

Thermodynamic studies of dissociation reactions of some dicarboxylic acids in 20% (w/w) acetonitrile – water mixture

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pK_1 and pK_2 values at zero ionic strength of some dicarboxylic acids (succinic, tartaric, malonic, malic and maleic) in 20% (w/w) acetonitrile–water at temperatures ranging from 30 °C to 60 °C have been determined using a precise EMF method. The thermodynamic parameters ΔH° , ΔG° and ΔS° of the first and the second dissociation reactions are calculated from well known equations and discussed in terms of solute–solvent interactions. An extrathermodynamic analysis of the obtained results has been performed and indicates that these dissociation reactions are entropy-controlled reactions where solute–solvent interaction plays an important role.

Keywords: dicarboxylic acids, dissociation constants, solvent effects, thermodynamic parameters

The systematic determination of solvent effects on acid dissociation constants and their thermodynamic functions is a subject of both practical and theoretical importance in chemical and biochemical analysis and leads to practical information concerning solute–solvent interactions. Therefore, the nature and the effect of solvents on ionic dissociation especially the dissociation of organic acids have been extensively documented.^{1–7} Several techniques have been used to measure the acid-dissociation constants.^{8–12} The EMF method with the glass electrode/HCl, H₂L, Na₂CO₃/AgCl, Ag cell (where H₂L represents the dicarboxylic acid) developed by Monk and Amira is the most precise method for the determination of K_1 and K_2 at zero ionic strength.^{13,14} Dissociation constants have been determined for some dicarboxylic acids in an aqueous medium and in mixed solvents.^{15–21}

Acetonitrile (MeCN) is one of the most important dipolar aprotic solvents, it is used extensively as a reaction medium for mechanistic studies, in electrochemistry, and in HPLC and it is also employed as a solvent for non aqueous titrations.²² MeCN behaves as a weaker base and as a much weaker acid than water. It has a relatively high dielectric constant ($\epsilon = 36$) and a small autoprotolysis constant ($pK_s = 33.6$). Accordingly, MeCN acts as a strongly differentiating solvent with a modest solvating power for many polar ionic solutes.²³

Barbosa *et al.*¹⁸ studied the effect of added acetonitrile in water up to 70% (w/w) on the pK_1 and pK_2 values of some dicarboxylic acids at constant temperature (25 °C), while the present work is concerned with the studies of a selected dicarboxylic acids (succinic, tartaric, malic, malonic, maleic acids) which are of special interest due to their reactivity spectrum toward ion solvation, where the first and the second dissociation constants K_1 and K_2 have been determined using the cell mentioned above in 20% (w/w) MeCN/water solvent and over a wide range of temperatures from 30 to 60 °C in order to study the thermodynamic behaviour of these acid dissociation reactions in an acetonitrile–water medium. The related thermodynamic parameters for these dissociation reactions are computed from well known thermodynamic relationships, in order to throw light on the effects of solvent–solvent and solute–solvent interactions.

Experimental

Chemicals and reagents

Analytical reagent grade chemicals were used, unless otherwise indicated. The dicarboxylic acids studied (succinic, tartaric, malonic, maleic and malic) were purchased from Fluka and used as delivered. Pure co-solvent MeCN (HPLC grade), was supplied by Merck and mixtures of 20% (w/w) in water were prepared using double distilled water. Sodium carbonate (dried at 300 °C for 3 h) was supplied from Fluka. Stock solution of HCl ($\cong 0.035$ M) was analysed with primary

standard base, and stock buffer solutions of H₂L and Na₂CO₃ were prepared.

Procedures and EMF measurements

K_1 and K_2 determinations were based on the EMF measurements of the cell described above. The buffer compositions were taken as [H₂L]: [Na₂CO₃] \cong 3 : 1 for K_1 determination and 1.2 : 1 for K_2 determination. In the first step, the cell was calibrated by introducing about 230 g of 20% MeCN into the cell with sufficient dilute HCl ($\cong 0.035$ M) containing 20% MeCN in order to determine the standard cell EMF E° value before making successive additions of stock buffer solutions. With the electrode in position, the cell was equilibrated at the desired temperature (± 0.1 °C). The HCl solution was then given a short stir until the EMF was constant. Up to six additions of stock buffer were then made by weighing pipette (after each addition the solution was stirred and the EMF of the cell was monitored to constancy). The time needed could vary from 1 h for the first addition for a K_2 series down to 15 min for other additions and 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 Micro 2-pH/ion meter.

Results and discussion

The expressions used for calculating the first and the second dissociation constants, K_1 and K_2 , of the studied dicarboxylic acids under investigation in 20% (w/w) MeCN–water mixture at temperatures from 30 to 60 °C are:

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

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

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

$$-\log \gamma_i = AZ_i^2 [I^{1/2} / (1 + 1.3 I^{1/2}) - 0.3I] \quad (4)$$

$$E(\text{cell}) = E^\circ(\text{cell}) - k' \log ([\text{H}^+][\text{CL}^-] \gamma_{\text{H}} \gamma_{\text{CL}}) \quad (5)$$

$$(k' = 2.3026 RT/F)$$

Where I and γ represent the ionic strength and the activity coefficient respectively. Firstly $E^\circ(\text{cell})$ was calculated from equations (4) and (5) by knowing $E(\text{cell})$ of the diluted HCl solution ($I = [\text{HCl}]$). If the stoichiometric molal concentrations of HCl, H₂L and Na₂CO₃ are m_1 , m_2 and m_3 respectively, the following equations are used (with equations (1) – (5)) for calculating K_1 .

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

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

Approximate values of $[\text{H}^+]$ on the addition of buffer solution were calculated from equations (4) and (5) with $I = m_1$ followed by applying equations (6) and (7) with $[\text{L}^{2-}] = [\text{NaL}^-] = 0$ in the first cycle. The subsequent value of I was used to recalculate $[\text{H}^+]$ followed by calculation of $[\text{L}^{2-}]$ using equation (2) with the estimated values of K_2 , and $[\text{NaL}^-]$ was calculated using equation (3). If the estimates of K_2 were significantly different, the calculations were repeated until

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Table 1 Determination of K_1 for succinic acid in 20% (v/v) MeCN/water at different temperatures

20%			T = 30 °C	
	$10^3 m_1 = 2.999$	$-E_1/mV = 230.3$	$-E^\circ/mV = 537.3$	
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^5 K_1$
11.851	2.963	141.5	6.111	3.233
18.470	4.617	133.7	9.526	3.616
25.381	6.345	129.4	13.128	3.751
31.097	7.774	127.9	16.106	3.964
37.096	9.274	126.5	19.236	4.117
42.081	10.52	125.8	21.83	4.282

20%			T = 35 °C	
	$10^3 m_1 = 2.961$	$-E_1/mV = 234.5$	$-E^\circ/mV = 547.3$	
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^5 K_1$
12.838	3.210	144.6	6.552	3.786
20.255	5.064	136.6	10.274	4.162
28.559	7.140	133.5	14.460	4.598
36.130	9.031	131.0	18.282	4.759
41.844	10.461	130.0	21.167	4.958
46.599	11.650	129.3	23.567	5.119

20%			T = 40 °C	
	$10^3 m_1 = 3.335$	$-E_1/mV = 239.7$	$-E^\circ/mV = 551.4$	
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^5 K_1$
13.532	3.383	148.5	6.938	3.936
20.807	5.202	140.1	10.622	4.310
28.252	7.063	136.7	14.417	4.677
34.443	8.611	134.6	17.58	4.863
40.818	10.204	133.4	20.835	5.123
44.996	11.249	132.7	22.968	5.276

20%			T = 45 °C	
	$10^3 m_1 = ?$	$-E_1/mV = 238.5$	$-E^\circ/mV = 565.9$	
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^5 K_1$
13.925	3.481	146.6	7.097	4.232
22.740	5.685	140.1	11.527	4.774
29.989	7.497	137.8	15.181	5.126
35.230	8.807	136.4	17.824	5.294
40.837	10.209	135.5	20.653	5.526
46.706	11.676	134.8	23.613	5.778

20%			T = 50 °C	
	$10^3 m_1 = ?$	$-E_1/mV = 240.4$	$-E^\circ/mV = 574.4$	
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^5 K_1$
14.391	3.596	147.2	7.330	4.362
21.722	5.430	141.7	11.011	4.797
27.677	6.919	139.2	14.010	5.027
34.014	8.503	138.4	17.204	5.439
39.901	9.975	137.0	20.172	5.604
45.384	11.346	136.3	22.936	5.838

20%			T = 60 °C	
	$10^3 m_1 = ?$	$-E_1/mV = 250.4$	$-E^\circ/mV = 594.4$	
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^5 K_1$
14.878	3.720	152.7	7.573	4.228
23.625	5.906	146.9	11.972	4.794
30.049	7.512	144.8	15.211	5.036
36.022	9.005	143.4	18.223	5.264
41.589	10.397	142.6	21.032	5.508
47.417	11.854	142.8	23.969	5.944

Table 2 Determination of K_2 for succinic acid in 20% (v/v) MeCN/water at different temperatures

20%			T = 30 °C		
	$10^3 m_1 = 2.738$	$-E_1/mV = 226.7$	$-E^\circ/mV = 538.1$		
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^6 K_2$	
6.466	5.173	59.8	12.231	1.660	
10.474	8.379	39.7	20.726	1.084	
13.758	11.007	34.7	27.862	1.079	
16.810	13.448	32.2	34.291	1.117	
19.996	15.997	30.4	41.071	1.150	
22.946	18.357	29.1	47.318	1.179	
20%			T = 35 °C		
	$10^3 m_1 = 2.694$	$-E_1/mV = 271.5$	$-E^\circ/mV = 589.2$		
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^7 K_2$	
6.591	5.273	82.8	12.220	6.031	
9.981	7.985	73.7	19.593	7.026	
13.134	10.507	69.8	26.330	7.615	
16.073	12.858	67.7	32.626	8.056	
18.820	15.056	66.4	38.480	8.434	
21.393	17.114	65.6	43.939	8.807	
20%			T = 40 °C		
	$10^3 m_1 = 2.467$	$-E_1/mV = 230.4$	$-E^\circ/mV = 557.9$		
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^6 K_2$	
5.724	4.579	55.2	10.651	1.110	
9.190	7.352	42.5	18.123	1.137	
12.410	9.928	37.1	25.124	1.149	
15.770	12.616	33.7	32.238	1.172	
18.881	15.105	31.7	38.868	1.196	
21.771	17.417	30.4	44.996	1.226	
20%			T = 45 °C		
	$10^3 m_1 = 3.565$	$-E_1/mV = 285.3$	$-E^\circ/mV = 598.7$		
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^7 K_2$	
6.281	5.025	96.2	10.958	4.875	
9.347	7.478	80.9	17.532	6.075	
12.614	10.091	74.9	24.653	6.995	
15.286	12.229	71.6	30.338	7.416	
18.146	14.517	69.3	36.469	7.812	
21.141	16.913	67.9	42.864	8.299	
20%			T = 50 °C		
	$10^3 m_1 = 2.474$	$-E_1/mV = ?$	$-E^\circ/mV = ?$		
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^7 K_2$	
6.205	4.964	82.9	11.366	5.405	
10.069	8.055	72.4	19.771	6.896	
13.626	10.901	67.5	27.390	7.368	
16.913	13.531	65.8	34.437	7.991	
19.632	15.706	64.6	40.232	8.351	
22.178	17.743	63.6	45.636	8.619	
20%			T = 60 °C		
	$10^3 m_1 = 2.837$	$-E_1/mV = 292.6$	$-E^\circ/mV = 633.7$		
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 I$	$10^7 K_2$	
6.578	5.262	87.5	12.072	5.348	
9.744	7.795	76.9	18.912	6.197	
13.412	10.730	71.4	26.828	6.744	
16.794	13.435	68.8	34.087	7.187	
19.315	15.452	65.5	39.452	6.926	
21.974	17.579	67.1	45.138	7.977	

the difference between successive values of $[H^+]$ agreed to $\leq 1 \times 10^{-9}$ m, and then K_1 was obtained from equations (1) and (4).

For K_2 , $[H^+]$ is calculated as described above and then by using equations (8) and (9).

$$[HL^-] = m_1 + 2 m_2 - 2 m_3 - [H^+] + 2[H_2L] \quad (8)$$

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

With $[H_2L] = [NaL^-] = 0$ in the first cycle followed by the use of equations (1) and (3) for calculating $[H_2L]$ and $[NaL^-]$ respectively, K_2 was calculated from equations (2) and (4) when the difference between successive values of $[H^+]$ agreed to $\leq 1 \times 10^{-9}$ m. All computations were made by GW-BASIC computer programs.

Tables 1 and 2 represent some examples of detailed runs of succinic acid in 20% (w/w) MeCN for different temperatures and for different ionic strengths. It is obvious that most of the K_1 and K_2 values for one run varied with the ionic strength. Accordingly extrapolated values of K_1 and K_2 values at zero ionic strength were obtained from the linear least square plots of K_1 and K_2 against ionic strength.

The computed pK_1 and pK_2 values at zero ionic strength of the studied dicarboxylic acids in 20% (w/w) acetonitrile for different temperatures are given in Tables 3 and 4.

It can be seen from Tables 3 and 4 that the pK_1 and pK_2 values of the studied acids are found to be greater in 20% acetonitrile than in water.^{20,21} These results are in agreement with Born's equation for predicting ionisation constants.²⁴ Comparison of the interpolated pK_1 and pK_2 values of tartaric acid at 25 °C in 20% (w/w) acetonitrile–water mixture obtained by Barbosa *et al.*¹⁸ are 3.48 and 4.78 respectively were found to be quite near to that obtained in the present work at 30 °C, 3.47 and 4.52 respectively. The small difference in pK_2 arises from the effect of temperature as pK_2 is more sensitive to temperature variation than pK_1 .

Thermodynamics of acid dissociation

The standard thermodynamic parameters ΔG° , ΔH° and ΔS° of the first and second dissociations for all dicarboxylic acids in 20% MeCN were computed from well-known thermodynamic relationships. The plots of pK_1 or pK_2 against $1/T$ shown in Figs 1 and 2 give straight lines for both dissociations and for all dicarboxylic acids, which shows that ΔH°_1 and ΔH°_2 may be treated as sensibly constant over the temperature range used here. From the slopes of these plots, values of ΔH°_1 and ΔH°_2 have been calculated. These are listed in Tables 5 and 6 with the computed values of ΔG°_1 , ΔG°_2 , ΔS°_1 and ΔS°_2 for the first and second dissociations.

ΔG°_1 and ΔG°_2 have positive values which indicate the preferential stabilisation of H_2L in the first dissociation reaction, and of the HL^- in the second dissociation reaction. Moreover, their high values give a good indication of the pronounced solvation of both anions HL^- and L^{2-} of the acids in a 20% (w/w) MeCN–water mixture.

A useful comparison can be made with the standard entropies of the present work from which the negative values ΔS°_1 were found to be increasing in the following order: maleic < tartaric < malonic < malic < succinic. These acids have the general formula $R-COOH$

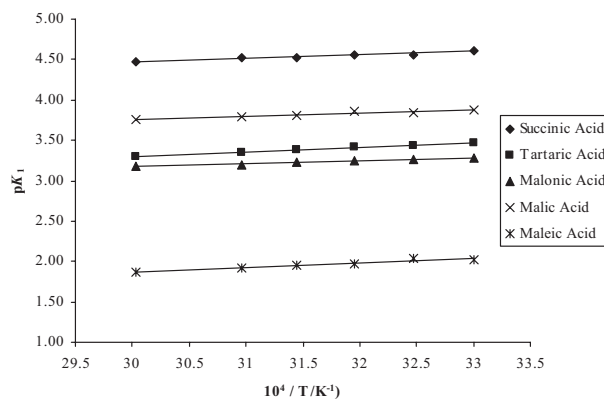


Fig. 1 Van't Hoff plots for the first dissociation reactions of dicarboxylic acids.

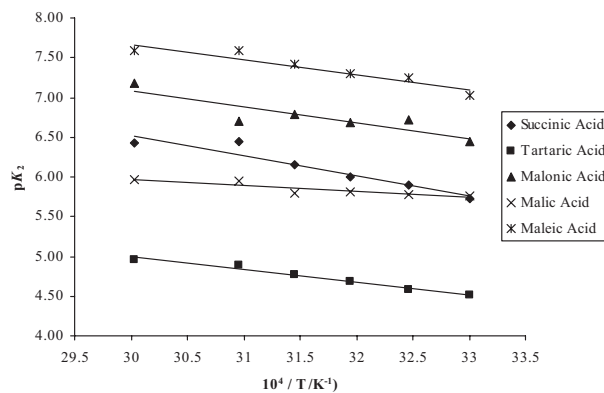


Fig. 2 Van't Hoff plots for the second dissociation reactions of dicarboxylic acids.

where R represents $-CH_2-COOH$ in malonic, $-CH_2-CH_2-COOH$ in succinic, $-CH_2-CH(OH)-COOH$ in malic, $-CH(OH)-CH(OH)-COOH$ in tartaric and $-CH=CH-COOH$ in maleic. The tendency is mainly attributed to the electrostatic action on the carboxylic groups, transmitted through the CH_2 -group for malonic and succinic acids, to hydroxyl substituents for malic and tartaric acids and also to conjugation effects for maleic acid. Furthermore, the electrostatic action transmitted through solvent molecules (field effect) also governs these solute-solvent interactions and their thermodynamics results. The charged anions (HL^- , L^{2-}) of these acids impose order

Table 3 pK_1 values of some dicarboxylic acids in 20% (w/w) MeCN/water at different temperatures

Acid	pK_1					
	30 °C	35 °C	40 °C	45 °C	50 °C	60 °C
Succinic	4.61	4.56	4.55	4.53	4.52	4.47
Malic	4.55	4.53	4.52	4.47		
Tartaric	3.87	3.85	3.85	3.80	3.79	3.76
Malonic	3.47	3.43	3.41	3.38	3.35	3.30
Maleic	3.28	3.26	3.24	3.23	3.19	3.17
	2.02	2.03	1.96	1.94	1.92	1.87

Table 4 pK_2 values of some dicarboxylic acids in 20% (w/w) MeCN/water at different temperatures

Acid	pK_2					
	30 °C	35 °C	40 °C	45 °C	50 °C	60 °C
Succinic	5.73	5.89	5.99	6.15	6.44	6.42
Malic	5.75	5.77	5.82	5.79	5.95	5.97
Tartaric	4.52	4.58	4.68	4.76	4.88	4.96
Malonic	6.44	6.71	6.69	6.79	6.69	7.18
Maleic	7.03	7.24	7.29	7.41	7.59	7.58

Table 5 Thermodynamic parameters for the first dissociation constant in 20% (w/w) MeCN/water at different temperatures (ΔH° , $\Delta G^\circ/\text{kJ mol}^{-1}$ and $\Delta S^\circ/\text{J mol}^{-1}\text{K}^{-1}$)

T/°C		Succinic	Tartaric	Malonic	Malic	Maleic
30	ΔH°_1	8.27	10.56	7.35	6.96	10.41
	ΔG°_1	26.77	20.15	19.07	22.48	11.75
	$-\Delta S^\circ_1$	61.04	31.62	38.67	51.17	4.40
35	ΔH°_1	8.27	10.56	7.35	6.96	10.41
	ΔG°_1	26.90	20.25	19.26	22.66	11.98
	$-\Delta S^\circ_1$	60.47	31.42	38.66	50.79	5.07
40	ΔH°_1	8.27	10.56	7.35	6.96	10.41
	ΔG°_1	27.31	20.46	19.46	23.11	11.76
	$-\Delta S^\circ_1$	60.80	31.60	38.68	51.56	4.31
45	ΔH°_1	8.27	10.56	7.35	6.96	10.41
	ΔG°_1	27.59	20.61	19.69	23.16	11.85
	$-\Delta S^\circ_1$	60.72	31.56	38.78	50.89	4.51
50	ΔH°_1	8.27	10.56	7.35	6.96	10.41
	ΔG°_1	27.98	20.76	19.78	23.48	11.90
	$-\Delta S^\circ_1$	60.99	31.55	38.48	51.10	4.61
60	ΔH°_1	8.27	10.56	7.35	6.96	10.41
	ΔG°_1	28.51	21.07	20.25	23.99	11.95
	$-\Delta S^\circ_1$	60.76	31.54	38.73	51.11	4.62

Table 6 Thermodynamic parameters for the second dissociation constant in 20% (w/w) MeCN/water at different temperatures (ΔH° , ΔG° , /kJ mol⁻¹ and $\Delta S^\circ/\text{J mol}^{-1}\text{K}^{-1}$)

T/°C		Succinic	Tartaric	Malonic	Malic	Maleic
30	$-\Delta H^\circ_2$	48.71	30.36	38.02	15.26	36.37
	ΔG°_2	33.27	26.23	37.39	33.42	40.81
	$-\Delta S^\circ_2$	270.45	186.70	248.77	160.58	254.64
35	$-\Delta H^\circ_2$	48.71	30.36	38.02	15.26	36.37
	ΔG°_2	34.79	27.06	38.58	34.05	42.72
	$-\Delta S^\circ_2$	271.00	186.37	251.85	160.03	256.71
40	$-\Delta H^\circ_2$	48.71	30.36	38.02	15.26	36.37
	ΔG°_2	35.93	28.09	40.10	34.89	43.74
	$-\Delta S^\circ_2$	270.31	186.66	249.50	160.15	255.86
45	$-\Delta H^\circ_2$	48.71	30.36	38.02	15.26	36.37
	ΔG°_2	37.50	29.03	41.35	35.29	45.15
	$-\Delta S^\circ_2$	271.33	186.71	249.51	158.90	256.27
50	$-\Delta H^\circ_2$	48.71	30.36	38.02	15.26	36.37
	ΔG°_2	39.84	30.21	41.42	36.83	46.96
	$-\Delta S^\circ_2$	274.04	187.48	245.86	161.20	257.89
60	$-\Delta H^\circ_2$	48.71	30.36	38.02	15.26	36.37
	ΔG°_2	40.95	31.66	45.81	38.10	48.36
	$-\Delta S^\circ_2$	269.13	186.20	251.65	160.17	254.36

on the surrounding solvent molecules, which interferes with internal rotation of the alkyl chain of the acid, and thus the partial molal entropies of the anions become smaller (relative to the neutral acid) and hence ΔS°_1 of the dissociation should be more negative as the length of the alkyl chain increases. ΔS°_2 values are more negative than ΔS°_1 values, since solvent interactions in anion L^{2-} are properly higher than that of mono-anion HL⁻.

From the above discussions, the order imposed on the solvent about mono-succinate anion should restrict internal rotation in an $-\text{CH}_2-\text{CH}_2-\text{COOH}$ group more than in the $-\text{CH}_2-\text{COOH}$ group in the case of mono-malonate anion. This restriction of internal rotation lowers the partial molal entropy of the succinate mono-anion compared with the corresponding malonate mono-anion, and thus the ΔS°_1 value of succinate mono-anion becomes more negative.

The higher negative ΔS°_1 value of succinic acid compared with malic and tartaric acids could be explained in the light of hydrogen bonding, which mainly exists in malic and tartaric acids. This effect causes a lowering in the basicity of both malate and tartarate mono anions with subsequent decreases of solvation and correspondingly less negative ΔS°_1 values compared with succinic acid. Accordingly, the basicity of the succinate mono anion becomes higher, and thus,

the extent of its solvation is increased giving more lowering of its partial molal entropy compared to that of malate and tartarate mono anions; thus the negative ΔS°_1 of the succinate mono anion should be higher than that of the malate and tartarate mono anions. However, the higher conjugation effect in the maleate mono anion give less basicity for the anion species with a subsequent decreasing of solvation (compared with the rest of the studied series) and correspondingly a relatively less negative ΔS°_1 is obtained. Moreover, the first dissociation process is more favoured for the formation of mono-maleate anion. This allows maleic acid to be the strongest of the studied acids (lowest $\text{p}K_1$ values). The trend in ΔS°_2 values among the studied acids is similar to that obtained for ΔS°_1 except for maleic acid where the conjugation stabilised the negative charge on the two carboxylate oxygen atoms yielding more solvent electrostriction than in the case of ΔS°_1 due to the repulsion between the two carboxylate anions.

The negative values of ΔH°_2 for the second ionisation reaction reflect exothermic dissociation while the positive values of ΔH°_1 for the first dissociation reaction reflect endothermic dissociation.

Extrathermodynamic Analysis

An extrathermodynamic analysis of the obtained results has been performed to test the isoequilibrium correlation among different dicarboxylic acids. This correlation is shown in Figure 3 which represents $\Delta H^\circ - \Delta S^\circ$ for the first and second dissociation reactions for the studied dicarboxylic acids at 40°C. This correlation was found to be linear with a slope (β) of 55.3 K for the first dissociation and 236.2 K for the second dissociation. These isoequilibrium temperatures of both dissociation reactions are found to be lower than the experimental temperature (313 K) indicating that these dissociation reactions are entropy controlled reactions²⁵ where solute-solvent interaction plays an important role.

Conclusion

In this work, pK_1 and pK_2 values at zero ionic strength of succinic, tartaric, malonic, malic and maleic acids have determined using a precise EMF method and have been found to be in agreement with Born's equation. The thermodynamic parameters of the first and the second dissociation reactions have been calculated. The positive values of ΔG°_1 and ΔG°_2 indicate the preferential stabilisation of H_2L and HL^- . Moreover, their higher values give a good indication of the pronounced solvation of both anions HL^- and L^{2-} of the acids.

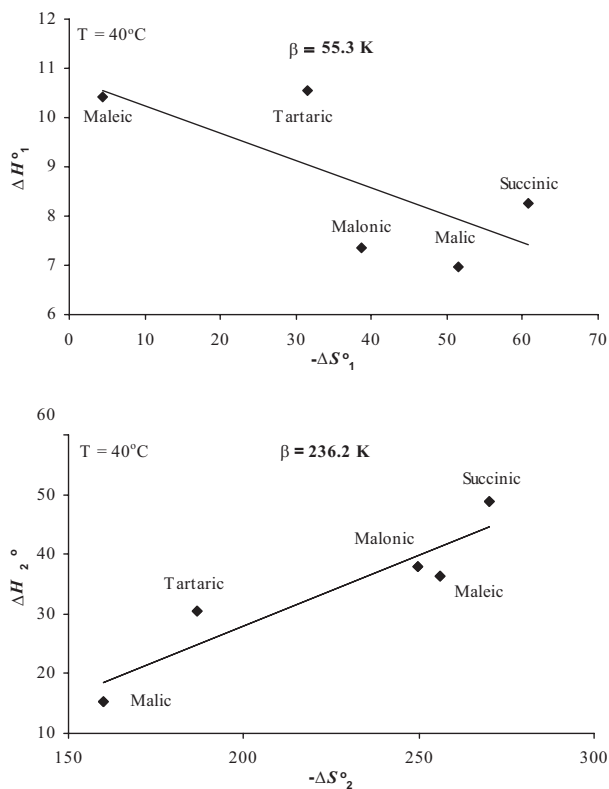


Fig. 3 Isoequilibrium plots for the acid dissociation reactions at 40°C.

The negative values of ΔH°_2 reflect exothermic dissociation, while the positive values of ΔH°_1 reflect endothermic dissociation. The negative values of ΔS°_1 were found to increase in the following order: maleic < tartaric < malonic < malic < succinic acids. A similar trend was found for ΔS°_2 values except for maleic acid where conjugation stabilised the negative charge on the two carboxylate oxygen atoms yielding more solvent electrostriction than in the case of ΔS°_1 due to the repulsion between the two carboxylate anions. The isoequilibrium temperatures of both dissociation reactions were found to be lower than the experimental temperature (313 K) indicating that these dissociation reactions are entropy controlled reactions where solute-solvent interaction plays an important role.

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References

- 1 F. Mardn, D. Celadon, M.G. Serverin and E. Vianello, *J. Am. Chem. Soc.*, 1991, **113**, 9320.
- 2 A.A. El-Bardan, N.M. El-Mallah and E.A. Hamed, *J. Phys. Org. Chem.*, 1992, **5**, 239.
- 3 A.H. Azab, A. Hassan and Z.A. Khafagy, *J. Chem. Eng. Data*, 1993, **38**, 231.
- 4 A. Cladera, C. Tomas, J.M. Estela and V. Cedra, *Anal. Chim. Acta.*, 1994, **286**, 253.
- 5 G.E. Jackson and L.F. Seymour, *Talanta*, 1995, **42**, 5.
- 6 A.A. Boraie, I.T. Ahmed and M.M. Hamed, *J. Chem. Eng. Data*, 1996, **41**, 787.
- 7 F.R. Trull, S. Bioadjiev and A.F. Mc Donagh, *J. Lipid Res.*, 1997, **38**, 1178.
- 8 A.G. Gonzalez, D. Rosales, J.L. Gomez Ariza and J.F. Sanz, *Anal. Chim. Acta*, 1990, **228**, 301.
- 9 L. Chmurzynski, A. Wawrzynow and Z. Pawlak, *Electrochim. Acta*, 1990, **35**, 665.
- 10 L. Chmurzynski, A. Liwo and P. Barczynski, *Anal. Chim. Acta*, 1996, **335**, 147.
- 11 A.G. Gonzalez, M.A. Herrador and A.G. Asuero, *Anal. Chim. Acta*, 1991, **246**, 429.
- 12 Z. Guo, H. Miyoshi, K. Nagatani, T. Komyoji, T. Haga and T. Fujita, *J. Org. Chem.*, 1991, **56**, 3692.
- 13 C.B. Monk and M.F. Amira, *J. Chem. Soc. Faraday Trans. I*, 1978, **74**, 1170.
- 14 C.B. Monk and M.F. Amira, *J. Chem. Soc. Faraday Trans. I*, 1980, **76**, 1773.
- 15 M.F. Amira, Sh. El-Shazly and M.M. Khalil, *Thermochem. Acta.*, 1987, **115**, 1.
- 16 G. Younes, G. El-Subruiti, K. Hamdan and M. Amira, *Proc. Int. Conf. on RTST*, Lebanese American University, Beirut, Lebanon, 4-6 March 2002, 115.
- 17 A.A. Zaghoul, G.A. El Naggat, Sh. A. El Shazly and M.F. Amira, *Talanta*, 1997, **45**, 189.
- 18 J. Barbosa, J.L. Beltran and V. Sanz-Nebot, *Anal. Chim. Acta*, 1994, **288**, 271.
- 19 A.A. Zaghoul, *Afinidad*, 1996, **462**, 123.
- 20 A.A. Zaghoul, G.A. El Naggat and M.F. Amira, *Gazz. Ital.*, 1996, **126**, 735.
- 21 G.A. El Naggat, S.M. Selim, A.A. Zaghoul and M.F. Amira, *Z. Phys. Chem.*, 2002, **216**, 1239.
- 22 J. Barbosa and V. Sanz-Nebot, *Talanta*, 1989, **36**, 837.
- 23 G. Jahanbakhsh, A. Shahin, K. Mikael and F. Amin, *J. Chem. Eng. Data*, 2003, **48**, 1178.
- 24 M. Born, *Z. Phys. Chem.*, 1920, **45**, 1.
- 25 J. E. Leffler and E. Grunwald, *Rates and equilibria of organic reactions*, John Wiley and Sons, New York, 1963. p.155.