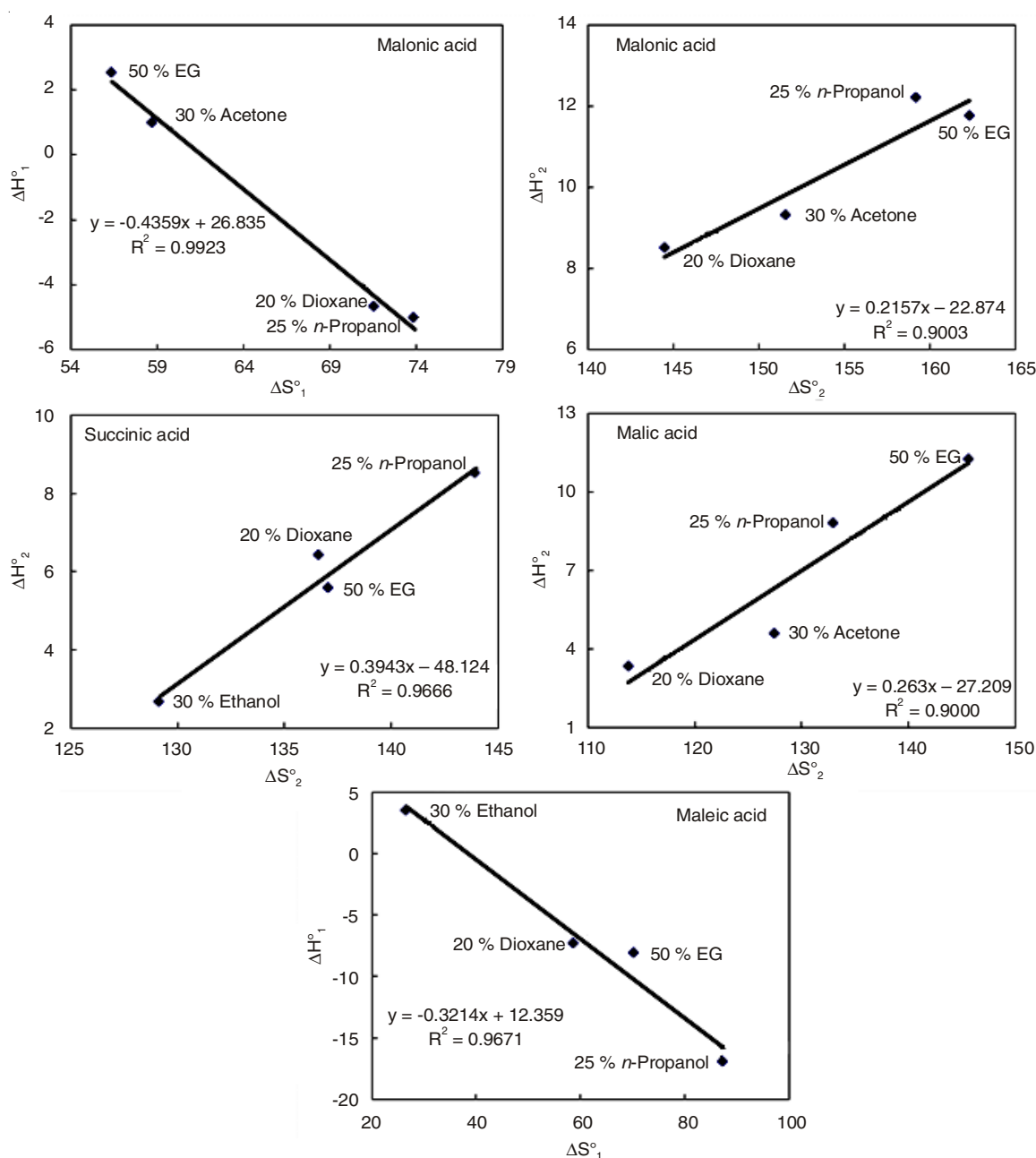


Fig. 4. Represented data for isoequilibrium for the first and the second dissociation reaction of dicarboxylic acids in isodielectric medium at 40 °C

by the particular coupling of the enthalpy levels with the corresponding entropy levels for the specific series of reactions. The plot of $\Delta H_1^\circ - \Delta S_1^\circ$ correlation reported in the present work reflects an appreciable shielding effect [33] induced by the solvent on the properties of each acid in the series which causes differences in the specific properties of the different acids, thus in a homologous series of reactions with a precise $\Delta H^\circ - \Delta S^\circ$ interplay, it is not necessarily for the mutual influence between the changes in the values of parameters to be compensative in nature.

Moreover, on testing correlation for the first and second dissociation reactions of maleic acid, malonic acid, malic acid, tartaric acid, phthalic acid and succinic acid in other media [1,2,4-6,11] (Fig. 4) which are isodielectric with our studied medium is linear. Higher correlation coefficients are obtained for all cases studied except for the first dissociation reaction of malic acid, phthalic acid, tartaric acid and succinic acid like our present investigation. The linear relation between ΔH° and ΔS° indicates parallel changes in ΔH° and ΔS° . Such parallelism between $\partial \Delta H^\circ$ and $\partial \Delta S^\circ$ among the different isodielectric media for the first and second dissociation reactions indicate that these dissociation reactions are occurring in a similar way in all these media. These media are of different polarities, ion-solvent, solvent-solvent and hydrogen-bonding interactions which means that these dissociation processes are not strongly affected by such type of interactions. It seems that Born-type electrostatic effects through relative permittivity are more important. This behaviour was confirmed before from the non-linear variation observed in ΔH° and ΔS° interplay for fixed acids in the systems: ethanol-water [5,6], ethylene glycol-water [4] and acetone-water [1,2] in which the relative permittivity was varied in each system.

Conclusion

The dissociation constants of the first and second dissociation reactions of dicarboxylic acids have been determined in 20 wt % 1,4-dioxane-water mixture at different temperatures. These dissociation constants are of great interest and can be used in a number of areas of chemistry and biochemistry. 1,4-Dioxane is a non-polar aprotic solvent, acts as a Lewis base in aqueous medium, able to associate by hydrogen bonding due to its etheric oxygen. Thus in 20 wt % 1,4-dioxane the number of hydrogen bonds is lower than in pure water. So, pK values are higher in 20 wt % 1,4-dioxane than in pure water.

On testing the isoequilibrium relationship among the studied acids, the correlation was found to be linear for some acids and non-linear for others. The linear dependence was explained in terms of the smaller dissociation reactions of these acids in such medium. The non-linear correlation was discussed in terms of the shielding effect induced by the solvent on the

properties of each acid, that caused some differences of specific properties of the acids at these particular solvent mixtures.

REFERENCES

1. L.A. Al-Alwan, L.A. Al-Juhaiman and A.A. Zaghloul, *J. Saudi Chem. Soc.*, **12**, 555 (2008).
2. L.A. Al-Juhaiman, L.A. Al-Alwan and A.A. Zaghloul, *Z. Phys. Chem.*, **220**, 1181 (2006).
3. G.A. El-Naggar, M. El-Batouti and A.A. Zaghloul, *Bull. Electrochem.*, **17**, 65 (2001).
4. G.A. El-Naggar, S.M. Selim, A.A. Zaghloul and M.F. Amira, *Z. Phys. Chem.*, **216**, 1239 (2002).
5. G.A. El-Naggar, A.A. Zaghloul and M. El-Batouti, *Egypt. J. Chem.*, **45**, 33 (2002).
6. A.A. Zaghloul, G.A. El-Naggar and M.F. Amira, *Gazz. Chim. Ital.*, **126**, 735 (1996).
7. A.A. Zaghloul, G.A. El-Naggar, S.A. El-Shazly and M.F. Amira, *Talanta*, **45**, 189 (1997).
8. M. Mohamed, A.A. Zaghloul, A.M. Saad, A.M. El-Bahnasawy and M.F. Amira, *Afindad*, **21**, 2219 (1997).
9. R.K. Kvaratskhelia and E.R. Kvaratskhelia, *Russ. J. Electrochem.*, **46**, 952 (2010).
10. O. Kilic and E. Birol, *J. Serb. Chem. Soc.*, **71**, 43 (2006).
11. G.A. Ebrahim, M.Sc. Thesis, Electrochemical Studies on the Formation of Ion-Pairs of Some Metal Complexes in Mixed Solvents, Alexandria University, Egypt (2010).
12. A.R.M. Miller and M.R. Fleming, *Vitae*, **16**, 327 (2009).
13. O. Iulian and O. Ciocirlan, *Rev. Roum. Chim.*, **55**, 45 (2010).
14. H. Demirelli and F. Köseoglu, *J. Solution Chem.*, **33**, 1501 (2004).
15. W.L.F. Armarego and D.D. Perrin, *Purification of Laboratory Chemicals*, Elsevier, edn 4 (1997).
16. C.B. Monk and M.F. Amira, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1170 (1978).
17. C.B. Monk and M.F. Amira, *J. Chem. Soc., Faraday Trans. 1*, **76**, 1773 (1980).
18. H.A. Azab and K.M. Aboul Nour, *J. Chem. Eng. Data*, **44**, 678 (1999).
19. B.M. Lowe and D.G. Smith, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1934 (1973).
20. F. Franks and D.J.G. Ives, *Q. Rev. Chem. Soc.*, **20**, 1 (1966).
21. H.P. Bennetto, D. Feakins and D.J. Turner, *J. Chem. Soc. A*, 1211 (1966).
22. D. Feakins, K.G. Lawrence and R.P.T. Tomkins, *J. Chem. Soc. A*, 753 (1967).
23. B.K. Dolui, S.K. Bhattacharya and K.K. Kundu, *J. Solution Chem.*, **37**, 987 (2008).
24. A. Hassan, H.A. Azab, S.A.E. Gyar and Z.A. Khafagy, *Can. J. Chem.*, **70**, 1684 (1992).
25. N. Bjerrum, *Z. Phys. Chem.*, **106**, 219 (1923).
26. R. Gane and C.K. Ingold, *J. Chem. Soc. A*, 1594 (1928).
27. R. Gane and C.K. Ingold, *J. Chem. Soc. A*, 2267 (1928).
28. R. Gane and C.K. Ingold, *J. Chem. Soc. A*, 2153 (1931).
29. E.J. King, *J. Am. Chem. Soc.*, **73**, 155 (1951).
30. D.H. Everett and B.R.W. Pinsent, *Proc. R. Soc. Lond. A Math. Phys. Sci.*, **215**, 416 (1952).
31. E.J. King and G.W. King, *J. Am. Chem. Soc.*, **78**, 1089 (1956).
32. K.J. Laidler, *Chemical Kinetics*. New York, McGraw-Hill (1965).
33. D. De Marco, A. Giannetto and W. Linert, *Thermochim. Acta*, **286**, 387 (1996).