Thermochimica Acta, 115 (1987) 1–10
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF ELECTROLYTIC DISSOCIATION. FIRST AND SECOND DISSOCIATION CONSTANTS OF SOME DICARBOXYLIC ACIDS IN 10% (V/V) ACETONE

M.F. AMIRA *, SH. A. EL-SHAZLY and M.M. KHALIL

Chemistry Department, Faculty of Science, Alexandria University, Alexandria (Egypt)

(Received 28 May 1986)

ABSTRACT

First and second dissociation constants (K_1 and K_2) of some dicarboxylic acids (succinic, malic, tartaric, malonic, maleic and phthalic) in 10% (v/v) acetone has been determined at different temperatures (30–60 °C) using the chemical cell, glass electrode/HCl, H_2L, $Na_2CO_3/AgCl_{(s)}$, Ag. The thermodynamic parameters ΔG^0, ΔH^0 and ΔS^0 for the first and the second dissociation reactions of these acids have been calculated and discussed. An extra thermodynamic analysis has been examined, in the light of the isoequilibrium relationship, where the isoequilibrium temperature values for both dissociation reactions indicate that these reactions are entropy-controlled reactions.

INTRODUCTION

Although the pKs of several monobasic acids in mixed solvents have been reported [1–6], there seems to be little similar information about dibasic acids. Recently, Monk and Amira [7,8] used the glass electrode–AgCl cell in the determination of K_1 and K_2 of some dibasic acids in aqueous and 10% (v/v) ethanol solutions at 40 °C. They attempted to reduce the dependence of the pK values at zero ionic strength (for pKs < 2.5) upon the ion-size parameters value (σ) of the Debye–Hückel activity coefficient expression. Their method provides a simple and precise way of pK determination. The present work deals with the determination of K_1 and K_2 in 10% (v/v) acetone for six different dicarboxylic acids (succinate, malic, tartaric, malonic, maleic and phthalic) in a wide temperature range (30–60 °C). This study will help to elucidate the thermodynamics of acid dissociation in the acetone–water medium for the given dicarboxylic acids. Moreover, the structure effect of these acids on the S_1^0 and S_2^0 values can now be understood.

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* To whom all correspondence should be addressed.

EXPERIMENTAL

Stock solutions of HCl (~ 0.2 mol kg^{-1}) were analyzed by AgCl weighings, and stock solutions of dicarboxylic acids (H_2L) and Na_2CO_3 (dried at 300 °C for 3 h) were made up, by weight, from B.D.H. Analar samples. The H_2L: Na_2CO_3 molar ratios were 3:1 for the K_1 and $\sim 1.2:1$ for the K_2 determinations, respectively. For phthalic acid, potassium hydrogen phthalate and HCl solutions were used for the K_1 and a potassium hydrogen phthalate: Na_2CO_3 molar ratio of $\sim 2:1$ for the K_2 determinations, respectively. About 200 g of 10% (v/v) acetone (to ± 0.01 g) was weighed into the cell, together with sufficient diluted stock HCl containing 10% (v/v) acetone (~ 0.03 mol kg^{-1}) to make ~ 0.0015–0.0025 mol kg^{-1} HCl (addition by weight pipette to ± 0.01 mg). With the electrodes in position, the cell was equilibrated at the desired temperature (±0.01 °C). This could take up to 3 h. The HCl was then given a short stir (~ 5 s) by a fitted microstirrer and left to settle until the e.m.f. was constant (~ 0.5 h). Up to six additions of stock buffer were then added by weight pipette. Each addition was stirred and the e.m.f. of the cell then monitored to constancy. The time needed could vary from ~ 1 h for the first addition for a K_2 series, i.e. the point of greatest e.m.f. change, down to ~ 15 min for later additions and for all of a particular K_1 series. Under the above conditions the solutions were free of evolved CO_2.

Measurements to ± 0.1 mV were made with a digital pH meter (Beckman 4500 type). The AgCl electrode was made by plating a thin Pt wire spiral with Ag in 0.5% $KAg(CN)_2$ for ~ 1 h with a 9 V battery followed by electrolysis for AgCl in 0.05 M HCl at 9 V for 20 s. The ultra water thermostat, working to ± 0.01 °C, was used.

RESULTS AND DISCUSSION

The expressions used for calculating K_1 and K_2 were

$$K_1 = ([H^+][HL^-] f_H f_{HL})/[H_2L] \tag{1}$$

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

$$-\log f_1 = AZ_i^2 [I^{1/2}/(1 + BI^{1/2}) - QI] \tag{3}$$

($B = 1.3$ and $Q = 0.3$)

$$E(\text{cell}) = E^0(\text{cell}) - k' \log([H^+][Cl^-] f_H f_{Cl}) \tag{4}$$

where I represents ionic strength and f represents the activity coefficients. The value of the Debye–Hückel constant, A, varied with either temperature or dielectric constant, while k' ($= 2.3026\ RT/F$) values varied with temperature. Firstly, E^0 (cell) was calculated from eqns. (3) and (4) via E(cell) of the initial HCl solution. Approximate values of $[H^+]$ on the addition of buffer solution were calculated from eqns. (3) and (4) with $I = m_1$, followed by use of

$$[H_2L] = m_1 + m_2 - 2m_3 - [H^+] + [L^{2-}] \tag{5}$$

$$[HL^-] = m_2 - [H_2L] - [L^{2-}] \tag{6}$$

with $[L^{2-}] = 0$ in the first cycle. The subsequent value of I was used to recalculate $[H^+]$, followed by calculation of $[L^{2-}]$ via eqn. (2) with theoretical published values of K_2 [8]. When successive values of $[H^+]$ agreed to within $\leqslant 1.0 \times 10^{-6}$ mol kg^{-1}, K_1 was obtained from eqns. (1) and (3).

For K_2, $[H^+]$ was calculated as described above and, then,

$$[HL^-] = m_1 + 2m_2 - 2m_3 - [H^+] - 2[H_2L] \tag{7}$$

$$[L^{2-}] = m_2 - [H_2L] - [HL^-] \tag{8}$$

found with $[H_2L] = 0$ in the first cycle followed by use of eqn. (1). K_2 was calculated from eqns. (2) and (3) when successive values of $[HL^-]$ agreed to within $\leqslant 5.0 \times 10^{-7}$ mol kg^{-1}. The computations were performed by means of BASIC computer programs.

Some examples of the present work are shown in Table 1, which contains the e.m.f. values with the corresponding computed K_1 or K_2 values for different dicarboxylic acids used at different temperatures. For each run, the extrapolated K_1 and K_2 values were obtained from the linear least mean squares plots of K_1 (or K_2) versus I. The computed pK_1 and pK_2 values for different acids at different temperatures are shown in Table 2 (some published values are included in this table for critical comparisons).

Thermodynamics of acid dissociation

It is well known that the ionization of acids in a pure aqueous medium is a process for which ΔC_p is quite large [9]. At the same time, water is a solvent whose microstructure is believed to change considerably with temperature. For this reason, it is difficult to explain structural effects using the standard enthalpy and entropy changes for acid dissociation in a pure aqueous medium [10]. In the present work, the thermodynamics of acid dissociation in a 10% acetone medium were discussed, since greater ion association occurs in this solvent, thereby giving more favourable conditions for high-lighting any dependency of ΔH^0 and ΔS^0 values on the acid structure. The thermodynamic properties, ΔG_1^0, ΔH_1^0 and ΔS_1^0, of the first and the second dissociation reactions, ΔG_2^0, ΔH_2^0 and ΔS_2^0, in 10% acetone were determined. The enthalpy of dissociation (ΔH^0) was computed from the slope of the best fitting Van't Hoff plots (some examples are shown in Fig. 1), while ΔG^0 and ΔS^0 were calculated according to the following equations:

$$\Delta G^0 = -RT \ln K$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

TABLE 1

Examples of K_1 and K_2 determinations

Succinic (50 ° C)				Tartaric (60 ° C)				Malic (35 ° C)			
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^5 K_1$	$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^4 K_1$	$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^5 K_1$
13.208	3.472	9.10	5.460	11.174	29.085	81.40	7.043	15.710	4.123	47.00	2.671
19.931	5.240	2.50	5.646	17.300	45.032	78.10	7.220	21.474	5.636	44.00	2.780
25.545	6.716	−0.10	5.872	22.875	59.543	76.60	7.473	26.401	6.929	41.00	2.702
29.782	7.830	−3.40	5.631	26.580	69.187	75.50	7.504	33.732	8.853	39.00	2.776
34.109	8.967	−4.60	5.757	30.412	79.162	74.00	7.370	36.988	9.708	38.00	2.776
36.826	9.681	−5.10	5.865	35.362	92.045	72.70	7.365	40.769	10.700	37.00	2.785
Malic (50 ° C)				Maleic (60 ° C)				Tartaric (40 ° C)			
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^4 K_1$	$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 K_1$	$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^4 K_1$
13.546	3.555	42.00	2.978	15.960	4.197	133.60	10.645	15.166	3.948	77.20	7.218
19.993	5.247	37.00	2.941	22.855	6.010	135.70	10.783	20.438	5.320	75.00	7.203
26.364	6.920	35.00	3.055	28.861	7.589	136.70	10.820	25.834	6.725	73.60	7.298
30.773	8.077	33.00	3.005	36.282	9.540	137.00	10.617	31.252	8.135	72.20	7.299
34.432	9.037	31.00	2.906	40.051	10.531	137.10	10.620	35.061	9.126	71.20	7.263
38.494	10.103	30.00	2.927					38.556	10.036	70.60	7.323
Malonic (30 ° C)				Phthalic (60 ° C)				Maleic (30 ° C)			
$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 K_1$	10^2 (KHph)	10^3 (HCl)	$-E$ (mV)	$10^4 K_1$	$10^3 m_2$	$10^3 m_3$	$-E$ (mV)	$10^3 K_1$
15.707	4.138	89.80	1.099	0.778	4.237	95.80	7.935	13.464	3.540	122.10	11.702
20.658	5.442	87.90	1.101	1.121	5.336	99.50	8.161	18.984	4.992	123.90	11.237
25.283	6.661	86.50	1.104	1.474	6.468	102.90	8.186	25.712	6.761	125.70	11.482
30.415	8.013	85.00	1.099	1.976	8.076	107.00	8.075	31.322	8.236	126.30	11.334
35.548	9.365	84.00	1.111	2.371	9.345	110.30	8.114	35.227	9.263	126.60	11.320
39.060	10.290	83.40	1.122	2.668	10.295	112.50	8.112	39.580	10.407	126.90	11.404

TABLE 1 (continued)

Succinate (30 ° C)				Malonic (50 ° C)				Tartaric (60 ° C)			
$10^3 m_2$	$10^3 m_3$	E (mV)	$10^6 K_2$	$10^3 m_2$	$10^3 m_3$	E (mV)	$10^7 K_2$	$10^3 m_2$	$10^3 m_3$	E (mV)	$10^5 K_2$
9.382	7.922	85.60	1.369	5.879	4.918	81.70	7.672	7.017	5.781	1.70	2.883
12.935	10.922	90.90	1.401	8.909	7.452	94.00	8.371	10.082	8.306	9.60	2.888
15.443	13.039	93.70	1.395	11.113	9.296	98.70	8.550	12.454	10.260	13.80	2.825
19.466	16.436	96.70	1.404	12.874	10.769	101.90	8.473	14.552	11.988	15.60	2.891
21.943	18.527	98.40	1.396	14.975	12.526	104.20	8.589	16.970	13.979	16.90	2.990
				17.997	15.054	106.30	8.844	18.903	15.572	17.60	3.078
Malic (55 ° C)				Malic (40 ° C)				Malonic (50 ° C)			
$10^3 m_2$	$10^3 m_3$	E (mV)	$10^6 K_2$	$10^3 m_2$	$10^3 m_3$	E (mV)	$10^6 K_2$	$10^3 m_2$	$10^3 m_3$	E (mV)	$10^7 K_2$
6.977	5.650	51.50	3.891	6.032	4.885	51.40	4.566	5.979	5.001	107.50	6.366
10.169	8.235	59.50	4.253	10.283	8.328	62.60	4.838	8.535	7.140	113.70	7.016
13.311	10.779	63.00	4.547	13.590	11.005	66.60	4.917	11.851	9.913	117.20	7.605
15.531	12.577	64.40	4.745	15.973	12.935	68.30	5.010	14.035	11.740	118.30	7.962
17.681	14.318	68.30	4.409	17.689	14.324	70.30	4.865	16.174	13.529	121.90	7.480
20.155	16.321	70.60	4.337	19.607	15.878	72.00	4.782	18.265	15.278	122.80	7.630
Tartaric (50 ° C)				Phthalic (35 ° C)				Maleic (30 ° C)			
$10^3 m_2$	$10^3 m_3$	E (mV)	$10^5 K_2$	$10^3 m_2$	$10^3 m_3$	E (mV)	$10^6 K_2$	$10^3 m_2$	$10^3 m_3$	E (mV)	$10^7 K_2$
5.960	4.910	0.00	2.829	0.957	4.039	85.90	1.902	8.310	6.995	117.00	3.546
8.545	7.039	7.50	2.950	1.207	5.093	90.40	1.998	10.902	9.176	121.00	3.666
11.103	9.147	11.60	3.023	1.658	6.998	95.70	2.098	13.289	11.186	123.00	3.792
13.163	10.843	14.60	2.971	2.184	9.220	99.40	2.189	15.200	12.643	124.20	3.849
15.099	12.439	17.00	2.911	2.514	1.061	102.30	2.136	17.345	14.600	125.70	3.882
17.389	14.325	18.80	2.913	2.882	1.216	106.00	2.011				

TABLE 2

pK_1 and pK_2 values of some dicarboxylic acid in 10% acetone at different temperatures

Acid	pK_1									pK_2								
	25 °C [a]	30 °C	35 °C	40 °C [a]	40 °C	45 °C	50 °C	55 °C	60 °C	25 °C [a]	30 °C	35 °C	40 °C [a]	40 °C	45 °C	50 °C	55 °C	60 °C
Succinic	4.362	4.292	4.268	4.339	4.301	4.347	4.252	4.301	4.292	5.816	5.854	5.903	5.836	5.903	5.854	5.920	5.978	5.971
	4.209 [b]			4.193 [b]						5.647 [b]			5.664 [b]					
Malic	3.599	3.556	3.561	3.588	3.565	3.544	3.527	3.573	3.553	5.258	5.269	5.301	5.304	5.316	5.324	5.305	5.360	5.377
Tartaric	3.196	3.151	3.180	3.174	3.139	3.139	3.175	3.180	3.130	4.534	4.532	4.529	4.542	4.627	4.545	4.533	4.525	4.534
Malonic	2.982	2.956	2.967	2.984	2.971	3.013	2.980	2.957	2.991	5.942	5.973	6.004	6.005	6.008	6.142	6.154	6.199	6.191
	2.85 [c]									5.692 [b]			5.477 [b]					
Maleic	1.970	1.943	1.955	2.000	1.958	1.947	1.911	1.964	1.971	6.509	6.493	6.585	6.624	6.611	6.553	6.676	6.788	6.730
	1.960 [d]									6.242			6.276 [b]					
Phthalic	3.134	3.077	3.090	3.155	3.119	3.134	3.118	3.077	3.092	5.673	5.769	5.764	5.729	5.821	5.863	5.865	6.017	6.045

[a] Values in 10% ethanol taken from ref. 8.

[b] Water, ref. 8.

[c] Water, ref. 8.

[d] Water, ref. 7.

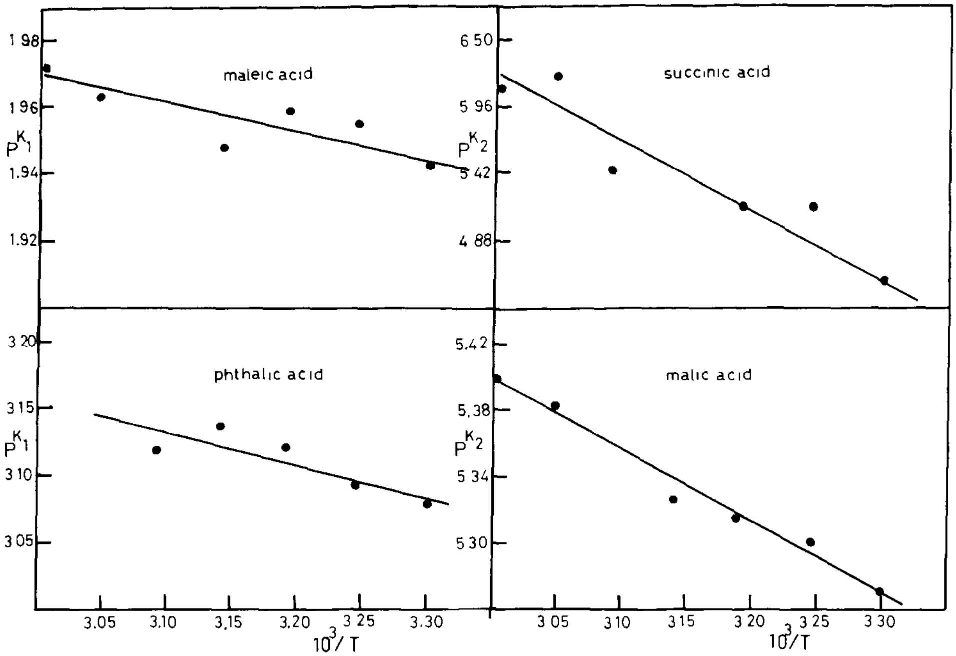

Fig. 1. Van't Hoff plots for the first and second dissociation reactions of dicarboxylic acids.

The computed values of ΔG_1^0, ΔH_1^0 and ΔS_1^0 for the first acid dissociation constant are given in Table 3, while ΔG_2^0, ΔH_2^0 and ΔS_2^0 values for the second dissociation reaction are displayed in Table 4. A critical comparison of ΔH_2^0 and ΔS_2^0 values can be made with those reported in a pure aqueous medium. For example, ΔH_2^0 and ΔS_2^0 values of malonic acid in a pure aqueous medium were reported as -4.81 kJ mol^{-1} and -125.10 J mol^{-1} K^{-1}, respectively [11,12], while the corresponding values in 10% (v/v) acetone at 30 °C (present work) are -17.99 kJ mol^{-1} and -171.2 J mol^{-1} K^{-1}, respectively. The relatively higher negative ΔH_2^0 and ΔS_2^0 values in 10% acetone can be attributed to the increase of the extent of the ion-solvation in 10% acetone than in water with a subsequent negative increase of ΔH_2^0 and ΔS_2^0 values. In addition, electrostatic, hydrogen-bonding and solvent basicity govern these thermodynamics variations.

The negative value of ΔS_1^0 (Table 1) was found to increase in the order: maleic < malonic < tartaric < malic < phthalic < succinic. This trend is primarily because of the electrostatic action on the carboxylic groups transmitted through–CH_2–groups (malonic and succinic) and its hydroxy substituents (malic and tartaric), and is also due to the conjugation effects of maleic and phthalic acids. Moreover, the electrostatic action transmitted through solvent molecules (field effect) also govern these types of interactions. Evan and Hamann [13] suggested that there is significant interaction of the positive charge on NH_4^+ with surrounding water molecules. This

TABLE 3

Thermodynamic parameters ΔG_1^0, ΔH_1^0 and ΔS_1^0 for the first dissociation constant K_1 in 10% acetone (ΔG_1^0 in kJ mol^{-1}, ΔH_1^0 in kJ mol^{-1} and ΔS_1^0 in J mol^{-1} K^{-1})

Acid	Parameter	Temperature (° C)						
		30	35	40	45	50	55	60
Succinic	ΔG_1^0	24.909	25.178	25.784	26.476	26.304	27.019	27.374
	$-\Delta H_1^0$	0.766	0.766	0.766	0.766	0.766	0.766	0.766
	$-\Delta S_1^0$	84.690	84.190	84.780	85.600	83.800	84.700	84.500
Malic	ΔG_1^0	20.637	21.007	21.372	21.585	21.819	22.446	22.660
	$-\Delta H_1^0$	1.149	1.149	1.149	1.149	1.149	1.149	1.149
	$-\Delta S_1^0$	71.900	71.900	71.900	71.500	71.100	71.900	71.500
Tartaric	ΔG_1^0	18.287	18.760	18.818	19.119	19.642	19.977	19.962
	$-\Delta H_1^0$	2.297	2.297	2.297	2.297	2.297	2.297	2.297
	$-\Delta S_1^0$	67.000	68.300	67.400	67.300	67.900	67.900	66.810
Malonic	ΔG_1^0	17.155	17.503	17.811	18.351	18.435	18.576	19.076
	$-\Delta H_1^0$	2.680	2.680	2.680	2.680	2.680	2.680	2.680
	$-\Delta S_1^0$	65.400	65.500	65.400	66.100	65.300	64.800	65.300
Maleic	ΔG_1^0	11.276	11.533	11.738	11.859	11.822	12.338	12.571
	$-\Delta H_1^0$	1.531	1.531	1.531	1.531	1.531	1.531	1.531
	$-\Delta S_1^0$	42.200	42.400	42.400	42.100	41.300	42.300	42.300
Phthalic	ΔG_1^0	17.857	18.229	18.698	19.088	19.289	19.330	19.720
	$-\Delta H_1^0$	5.743	5.743	4.40	5.743	5.743	5.743	5.743
	$-\Delta S_1^0$	77.800	77.800	73.77	78.000	77.500	76.400	76.400

interaction imposes a certain ordering and thus loss of entropy on the solvent. They also suggested that the order imposed on the solvent about the cation could restrict internal rotation in an alkyl substituent. This restriction of internal rotation lowers the entropy of the acid cation relative to that of the neutral base and therefore causes the entropy of ionization to become less negative as the length of an alkyl substituent increases. In the present investigation it is the charged anion that imposes order on the surrounding solvent molecule, which in turn interferes with internal rotation in the alkyl chain, partial molal entropies of the anions become smaller (relative to the neutral acid) and, thus, ΔS_1^0 should become correspondingly more negative as the length of the alkyl chain increases, in accordance with the observed ΔS_1^0 values of malonic and succinic acids. The higher negative ΔS_1^0 value of succinic acid (compared to malic and tartaric acids) can be largely attributed to the hydrogen bonding effect which mainly exists in malic and tartaric acids. This effect causes a lowering in the basicity of both malate and tartrate mono anions with subsequent decrease of the entropy of solvation and correspondingly less negative ΔS_1^0 values compared to succinic acid. The relatively higher negative ΔS_1^0 value of malic acid than tartaric acid was

TABLE 4

Thermodynamic parameters ΔG_2^0, ΔH_2^0 and ΔS_2^0 for the second dissociation constant K_2 in 10% acetone (ΔG_2^0 in kJ mol^{-1}, ΔH_2^0 kJ mol^{-1} and ΔS_2^0 J mol^{-1} K^{-1})

Acid	Parameter	Temperature (° C)						
		30	35	40	45	50	55	60
Succinic	ΔG_2^0	33.974	34.823	35.388	35.655	36.623	37.554	38.082
	$-\Delta H_2^0$	8.040	8.040	8.040	8.040	8.040	8.040	8.040
	$-\Delta S_2^0$	138.600	139.100	138.700	137.300	138.200	139.900	138.400
Malic	ΔG_2^0	30.579	31.272	31.869	32.427	32.819	35.368	34.294
	$-\Delta H_2^0$	4.020	4.020	4.020	4.020	4.020	4.020	4.020
	$-\Delta S_2^0$	114.100	114.500	114.600	114.600	114.000	112.000	115.000
Tartaric	ΔG_2^0	26.301	26.718	27.739	27.682	28.043	28.426	28.917
	$-\Delta H_2^0$	18.684	18.684	18.684	18.684	18.684	18.684	18.684
	$-\Delta S_2^0$	148.400	147.300	148.200	146.000	145.000	144.000	143.000
Malonic	ΔG_2^0	34.664	35.419	36.018	37.409	38.071	38.943	39.485
	$-\Delta H_2^0$	17.995	17.995	17.995	17.995	17.995	17.995	17.995
	$-\Delta S_2^0$	171.200	170.900	170.000	171.700	171.100	171.200	170.200
Maleic	ΔG_2^0	37.682	38.846	39.632	39.912	41.300	42.642	42.923
	$-\Delta H_2^0$	17.230	17.230	17.230	17.230	17.230	17.230	17.230
	$-\Delta S_2^0$	181.100	182.000	181.600	179.600	181.100	182.400	180.600
Phthalic	ΔG_2^0	33.480	34.003	34.897	35.710	36.283	37.799	38.554
	$-\Delta H_2^0$	15.698	15.698	15.698	15.698	15.698	15.698	15.698
	$-\Delta S_2^0$	162.200	161.300	161.600	161.600	160.900	163.000	162.800

due to the relatively higher hydrogen bonding effect present in the latter acid. The higher conjugation effect acting in the phthalate mono anion compared to the maleate mono anion causes more basicity in the former (higher pK_1). Accordingly, the extent of ion solvation should be higher in phthalate mono anions than that of maleate mono anions and, consequently, the negative ΔS_1^0 value of phthalate is the higher, in accordance with the results obtained.

For the second dissociation reaction, an extra thermodynamic analysis has been examined in the light of the ΔH_2^0-ΔS_2^0 relationship. The plot of $-\Delta H_2^0$ versus $-\Delta S_2^0$ for the six dicarboxylic acids studied gives a good straight line (except for tartaric acid), as shown in Fig. 2. This indicates that this series of dicarboxylic acids in fitted by an isoequilibrium line with a slope equal to 230 K. This slope which represents the isoequilibrium temperature (β) is much smaller than the experimental temperature, which gives a good indication that this dissociation reaction is entropy controlled [14].

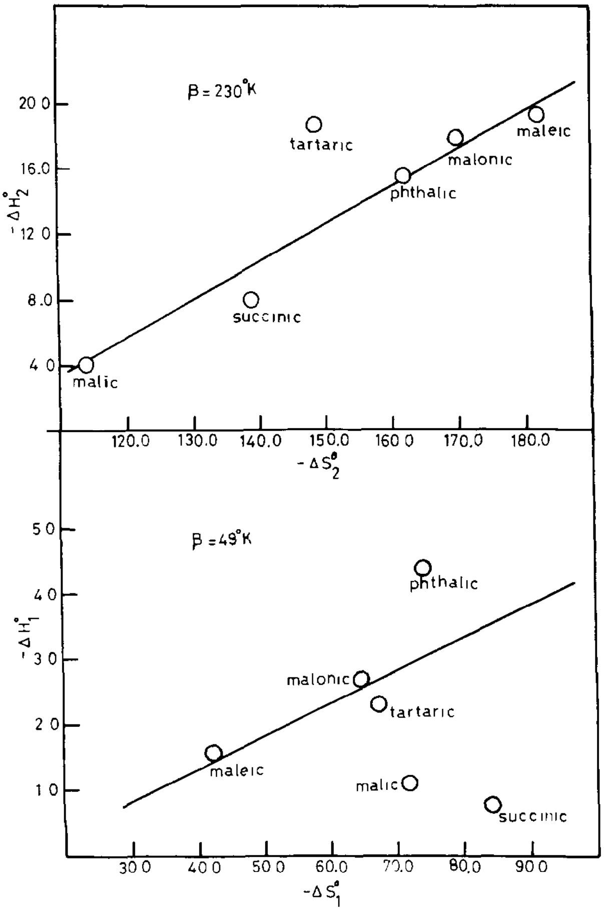

Fig. 2. Isoequilibrium plots for the first and second dissociation reactions.

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