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THERMODYNAMICS OF DISSOCIATION OF DICARBOXYLIC ACIDS IN WATER + DIOXANE MIXTURES

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ABSTRACT

From e.m.f. measurements on cells of the type Pt, $H_2(g)|H_2A(m_1)$, $MHA(m_2)$, $MCl(m_3)|AgCl(s)$, Ag and Pt, $H_2(g)|MHA(m_1)$, $M_2A(m_2)$, $MCl(m_3)|AgCl(s)$, Ag, the first and second dissociation constants of oxalic, malonic, succinic, glutaric, adipic, tartaric and phthalic acids have been determined at different temperatures in water +10, +20, +30 and +40 mass% dioxane. From the temperature coefficients, the thermodynamic quantities, ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0, of the dissociation process have been evaluated. The results have been discussed in terms of preferential solvation of dicarboxylate ions. The additivity in the thermodynamic quantities for the homologous series of dicarboxylic acids has been examined. The distances between the carboxylic groups have been calculated from the ratio of the successive dissociation constants in these media.

INTRODUCTION

Dash and Nayak [1] reported the dissociation constants of a number of dicarboxylic acids in aqueous and non-aqueous media using cells without liquid junction potentials. Relatively little work has been done on the determination of the dissociation constants of dicarboxylic acids in mixed solvent systems [2]. However, Das et al. [3] made similar studies on *dl*-malic, maleic and fumaric acids in different water–dioxane mixtures over a range of temperatures and discussed the results in terms of ion–solvent interactions. With a view to extending such studies to other dicarboxylic acids, the present work has been undertaken to determine the dissociation constants of oxalic, malonic, succinic, glutaric, adipic, tartaric and phthalic acids in different water + dioxane compositions (10, 20, 30 and 40 mass% dioxane) at five different temperatures ranging from 15 to 35°C. For this purpose, cells of the type

$$\text{Pt, } H_2(g)\,|\,H_2A(m_1),\ MHA(m_2),\ MCl(m_3)\,|\,AgCl(s),\ Ag \qquad (A)$$

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and

$$\mathrm{Pt,\ H_2(g)\,|\,MHA(m_1),\ M_2A(m_2),\ MCl(m_3)\,|\,AgCl(s),\ Ag} \qquad \text{(B)}$$

where M is Na or K, and A is the dicarboxylate ion of the acid concerned, have been employed.

EXPERIMENTAL

Acids were Merck G.R. grade or B.D.H. AnalaR grade. Oxalic acid was dehydrated following the method of Paul and Srenathan [4] by heating to 100 °C and keeping in a vacuum for 18–20 h. Other acids were stored in a vacuum desiccator before use. Mono- and disodium salts of the acids were prepared by adding calculated quantities of sodium bicarbonate solution to known weights of pure acids, evaporating the solutions to dryness on a steam bath, and recrystallizing the products from 95% alcohol. The salts were dried at 110–120 °C for at least 2 h. Sodium oxalate (Merck) was dried at 125 °C for more than 4 h. Sodium chloride (Merck) was dried at 100 °C for 2 h. These salts were kept in a vacuum desiccator over calcium chloride until required. The purity of the mono- and disodium salts was checked by the standard method [3,5].

Dioxane (Merck) was purified by the method described earlier [6]. Solvents of different compositions were prepared (wt.%) from the conductivity water and purified solvent.

Preparation of the electrodes, setting up of the cells, e.m.f. measurements and other experimental details have been discussed earlier [7].

RESULTS AND DISCUSSION

The method of calculating the first dissociation constant, K_1, was based on the evaluation of the "apparent" hydrogen ion molality of the solution as recommended by Harned and Owen for moderately weak acids [8]. The "apparent" hydrogen ion molality, m'_{H^+}, is related to the e.m.f.s of cell (A) by the equation [3]

$$\begin{aligned} -\log m'_{\mathrm{H}^+} &= \frac{(\Delta E)F}{2.3026RT} + \log m_3 + 2\log\gamma \\ &= \frac{(\Delta E)F}{2.3026RT} + \log m_3 + \frac{2A\sqrt{Id_0}}{1 + Ba^0\sqrt{Id_0}} \end{aligned} \qquad (1)$$

where $\Delta E = E - E^0$.

The ionic strength, I, is given by $I = m_1 + m_3 + m'_{\mathrm{H}^+}$. The values of I and m'_{H^+} were calculated as described earlier [9]. The "apparent" first dissociation constant, K'_1, can be calculated from the expression

$$+\log K'_1 = \log\frac{m'_{\mathrm{H}^+}(m_2 + m'_{\mathrm{H}^+})}{(m_1 - m'_{\mathrm{H}^+})} - \frac{2A\sqrt{Id_0}}{1 + Ba^0\sqrt{Id_0}} \tag{2}$$

The "apparent" second dissociation constant, K'_2, obtained from cell (B) can be expressed by [3]

$$-\log K'_2 = \frac{(\Delta E)F}{2.3026RT} + \log\frac{m_1 m_3}{m_2} + \frac{2A\sqrt{Id_0}}{1 + Ba^0\sqrt{Id_0}} \tag{3}$$

where $\Delta E = E - E^0$. The ionic strength, I, in this case equals $m_1 + 3m_2 + m_3$. The true (thermodynamic) dissociation constants, K_1 and K_2, were obtained from the intercepts of the plots of log K'_1 and log K'_2, respectively, against the ionic strength.

The e.m.f. values of cell (A) were measured with different solutions, from $m_1 = 1.2 \times 10^{-3}$, $m_2 = 0.6 \times 10^{-2}$ and $m_3 = 0.9 \times 10^{-2}$ up to $m_1 = 1.1 \times 10^{-2}$, $m_2 = 1.2 \times 10^{-2}$ and $m_3 = 8.5 \times 10^{-2}$ mol kg^{-1}. The ionic strength of the solution in the cell was varied in the range (1.5–10.3) $\times 10^{-2}$ mol kg^{-1}. For the solutions of cell (B), m_1, m_2 and m_3 were varied in the range (0.6–1.4) $\times 10^{-3}$, (0.12–2.7) $\times 10^{-3}$ and (1.2–9.8) $\times 10^{-2}$ mol kg^{-1}, respectively, and the ionic strength was in the range (1.0–10.7) $\times 10^{-2}$ mol kg^{-1}.

E^0 values of the silver–silver chloride electrode in various water + dioxane mixtures were obtained from the literature [10]. d_0 values and the Debye–Hückel constants (A and B) were also obtained from the literature [8,10] or calculated on the molal scale by usual methods. The e.m.f. values obtained for cells (A) and (B) were corrected for the atmosphere [11].

TABLE 1

Values of ion size parameter, a^0 (Å), for different acids in water and water + dioxane mixtures

Acid	Mass% dioxane				
	0 [a]	10	20	30	40
Oxalic	4.5	5.0	5.5	5.0	5.0
Malonic	5.0	5.5	5.0	5.5	6.0
Succinic	5.0	6.0	6.0	5.5	5.5
Glutaric	5.5	5.0	5.5	5.5	6.0
Adipic	5.5 [b]	2.5	2.5	5.0	5.5
Tartaric	5.0 [c]	2.5	3.5	4.0	6.0
Phthalic	5.0 [c]	6.0	6.0	5.5	5.5

[a] Ref. 15.

[b] Ref. 1e.

[c] Ref. 16.

For the suitable choice of the ion size parameter (a^0), the first dissociation constants of the acids at 25 °C were calculated for various values of a^0 in the range 2.5–6.0 Å [3,9] at an interval of 0.5 Å following the principle

TABLE 2

Values of pK_1 and pK_2 of oxalic, malonic, succinic, glutaric, adipic, tartaric and phthalic acids in water and water + dioxane mixtures at different temperatures

Mass% dioxane	Temperature (° C)									
	15		20		25		30		35	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
Oxalic acid										
0 [a]	1.375	4.280	–	–	1.354	4.303	–	–	1.308	4.338
10	1.601	4.653	1.592	4.662	1.580	4.673	1.571	4.684	1.559	4.691
20	1.861	4.940	1.853	4.948	1.846	4.953	1.839	4.960	1.834	4.968
30	2.188	5.360	2.182	5.366	2.175	5.372	2.170	5.379	2.164	5.385
40	2.576	5.879	2.570	5.884	2.565	5.892	2.559	5.899	2.552	5.906
Malonic acid										
0 [a]	2.860	5.683	–	–	2.848	5.701	–	–	2.850	5.731
10	3.101	5.941	3.092	5.952	3.081	5.961	3.070	5.970	3.062	5.981
20	3.360	6.233	3.352	6.240	3.346	6.246	3.340	6.254	3.335	6.261
30	3.686	6.679	3.680	6.670	3.675	6.662	3.668	6.668	3.661	6.675
40	4.068	7.164	4.061	7.170	4.055	7.178	4.048	7.184	4.042	7.190
Succinic acid										
0 [a]	4.246	5.650	–	–	4.224	5.661	–	–	4.201	5.671
10	4.480	5.968	4.471	5.975	4.462	5.982	4.454	5.989	4.443	5.997
20	4.744	6.254	4.738	6.261	4.731	6.267	4.725	6.274	4.718	6.280
30	5.070	6.669	5.061	6.675	5.055	6.681	5.046	6.690	5.040	6.697
40	5.453	7.185	5.447	7.191	5.440	7.198	5.434	7.204	5.428	7.213
Glutaric acid										
0 [a]	4.374	5.400	3.363	5.413	4.351	5.421	4.345	5.429	4.339	5.437
10	4.610	5.970	4.601	5.979	4.592	5.986	4.583	5.994	4.576	6.001
20	4.877	6.280	4.870	6.288	4.861	6.295	4.855	6.301	4.849	6.310
30	5.198	6.695	5.191	6.702	5.185	6.710	5.180	6.718	5.174	6.725
40	5.582	7.218	5.577	7.224	5.570	7.230	5.563	7.238	5.558	7.245
Adipic acid										
0 [b]	4.444	5.914	4.421	5.937	4.419	5.974	4.404	6.016	4.393	6.030
10	4.612	6.137	4.604	6.143	4.598	6.152	4.590	6.160	4.583	6.167
20	4.916	6.445	4.910	6.450	4.902	6.456	4.893	6.461	4.886	6.468
30	5.240	6.859	5.235	6.865	5.228	6.871	5.221	6.878	5.216	6.886
40	5.628	7.376	5.621	7.383	5.615	7.389	5.610	7.395	5.604	7.401
Tartaric acid										
0 [c]	3.235	4.370	3.218	4.386	3.201	4.400	3.195	4.409	3.190	4.413
10	3.458	4.632	3.450	4.644	3.442	3.653	3.431	4.662	3.422	4.670
20	3.726	4.917	3.720	4.925	3.713	4.932	3.705	4.941	3.698	4.948
30	4.050	5.338	4.040	5.341	4.038	5.345	4.030	5.351	4.025	5.358
40	4.440	5.862	4.433	5.866	4.425	5.862	4.419	5.868	4.413	5.875

TABLE 2 (continued)

Mass% dioxane	Temperature (°C)									
	15		20		25		30		35	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
Phthalic acid										
0 [c]	3.022	5.475	3.004	5.483	2.981	5.492	2.960	5.498	2.943	5.506
10	3.226	5.706	3.220	5.712	3.213	5.720	3.205	5.726	3.196	5.734
20	3.496	5.981	3.489	5.987	3.483	5.994	3.476	5.998	3.470	6.005
30	3.822	6.385	3.815	6.391	3.810	6.398	3.802	6.404	3.796	6.411
40	4.215	6.900	4.208	6.907	4.201	6.915	4.194	6.927	4.185	6.936

[a] Ref. 15.
[b] Ref. 1e.
[c] Ref. 16.

adopted by Roy et al. [12]. The same value of a^0 was used for the calculation of both K_1 and K_2. Values of a^0 are reported in Table 1.

Any possible error in the values of pK_1 and pK_2 due to deviations from the Debye–Hückel equation under the experimental conditions was compensated by the extrapolation method used and the adjustment of the parameter a^0 in our calculation procedure.

The values of pK_1 and pK_2 obtained from the linear extrapolation of pK_1' and pK_2' to $I = 0$ in water + dioxane mixtures at different temperatures are listed in Table 2. These values, obtained at different temperatures, were fitted by a least-squares method to an equation recommended by Harned and Robinson [13]

$$\mathrm{p}K = \frac{A}{T} + B + CT \tag{4}$$

The parameters A, B and C for pK_1 and pK_2 of the acids in different solvents are presented in Table 3. The average deviation between the observed values of pK_1 and pK_2 and those calculated from eqn. (4) are within the range 0.003–0.007 log units.

Using these parameters, the various thermodynamic quantities, ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0, for both the dissociation processes of the acids in their standard states have been calculated from the following equations:

$$\Delta G^0 = 2.3026R(A + BT + CT^2) \tag{5}$$

$$\Delta H^0 = 2.3026R(A - CT^2) \tag{6}$$

$$\Delta S^0 = -2.3026R(B + 2CT) \tag{7}$$

$$\Delta C_p^0 = -2.3026R(2CT) \tag{8}$$

Table 4 shows the values of these quantities at 25 °C.

The thermodynamic functions (on the mole fraction scale) for the transfer process at 25 °C between water (w) and water + dioxane mixtures (s) of

TABLE 3

Constants of eqn. (4) for the acids in water + dioxane mixtures

Constant	Mass% dioxane							
	10		20		30		40	
	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
Oxalic acid								
A	134.9615	98.8051	253.1224	255.5331	401.0748	57.2847	279.7928	516.7966
B	1.2998	3.4253	0.5528	2.8337	−0.1603	4.6135	1.0368	2.0110
$C \times 10^3$	−0.5	3.0	1.4	4.2	3.3	1.9	1.9	7.2
Malonic acid								
A	38.9204	−71.9265	379.1213	−228.7615	330.4923	651.4482	175.2313	−526.0218
B	3.4165	5.8609	1.1704	7.3681	1.8233	2.3574	3.2656	10.3194
$C \times 10^3$	−1.5	1.1	3.0	−1.1	2.4	7.1	0.6	−4.6
Succinic acid								
A	270.1373	−406.1615	117.6450	−383.9672	745.2714	103.0617	−76.6356	630.2043
B	3.1906	8.2824	4.3288	8.4609	0.4964	5.5678	6.3313	2.5546
$C \times 10^3$	1.2	−3.1	0	−3.0	6.8	2.5	−2.1	8.4

Glutaric acid								
A	736.9237	−177.1878	−353.8604	303.4140	−159.3887	−406.9147	50.5096	305.4718
B	0.1562	6.7185	7.6628	33.8235	6.6090	8.9911	5.6005	4.7767
$C\times10^3$	6.5	−0.4	−5.4	4.8	−2.9	−3.0	−0.6	4.7
Adipic acid								
A	238.1683	−267.6307	60.2466	706.0023	−192.4617	86.2801	155.5918	−513.6208
B	3.4270	7.4913	4.9563	1.3749	6.8905	5.8938	4.9238	10.4715
$C\times10^3$	1.2	−1.4	−0.8	9.0	−3.4	2.3	0.5	−4.5
Tartaric acid								
A	167.5328	−62.7326	83.9073	−187.9732	555.6751	246.7547	329.9320	474.0225
B	2.8585	4.5133	3.5730	5.7316	0.6613	3.3922	2.6163	2.5173
$C\times10^3$	0	1.1	−0.4	−0.5	5.0	3.7	2.3	5.8
Phthalic acid								
A	−217.7277	−124.3760	−40.6044	−336.2553	27.4989	−711.5252	380.9511	378.7485
B	5.1215	6.1386	4.1433	7.9011	4.0121	10.7914	2.0831	3.8257
$C\times10^3$	−3.9	0	−1.7	−2.6	−0.9	−6.7	2.8	6.1

TABLE 4

Standard thermodynamic quantities (molal scale) for the dissociation process of carboxylic acids in water and water + dioxane mixtures at 25 °C (first and second dissociation steps)

Mass% dioxane	ΔG^0 (kJ mol^{-1})		ΔH^0 (kJ mol^{-1})		ΔS^0 (kJ mol^{-1} K^{-1})		ΔC_p^0 (kJ mol^{-1} K^{-1})	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Oxalic acid								
0	7.700	24.393	5.354	−5.319	−0.008	−0.099	0.058	−0.319
10	10.848	26.531	3.433	−3.208	−0.019	−0.100	0.006	−0.034
20	10.379	28.196	2.465	−2.248	−0.027	−0.102	−0.016	−0.048
30	11.153	30.644	2.067	−2.133	−0.035	−0.109	−0.038	−0.022
40	14.500	33.604	2.126	−2.346	−0.042	−0.120	−0.022	−0.082
Malonic acid								
0	16.225	32.525	0.366	−4.594	−0.053	−0.125	−0.212	−0.214
10	17.684	33.927	3.295	−3.246	−0.048	−0.125	0.017	−0.013
20	19.034	35.782	2.157	−2.509	−0.057	−0.129	−0.034	0.013
30	20.807	37.988	2.246	0.401	−0.062	−0.126	−0.027	−0.081
40	23.003	40.978	2.334	−2.249	−0.069	−0.145	−0.007	0.053
Succinic acid								
0	23.992	32.273	3.743	−2.097	−0.068	−0.115	−0.040	−0.057
10	25.411	34.202	3.131	−2.505	−0.075	−0.123	−0.014	0.035
20	26.946	35.815	2.252	−2.250	−0.083	−0.128	0	0.034
30	28.658	37.984	2.706	−2.277	−0.087	−0.135	−0.078	−0.029
40	31.080	40.916	2.102	−2.215	−0.097	−0.145	0.024	−0.096

Glutaric acid								
0	24.700	30.777	3.657	−2.579	−0.071	−0.111	−0.171	−0.010
10	26.048	34.254	3.057	−2.711	−0.077	−0.124	−0.074	0.005
20	27.759	35.779	2.409	−2.351	−0.085	−0.128	0.062	−0.055
30	29.720	38.401	1.878	−2.689	−0.093	−0.138	0.033	0.034
40	31.895	41.086	1.986	−2.142	−0.100	−0.145	0.007	−0.054
Adipic acid								
0	25.200	34.030	3.830	−10.780	−0.072	−0.150	0.017	−0.686
10	26.148	35.231	2.519	−2.743	−0.079	−0.127	−0.014	0.016
20	28.066	36.657	2.513	−1.784	−0.086	−0.129	0.009	−0.103
30	29.843	39.183	2.095	−2.258	−0.093	−0.139	0.039	−0.026
40	31.916	42.253	2.128	−2.182	−0.100	−0.149	−0.006	0.051
Tartaric acid								
0	18.312	25.056	8.899	1.483	−0.032	−0.079	−0.512	0.037
10	19.513	26.415	3.207	−3.070	−0.055	−0.099	0	−0.013
20	21.308	28.248	2.286	−2.748	−0.064	−0.104	0.005	0.006
30	22.909	30.364	2.137	−1.566	−0.070	−0.107	−0.057	−0.042
40	25.150	33.294	2.405	−0.785	−0.076	−0.114	−0.026	−0.066
Phthalic acid								
0	16.890	31.181	6.734	−2.316	−0.034	−0.112	−0.076	−0.029
10	18.418	32.637	2.461	−2.381	−0.054	−0.118	0.045	0
20	19.968	34.215	2.112	−2.016	−0.060	−0.122	0.019	0.030
30	21.883	36.550	2.056	−2.230	−0.067	−0.130	0.010	0.076
40	23.935	39.444	2.532	−3.119	−0.072	−0.142	−0.032	−0.070

TABLE 5

Standard thermodynamic quantities (mole fraction scale) for the transfer of acids from water to water + dioxane mixtures at 25 ° C (first and second dissociation steps)

Mass% dioxane	ΔG_t^0 (kJ mol^{-1})		ΔH_t^0 (kJ mol^{-1})		ΔS_t^0 (kJ mol^{-1} K^{-1})		ΔC_{pt}^0 (kJ mol^{-1} K^{-1})	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Oxalic acid								
10	2.739	1.729	−1.921	2.111	−0.016	0.001	−0.052	0.285
20	1.822	2.946	−2.889	3.071	−0.016	0.001	−0.074	0.271
30	2.103	4.901	−3.287	3.186	−0.018	−0.006	−0.094	0.297
40	4.902	7.313	−3.228	2.973	−0.027	−0.015	−0.080	0.237
Malonic acid								
10	1.050	0.993	2.929	1.348	0.006	0.001	0.229	0.201
20	1.952	2.400	1.791	2.085	−0.001	−0.001	0.178	0.227
30	3.232	4.113	1.880	4.995	−0.005	0.003	0.185	0.133
40	4.880	6.555	1.968	2.345	−0.010	−0.014	0.205	0.267
Succinic acid								
10	1.010	1.520	−0.612	−0.408	−0.005	−0.007	0.026	0.092
20	2.097	2.685	−1.491	−0.153	−0.012	−0.010	0.040	0.091
30	3.316	4.361	−1.037	−0.180	−0.015	−0.015	−0.038	0.028
40	5.190	6.745	−1.641	−0.118	−0.023	−0.023	0.064	−0.039

Glutaric acid								
10	0.939	3.068	−0.600	−0.132	−0.005	−0.011	0.097	0.015
20	2.202	4.145	−1.248	0.228	−0.012	−0.013	0.233	−0.045
30	3.670	6.274	−1.779	−0.110	−0.018	−0.021	0.204	0.044
40	5.297	8.411	−1.671	0.437	−0.023	−0.027	0.178	−0.044
Adipic acid								
10	0.539	0.792	−1.311	8.037	−0.006	0.024	−0.031	0.702
20	2.009	1.770	−1.317	8.996	−0.011	0.024	−0.008	0.583
30	3.293	3.803	−1.735	8.522	−0.017	0.016	0.022	0.660
40	4.818	6.325	−1.702	8.598	−0.022	0.008	−0.023	0.737
Tartaric acid								
10	0.792	0.950	−5.692	−4.553	−0.022	−0.019	0.512	−0.050
20	2.139	2.335	−6.613	−4.231	−0.029	−0.022	0.507	−0.031
30	3.247	3.958	−6.762	−3.049	−0.034	−0.024	−0.005	−0.079
40	4.940	6.340	−6.494	−2.268	−0.038	−0.029	0.486	−0.103
Phthalic acid								
10	1.119	1.047	−4.273	−0.065	−0.018	−0.004	0.121	0.029
20	2.221	2.177	−4.622	0.030	−0.023	−0.007	0.095	0.059
30	3.643	4.019	−4.678	0.086	−0.028	−0.013	0.086	0.105
40	5.147	6.365	−4.202	−0.803	−0.031	−0.024	0.044	−0.041

TABLE 6

Values of γ (Å) in water and water + dioxane media at 25 °C

Mass% dioxane	Acid						
	Oxalic	Malonic	Succinic	Glutaric	Adipic	Tartaric	Phthalic
0	1.31	1.36	4.48	6.45	7.94	5.28	1.66
10	1.39	1.52	3.76	4.36	3.63	5.67	1.81
20	1.58	1.72	4.24	4.76	4.16	6.41	2.07
30	1.79	1.94	4.53	5.02	4.53	6.58	2.33
40	2.05	2.22	4.84	5.29	4.77	6.70	2.65

various compositions of the first and second dissociation processes of acids are listed in Table 5. The results are expressed on the mole fraction scale in order to eliminate any change in the thermodynamic quantities due to concentration changes. For this purpose the dissociation constant on the mole fraction scale has been calculated from the standard equation:

$$\mathrm{p}K(N) = \mathrm{p}K(m) + 2\log(1000/\overline{M}) \tag{9}$$

where $\overline{M}$ is the mean molar mass of the mixed solvent. The standard Gibbs free energy of transfer is given by the expression:

$$\Delta G_t^0(N) = 2.3026RT\left[{}_{\mathrm{s}}\mathrm{p}K(N) - {}_{\mathrm{w}}\mathrm{p}K(N)\right] \tag{10}$$

The values of other thermodynamic quantities for the transfer process (on the mole fraction scale) have been obtained from the usual relationships.

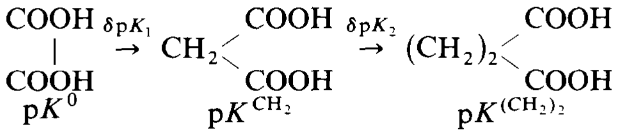
The distance r (Å) between the carboxylic groups of the acids in different solvents have been calculated from Bjerrum's equation [14]:

$$\ln(K_1/4K_2) = Ne^2/RTDr \tag{11}$$

where D is the effective dielectric constant of the solvent and r is the distance between the carboxylic groups. Other terms have their usual significance. The values are presented in Table 6 along with that in water.

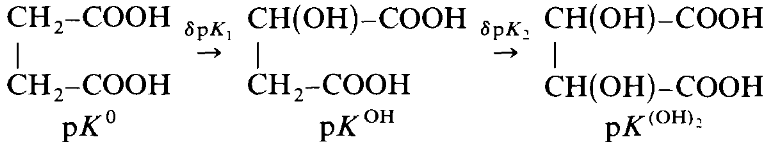
A perusal of Table 2 shows that the pK values of the acids are higher in water + dioxane mixtures than in water and tend to increase with increasing dioxane content. The magnitude of this increase is in accordance with the electrostatic charging (Born) effect corresponding to the monotonic increase of D^{-1} or the composition of water + dioxane mixtures. As observed, the pK values of the acids in various water + dioxane solvents increase with lengthening of the aliphatic carbon chain, i.e., with increasing CH_2 groups in the carboxylate ion. It can be concluded that the strength of the homologous dicarboxylic acids gradually decreases with an increase of the carbon chain length. However, the order of pK_1 values for glutaric and adipic acids and pK_2 values for malonic, succinic and glutaric acids is opposite in water to that in water + dioxane mixtures. This deviation might be due to the difference in anionic solvation of the dicarboxylate ions in these solvents. A comparison between the pK values of succinic, *dl*-malic [3] and tartaric acids shows that the introduction of a hydroxyl group into succinic acids favours ionization, i.e., pK values decrease with an increase in hydroxyl groups.

It is of interest to study the additive substituent effects for the proton ionization of the mono- and di-CH_2 substituted oxalic acids, and of the mono- and di-OH substituted succinic acids in these mixed solvents. Considering the CH_2 and OH substituent changes



$$\underset{\mathrm{p}K^{0}}{\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}} \xrightarrow{\delta\mathrm{p}K_1} \underset{\mathrm{p}K^{\mathrm{CH_2}}}{\mathrm{CH_2}\!<\!\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}} \xrightarrow{\delta\mathrm{p}K_2} \underset{\mathrm{p}K^{(\mathrm{CH_2})_2}}{(\mathrm{CH_2})_2\!<\!\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}}$$

and



$$\underset{\mathrm{p}K^{0}}{\begin{array}{l}\mathrm{CH_2{-}COOH}\\ |\\ \mathrm{CH_2{-}COOH}\end{array}} \xrightarrow{\delta\mathrm{p}K_1} \underset{\mathrm{p}K^{\mathrm{OH}}}{\begin{array}{l}\mathrm{CH(OH){-}COOH}\\ |\\ \mathrm{CH_2{-}COOH}\end{array}} \xrightarrow{\delta\mathrm{p}K_2} \underset{\mathrm{p}K^{(\mathrm{OH})_2}}{\begin{array}{l}\mathrm{CH(OH){-}COOH}\\ |\\ \mathrm{CH(OH){-}COOH}\end{array}}$$

perfect additivity in pK would give pK_1 equal to pK_2. If pK_1 = pK_2, i.e., $\mathrm{p}K^{\mathrm{X}} - \mathrm{p}K^{0} = \mathrm{p}K^{(\mathrm{X})_2} - \mathrm{p}K^{\mathrm{X}}$, where $X = \mathrm{CH_2}$ or OH, then $\mathrm{p}K^{(\mathrm{X})_2} = 2\mathrm{p}K^{\mathrm{X}} - \mathrm{p}K^{0}$. The p$K_1$ values of oxalic, malonic (mono-CH_2-substituted) and succinic (di-CH_2-substituted oxalic) and the pK_2 values of succinic, malic (mono-hydroxy succinic) and tartaric (di-hydroxy succinic) acids are in good agreement with the additivity on the corresponding proton ionizations in these mixed solvents.

The similarity between ΔH^0 values of the dissociation processes of the acids (except ΔH_2^0 for malonic acid in 30 wt% dioxane and tartaric acid in water) in water and water + dioxane mixtures indicates similar pattern of solvation in these solvents. The ΔS^0 values are expected to be negative in these solvents but in water + dioxane mixtures they are more negative. This may be due to the fact that the degree of reorientation and partial immobilization of the dioxane and water molecules by H^+ ion and mono- and di-carboxylate ions is greater in water + dioxane mixtures than in pure water. As apparent from Table 4, the standard changes in the heat capacity, ΔC_p^0 for both of the dissociation processes appear to be different in few solvents. This difference might be attributed to the contrary variation of ΔS^0 and ΔC_p^0 in the solvents concerned. Since electrostatic interactions between ions and dipolar solvent molecules should orient solvent molecules in the proximity of the ions, and hence should lead to decreased entropy and heat capacity (which is not observed in some cases), it is expected that there may be other interactions involved, such as "hydrophobic interactions", between the undissociated acid molecule and the water + dioxane solvent structure which may lead to the opposite trends in ΔS^0 and ΔC_p^0 values.

The increased positive values of ΔG_t^0 (except the first dissociation step of oxalic acid in 10 wt% dioxane) for the transfer from water to the mixed solvent of increased dioxane content indicate that the acids have more energy in the mixed media than in water. Unlike ΔG_t^0 values, ΔH_t^0 and ΔS_t^0 values are increasingly negative (except a few cases) in water + dioxane mixtures. This points to the fact that the mixed solvents are less associated (i.e., more structured) than pure water, thereby promoting an increased order in the solvation shells of the H^+ ion and the acid anions formed on dissociation in the mixed solvents.

The values of r, the distance between the carboxyl groups, are found to be more in water + dioxane mixtures than in water (except for succinic in 10 and 20 wt% dioxane and glutaric and adipic acids in all solvents). The values are presented in Table 6. As observed, the values of r in water + dioxane mixtures increase with increasing dioxane content. This increase may be attributed to the change in orientation of solvent molecules accompanying the acid ion–solvent interactions and solvation. When the proportion of dioxane increases, more solvent molecules (having two non-adjacent dipolar groups) enter the ionic field, thereby promoting a sort of ordering effect in the medium, and reducing the freedom of solvent molecules which would probably cause a separation between the carboxyl groups. This is reflected in the increased r value between the carboxyl groups with increasing dioxane content, contrary to the fact that the electrostatic interaction between the carboxyl groups and formation of intermolecular hydrogen bond in the acid ion are indicative of high K_1/K_2 ratios in these acids.

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