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DETERMINATION OF DISSOCIATION CONSTANTS OF MALONIC ACID IN (ETHYLENE GLYCOL-WATER)X% MIXED SOLVENT AT DIFFERENT TEMPERATURES USING ELECTROMOTIVE FORCE MEASUREMENTS

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ABSTRACT:
The first and second dissociation constants (pK_1 & pK_2) of malonic acid in different composition of (ethylene glycol-water)%, (10, 20 and 30)% mixed solvent determined using the electromotive force measurements of galvanic cells without liquid junction at nine different temperatures, $(278.15-318.15)$K at 5° interval, including the body temperature. The value of the first and second thermodynamic dissociation constants have been used to determine the thermodynamic quantities of two dissociation processes. These quantities involved the standard free energy, ΔG^0, standard enthalpy change, ΔH^0, standard entropy change, ΔS^0, and standard heat capacity change, $\Delta C_p{}^0$.

KEYWORDS: Electromotive force, Thermodynamic dissociation constant, Malonic acid, Ethylene glycol-water mixed solvent, and thermodynamic quantity.

1. INTRODUCTION

Malonic acid (also called propanedioic acid) is one of saturated dicarboxylic acids and is homologous series of oxalic acid[1]. The general structure for these acids is $HOOC-(CH_2)_n-COOH$, By using (x-ray) to obtain the crystal structure for malonic acid that has methylene group separating the carboxyl, the structure is $HOOC(CH_2)-COOH$. Malonic acid itself is rather unstable and has few applications[2][3]. The reactivity of its methylene group provides the sequence of reactions of alkylation, hydrolysis of the esters and decarboxylation resulting in substituted ketones. The dissociation constant ratio K_1/K_2 is much higher than in disubstituted than in mono substituted malonic acid. Some evidence has accumulated that this is due to intermolecular hydrogen bonding in the disubstituted malonic acid mono anions. Intermolecular hydrogen bonding did not take place in the mono substituted malonic acid[4]. There are four General methods for the measurement of dissociation constant of carboxylic acid, including Potentiometric titration method[5][6][7][8], Conductometric method[9][10][11], Spectrophotometric methods[12][13][14], and Electromotive force measurement method[15][16][17]. There are many studies on dissociation constant of carboxylic acid in different organic-water mixed solvents and at different temperatures[18][19][20][21][22][23][24][25].

The present work involved the determination of the first and second dissociation constants (pK_1 & pK_2) of malonic acid in different composition of ethylene glycol-water, (EG-water) mixed solvent, (10%, 20% and 30%) using the electromotive force measurements of galvanic cells without liquid junction containing standard hydrogen electrode and silver-silver chloride electrode at different temperatures in the range $(278.15-318.15\text{K})$ at 5° interval. The value of the first and second thermodynamic dissociation constants have been used to determine the thermodynamic quantities of two dissociation processes. These quantities involved the standard free energy, ΔG^0, standard enthalpy change, ΔH^0, standard entropy change, ΔS^0, and standard heat capacity change, $\Delta C_p{}^0$. However various studies employing electromotive measurement of cells without liquid junction using ethylene glycol-water mixture, there is still a need for investigation of this system with different dibasic carboxylic acid. In addition to its significance in understanding the role of high viscosity, density, as well as of low dielectric constant as compared with water on the phenomenon of solute-solute and solute-solvent interactions.

2. EXPERIMENTAL

All the chemicals used in this investigation were of analytical reagent grade purity. Malonic acid obtained from (Sigma-Aldrich, ≥ 99.95%), was used without further purification. Ethylene glycol (analytical reagent, Merck, 99.5%) was further purified by the method described earlier [26], freshly deionized water having a specific conductance of $0.2-0.9\ \mu s.cm^{-1}$ was used.

2.1 Cell A

The first thermodynamic dissociation constant of malonic acid is studied by emf measurement of the galvanic cell without liquid junction. Such measurement is performed with a cell of type:

$$\mathbf{Pt_{(S)},\ H_{2(g)}(1atm)|\ H_2Mal_{(m_1)},NaHMal_{(m_2)},\ NaCl_{(m_3)}in\ X\%\ EG+H_2O\ |\ AgCl_{(S)},Ag_{(S)}} \qquad \textbf{(A)}$$

Concentration of the malonic acid in the cell solution is 1M, concentration of standard sodium hydroxide is 1M and concentration of sodium chloride is 0.5M. Equal volumes of 1M sodium hydroxide with 1M of malonic acid were mixed to prepare a solution of 0.5M sodium salt of malonic acid. The different volume of 1M malonic acid, 0.5M sodium salt of malonic acid and 0.5M sodium chloride were mixed to prepare ten different molar concentrations of the malonic acid in cell solution in the range 0.01 to 0.1M. These solutions prepared in 10%, 20% and 30% $EG.\%+H_2O$ mixed solvent.

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2.2 Cell B

$$\mathbf{Pt_{(S)}, H_{2(g)}(1atm) \mid NaHA_{(m_1)},\ Na_2A_{(m_2)},\ NaCl_{(m_3)} \mid AgCl_{(S)},\ Ag_{(S)}} \qquad \textbf{(B)}$$

In this cell, the concentration of the malonic acid is 1M. Equal volumes of 1M malonic acid and 1M sodium hydroxide were mixed to prepare 0.5M HNaMal. And equal volumes of 1M malonic acid and 2M sodium hydroxide were mixed to prepare 0.5M Na_2Mal. The other solution of this cell is sodium chloride with concentration 0.5M, then the different volume of 0.5M HNaMal, 0.5M Na_2Mal and 0.5M NaCl was mixed to prepare ten different molar concentrations of malonic acid. These solutions prepared in 10%, 20% and 30% $\mathrm{EG.\%-water}$ mixed solvent.

2.3 Electromotive force measurements

The cell was, H-shape of all glass design, the dissolved air was removed from the cell by bubbling pure hydrogen which provided from electrolysis of acidified water [27] through the solution before the cell was filled. The cell was filled with solution and immersed in recirculating cooler for about 15 minute then prepared silver-silver chloride electrode [28][29] and standard hydrogen electrode[30][31] were dipped into the cell and pure hydrogen was passed (10-12 bubbles per second) through the electrode for about 1 hour to obtain stable emf the temperature was controlled to $\mp 0.1°\mathrm{C}$ over the range $(278.15-318.15\mathrm{K})$. The barometric pressure was recorded within1.0 mmHg. The hydrogen gas was presaturated at the experimental temperature prior to being introduced into the cell. Then the e.m.f. of the cell was measured by digital multimeter (Auto Range AC DC LINI-T UT804), with an accuracy of $\mp$0.1mV.

3. RESULTS

According to the Nernst equation

$$\mathbf{E = E_m^0 - \frac{RT}{F} Lna_{\pm}} \qquad (1)$$

The measurement of the electromotive force of each cell was corrected to a hydrogen partial pressure of 1atm in the usual way. The pH value of each buffer solutions at each temperature of measurement was estimated by the defining equation[32]

$$-\log m_{H^+} = \frac{(E_A - E_m^0)F}{2.303RT} + \log m_{Cl^-} - 2\log\gamma_{H^+} \qquad (2)$$

Where γ represents a molal activity coefficient; E_A and E_m^0 are the electromotive force and standard electromotive force, respectively of the cell A at the appropriate absolute temperature, R and F are the gas constant and the faraday respectively. Values of E_m^0 and 2.3026RT/F in absolute volts are summarized in an earlier publication[33].

The ionic strength (I_1) of the solution in the cell A [25] is given by equation (3)

$$\mathbf{I_1 = m_{H^+} + m_2 + m_3} \qquad \mathbf{(3)}$$

From dissociation of H_2Mal in different solvents composition, 10, 20, and 30% ethylene glycol-water mixed solvent, the apparent first dissociation constant $p\overline{K}_1$, was calculated from equation[23]

$$\mathbf{\frac{E_A - E_m^0}{K} + Log\frac{m_3(m_1 - m_{H^+})}{(m_2 + m_{H^+})} = -\beta I - logK_1} \qquad (4)$$

Where the left hand side of eq (4) is the apparent first dissociation constant $\overline{K}_1$, $(-\log K_1)$ of malonic acid and pK_1 is the intercept of the plot between the $p\overline{K}_1$ (y axis) with I_1 (x axis).

Table (1) shows the values of m_{H^+} of solution of the cell A. The table (2) shows ionic strength I_1 of solution of the cell A. The thermodynamic first dissociation constants, is obtained by a linear methods using (L.S.M) method of $p\overline{K}_1$ to $I_1 = 0$, according to the equation (4), and are listed in table (3). Thermodynamic functions of first dissociation constants pK_1 at different temperatures with other constants in X% Ethylene glycol-water mixtures are listed in tables (4). The values of pK_1 increase (acidity decreases) as mole fraction of Ethylene glycol increases in mixture with water because the solvation of the proton and intra-hydrogen bonding with the mono anion would be both hindered appreciably by the addition of larger and more viscous Ethylene glycol molecules. Hence a decrease acidity of malonic acid is expected to continue as mole fraction of Ethylene glycol increases.

Table 1. Concentration of hydrogen ion m_H for different concentrations of malonic acid in 10, 20, and 30% Ethylene glycol-water mixtures at different temperatures. $m_H = 10^{-2}$

10% EG									
Concentration	**Temperature ℃**								
m	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.009979	0.1590	0.1636	0.1668	0.1719	0.1820	0.1843	0.1859	0.1989	0.2010
0.019979	0.2194	0.2426	0.2620	0.2867	0.2961	0.3010	0.3127	0.3233	0.3314
0.030000	0.3144	0.3128	0.3359	0.2793	0.3254	0.3401	0.3604	0.3700	0.3852
0.040042	0.2740	0.2861	0.3246	0.3401	0.2468	0.2779	0.3024	0.3222	0.3352
0.050104	0.2295	0.2383	0.2648	0.2907	0.2888	0.3050	0.3097	0.3298	0.3505
0.060188	0.2471	0.2837	0.2920	0.3249	0.3373	0.3509	0.3745	0.3828	0.4363
0.070292	0.2932	0.3050	0.3169	0.3314	0.3461	0.3764	0.4129	0.4467	0.5035
0.080418	0.2664	0.2783	0.3010	0.3170	0.3256	0.3778	0.4756	0.4902	0.5631
0.090565	0.3022	0.3131	0.3213	0.3456	0.3565	0.4170	0.4981	0.5597	0.6267
0.100733	0.3303	0.3494	0.3629	0.3720	0.3962	0.4494	0.4926	0.6267	0.7144
m	**20% EG**								
0.009726	0.0988	0.1125	0.1192	0.1322	0.1351	0.1411	0.1451	0.1468	0.1507
0.019472	0.1597	0.1557	0.1659	0.1561	0.1727	0.1770	0.1854	0.1961	0.2040
0.029238	0.1873	0.2048	0.2224	0.2333	0.2560	0.2595	0.2638	0.2622	0.2733
0.039023	0.2027	0.2093	0.2320	0.2542	0.2778	0.2879	0.2992	0.3129	0.3139
0.048829	0.1941	0.2123	0.2449	0.2526	0.2676	0.2828	0.3076	0.3179	0.3318
0.058654	0.1813	0.2110	0.2563	0.2588	0.3017	0.3407	0.3488	0.3690	0.3982
0.068499	0.1979	0.2231	0.2577	0.2835	0.3133	0.3599	0.3935	0.4013	0.4241
0.078365	0.1923	0.2398	0.2517	0.2755	0.3457	0.3640	0.3927	0.4290	0.4607
0.088250	0.2200	0.2466	0.2787	0.2909	0.3502	0.3911	0.4256	0.4792	0.5089
0.098156	0.2335	0.2630	0.2857	0.3132	0.3463	0.4057	0.4623	0.5056	0.6039
m	**30% EG**								
0.009608	0.0898	0.0932	0.0990	0.1021	0.1036	0.1062	0.1056	0.1074	0.1104

0.019236	0.1188	0.1217	0.1257	0.1317	0.1340	0.1390	0.1439	0.1445	0.1441
0.028882	0.1194	0.1279	0.1355	0.1411	0.1484	0.1541	0.1603	0.1636	0.1699
0.038548	0.1320	0.1395	0.1508	0.1556	0.1616	0.1677	0.1719	0.1766	0.1888
0.048234	0.1222	0.1309	0.1388	0.1468	0.1563	0.1654	0.1760	0.1883	0.2093
0.057939	0.1251	0.1378	0.1488	0.1565	0.1650	0.1749	0.1879	0.1970	0.2155
0.067663	0.1123	0.1212	0.1310	0.1362	0.1466	0.1641	0.1723	0.1982	0.2287
0.077407	0.1161	0.1271	0.1381	0.1456	0.1556	0.1805	0.1897	0.2065	0.2360
0.087171	0.1237	0.1389	0.1451	0.1562	0.1778	0.2008	0.2110	0.2248	0.2704
0.096954	0.1421	0.1500	0.1606	0.1757	0.1915	0.2115	0.2328	0.2434	0.2794

Table 2. Ionic strength $\mathbf{I_1}$ at different molal concentrations from the cell A in 10, 20, and 30% Ethylene glycol-water mixtures at different temperatures. $\mathbf{I_1 = 10^{-3}}$

10% EG									
Concentration	**Temperature ℃**								
m	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.009979	21.546	21.592	21.624	21.675	21.776	21.799	21.815	21.945	21.966
0.019979	42.143	42.375	42.569	42.815	42.910	42.958	43.076	43.182	43.263
0.030000	63.123	63.106	63.338	62.772	63.233	63.380	63.582	63.679	63.830
0.040042	82.785	82.906	83.291	83.446	82.513	82.824	83.069	83.267	83.397
0.050104	102.44	102.53	102.797	103.06	103.04	103.20	103.25	103.45	103.65
0.060188	122.76	123.13	123.210	123.54	123.66	123.80	124.03	124.12	124.65
0.070292	143.40	143.52	143.638	143.78	143.93	144.23	144.60	144.94	145.50
0.080418	163.35	163.47	163.694	163.86	163.94	164.46	165.44	165.59	166.32
0.090565	183.96	184.07	184.152	184.39	184.50	185.11	185.92	186.54	187.21
0.100733	204.53	204.72	204.858	204.95	205.19	205.72	206.16	207.50	208.37
m	**20% EG**								
0.009726	20.438	20.576	20.642	20.772	20.801	20.862	20.901	20.918	20.957
0.019472	40.532	40.492	40.595	40.497	40.662	40.705	40.789	40.896	40.975
0.029238	60.328	60.504	60.679	60.788	61.016	61.050	61.094	61.078	61.189
0.039023	80.038	80.103	80.330	80.553	80.789	80.890	81.003	81.140	81.149
0.048829	99.542	99.724	100.05	100.13	100.28	100.43	100.68	100.78	100.92
0.058654	119.04	119.34	119.79	119.82	120.24	120.64	120.72	120.92	121.21
0.068499	138.87	139.12	139.47	139.72	140.02	140.49	140.82	140.90	141.13
0.078365	158.51	158.98	159.10	159.34	160.04	160.23	160.51	160.88	161.19
0.088250	178.52	178.78	179.11	179.23	179.82	180.23	180.57	181.11	181.41
0.098156	198.42	198.72	198.94	199.22	199.55	200.14	200.71	201.14	202.13
m	**30% EG**								
0.009608	20.112	20.146	20.205	20.236	20.250	20.277	20.271	20.288	20.318
0.019236	39.650	39.680	39.719	39.779	39.802	39.852	39.902	39.908	39.903
0.028882	58.939	59.024	59.100	59.156	59.229	59.285	59.348	59.381	59.444
0.038548	78.381	78.457	78.569	78.617	78.678	78.739	78.780	78.828	78.950
0.048234	97.635	97.722	97.801	97.881	97.976	98.067	98.173	98.296	98.506
0.057939	117.05	117.18	117.29	117.36	117.45	117.55	117.68	117.77	117.95
0.067663	136.34	136.43	136.53	136.58	136.69	136.86	136.94	137.20	137.51
0.077407	155.84	155.95	156.06	156.13	156.23	156.48	156.57	156.74	157.03
0.087171	175.40	175.55	175.62	175.73	175.94	176.17	176.27	176.41	176.87
0.096954	195.11	195.19	195.30	195.45	195.60	195.80	196.02	196.12	196.48

Table 3. Apparent first dissociation constant $\mathbf{p\bar{K}_1}$ at different temperatures and molal concentrations in 10, 20, and 30% Ethylene glycol-water mixtures.

10% EG									
Concentration	**Temperature ℃**								
m	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.009979	2.6953	2.6592	2.6342	2.6151	2.6073	2.6096	2.6027	2.5873	2.5865
0.019979	2.8193	2.7863	2.7418	2.7339	2.7344	2.7418	2.7327	2.7338	2.7296
0.030000	2.8622	2.8495	2.8125	2.8342	2.8342	2.8329	2.8266	2.8380	2.8298
0.040042	3.0047	2.9909	2.9350	2.9510	2.9800	2.9733	2.9729	2.9798	2.9752
0.050104	3.1069	3.0892	3.0444	3.0509	3.0603	3.0628	3.0754	3.0752	3.0716
0.060188	3.1795	3.1404	3.1048	3.1114	3.1190	3.1278	3.1315	3.1387	3.1265
0.070292	3.2135	3.1930	3.1556	3.1690	3.1768	3.1874	3.1869	3.1866	3.1817
0.080418	3.2646	3.2445	3.2029	3.2150	3.2291	3.2380	3.2267	3.2389	3.2175
0.090565	3.2958	3.2727	3.2437	3.2450	3.2611	3.2718	3.2620	3.2702	3.2585
0.100733	3.3349	3.3043	3.2664	3.2783	3.2918	3.3040	3.2952	3.2916	3.2823
m	**20% EG**								
0.009726	2.6953	2.6592	2.6342	2.6151	2.6073	2.6096	2.6027	2.5873	2.5865
0.019472	2.8193	2.7863	2.7418	2.7339	2.7344	2.7418	2.7327	2.7338	2.7296

0.029238	2.8622	2.8495	2.8125	2.8342	2.8342	2.8329	2.8266	2.8380	2.8298
0.039023	3.0047	2.9909	2.9350	2.9510	2.9800	2.9733	2.9729	2.9798	2.9752
0.048829	3.1069	3.0892	3.0444	3.0509	3.0603	3.0628	3.0754	3.0752	3.0716
0.058654	3.1795	3.1404	3.1048	3.1114	3.1190	3.1278	3.1315	3.1387	3.1265
0.068499	3.2135	3.1930	3.1556	3.1690	3.1768	3.1874	3.1869	3.1866	3.1817
0.078365	3.2646	3.2445	3.2029	3.2150	3.2291	3.2380	3.2267	3.2389	3.2175
0.088250	3.2958	3.2727	3.2437	3.2450	3.2611	3.2718	3.2620	3.2702	3.2585
0.098156	3.3349	3.3043	3.2664	3.2783	3.2918	3.3040	3.2952	3.2916	3.2823
m	**30% EG**								
0.009608	3.0161	2.9974	2.9648	2.9528	2.9460	2.9483	2.9469	2.9352	2.9340
0.019236	3.1330	3.1234	3.0996	3.0877	3.0845	3.0802	3.0711	3.0722	3.0928
0.028882	3.2346	3.2183	3.1975	3.1934	3.1821	3.1898	3.1890	3.1841	3.1848
0.038548	3.3423	3.3380	3.3084	3.3035	3.3002	3.3085	3.3105	3.3058	3.3042
0.048234	3.4417	3.4215	3.4022	3.4040	3.4004	3.3937	3.3917	3.3894	3.3887
0.057939	3.5079	3.4878	3.4667	3.4605	3.4578	3.4716	3.4598	3.4554	3.4687
0.067663	3.5595	3.5457	3.5200	3.5250	3.5156	3.5289	3.5232	3.5089	3.5245
0.077407	3.5991	3.5927	3.5603	3.5689	3.5549	3.5679	3.5609	3.5516	3.5697
0.087171	3.6366	3.6248	3.6056	3.6020	3.5941	3.6028	3.6010	3.5860	3.5936
0.096954	3.6621	3.6569	3.6324	3.6323	3.6253	3.6365	3.6291	3.6228	3.6303

Table 4. Thermodynamic functions of first dissociation constants $\mathbf{pK_1}$ at different temperatures obtained by (L.S.M.) with other constants in 10, 20, and 30% Ethylene glycol-water mixtures.

10% EG							
$\mathbf{T/K}$	$\boldsymbol{\beta \pm \sigma_\beta}$			$\mathbf{pK_1 \pm \sigma_{pK_1}}$			$\mathbf{R^2}$
278.15	3.5281	±	0.28221	2.6790	±	0.03587	0.9514
283.15	3.5395	±	0.94756	2.6525	±	0.03746	0.9476
288.15	3.5510	±	0.95654	2.6117	±	0.03409	0.9565
293.15	3.6341	±	0.95018	2.6082	±	0.03752	0.9502
298.15	3.7203	±	0.94364	2.6073	±	0.04101	0.9436
303.15	3.7743	±	0.30965	2.6056	±	0.03961	0.9489
308.15	3.7422	±	0.3426	2.6043	±	0.04396	0.9372
313.15	3.7659	±	0.36762	2.6031	±	0.04732	0.9292
318.15	3.687	±	0.36433	2.6026	±	0.04708	278.15
20% EG							
278.15	3.7340	±	0.23429	2.8983	±	0.02887	0.9696
283.15	3.4778	±	0.95345	2.8746	±	0.03354	0.9535
288.15	3.4606	±	0.95253	2.8317	±	0.03378	0.9525
293.15	3.5276	±	0.94731	2.8172	±	0.03643	0.9473
298.15	3.5029	±	0.94541	2.796	±	0.03696	0.9454
303.15	5.5736	±	0.30580	2.7932	±	0.03807	0.9447
308.15	3.5428	±	0.29927	2.7903	±	0.03733	0.946
313.15	3.59	±	0.30032	2.7894	±	0.03753	0.947
318.15	3.6285	±	0.33825	2.7888	±	0.04238	0.935
30% EG							
278.15	3.7072	±	0.307188	3.0150	±	0.03719	0.9480
283.15	3.7458	±	0.952117	2.9979	±	0.03598	0.9521
288.15	3.7626	±	0.949920	2.9708	±	0.03703	0.9499
293.15	3.8385	±	0.947081	2.9596	±	0.03891	0.9471
298.15	3.8146	±	0.944996	2.9549	±	0.03950	0.9450
303.15	3.8819	±	0.327071	2.9539	±	0.03976	0.9463
308.15	3.8584	±	0.327473	2.9516	±	0.03984	0.9455
313.15	3.8189	±	0.334330	2.9484	±	0.04071	0.9422
318.15	3.8529	±	0.337036	2.9519	±	0.04112	0.9423

Calculation of ionic strength and second dissociation constant

Ionic strength I_2 of the solution of the cell B is in the table (5) that is calculated from the equation (5).

$$\mathbf{I_2 = m_1 + 3m_2 + m_3} \qquad \textbf{(5)}$$

From dissociation of $HMal^-$

$$\frac{E_B - E_m^0}{K} - \mathrm{Log}\frac{m_{HMal^-} . m_{Cl^-}}{m_{Mal^{-2}}} + \frac{2A\sqrt{I_2}}{1+Ba^0\sqrt{I_2}} = -\beta I_2 - \log K_1 \qquad (6)$$

Where E_B is the emf of the cell B, E_m^0 is the standard emf of Ag-AgCl electrode, (m) is the molality. The apparent second dissociation constant $\overline{K}_2$, $(-\log K_2)$ of malonic acid from electromotive force of the cell B in different molal concentration and temperatures is obtained from the left hand side of eq (6)

The plot of $p\overline{K}_2$ is linear with $I_2$when a^0 is taken to be 4.3 at each temperature. The thermodynamic values pK_2 are listed in tables (6), the value of pK_2 reflect a larger increase (larger decrease in acidity of malonic acid) as mole fraction of Ethyle glycol increases. This may be due to the mono anion bering surrounded by the larger and highly viscous Ethylene glycol molecules. This slows down the second ionization step (decreases acidity of the acid) as mole fraction of ethylene glycol increases. The thermodynamic functions of the second dissociation constants pK_2 at different temperatures obtained by (L.S.M.) with other constants in X% Ethylene glycol-water mixtures show at the table (7). The pK_1 and pK_2 values decrease with the increase of temperature, the $pK_1$is less temperature dependent than pK_2. This is referred to the higher heat of the acid dissociation in the second stage of the dissociation as compared with the first stage as shown in table (8).

Table (5) Ionic strength I_2 at different molal concentrations for the cell B in 10% Ethylene glycol-water mixtures.

10% EG			**20% EG**			**30% EG**		
m	$\mathbf{I_2}$	$\mathbf{I_2^{1/2}}$	**m**	$\mathbf{I_2}$	$\mathbf{I_2^{1/2}}$	**m**	$\mathbf{I_2}$	$\mathbf{I_2^{1/2}}$
0.009979	0.0499	0.22339	0.009726	0.04864	0.220543	0.009608	0.0480488	0.2192
0.019979	0.09993	0.31612	0.019472	0.09739	0.312079	0.019236	0.0962099	0.31018
0.03	0.15008	0.3874	0.029238	0.14626	0.382443	0.028882	0.1444836	0.38011
0.040042	0.20035	0.4476	0.039023	0.19525	0.441869	0.038548	0.1928703	0.43917
0.050104	0.25074	0.50074	0.048829	0.24435	0.494317	0.048234	0.2413705	0.49129
0.060188	0.30125	0.54886	0.058654	0.29357	0.541819	0.057939	0.2899846	0.5385
0.070292	0.35189	0.5932	0.068499	0.3429	0.58558	0.067663	0.3387131	0.58199
0.080418	0.40265	0.63455	0.078365	0.39236	0.626384	0.077407	0.3875564	0.62254
0.090565	0.45354	0.67345	0.08825	0.44193	0.664777	0.087171	0.4365149	0.66069
0.100733	0.50455	0.71032	0.098156	0.49162	0.701155	0.096954	0.4855892	0.69684

Table 6. Appurant second dissociation constant $\mathbf{p\overline{K}_2}$ at different temperatures and molal concentrations in 10, 20, and 30% Ethylene glycol-water mixtures.

10% EG									
Concentration	**Temperature ℃**								
m	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15	318.15
0.009979	8.1899	8.1444	8.0861	8.0646	8.0470	8.0327	8.0179	8.0026	7.9746
0.019979	7.7348	7.6821	7.6277	7.6148	7.6022	7.5945	7.5811	7.5730	7.5478
0.030000	7.3835	7.3398	7.2925	7.2725	7.2648	7.2604	7.2467	7.2520	7.2264
0.040042	7.1796	7.1430	7.0957	7.0911	7.0796	7.0700	7.0642	7.0632	7.0405
0.050104	7.0812	7.0466	6.9910	6.9782	6.9757	6.9748	6.9628	6.9609	6.9464
0.060188	7.0032	6.9582	6.9153	6.9044	6.8952	6.8897	6.8763	6.8831	6.8625
0.070292	6.9301	6.8800	6.8429	6.8339	6.8301	6.8182	6.8050	6.8123	6.7887
0.080418	6.8555	6.8201	6.7745	6.7642	6.7607	6.7491	6.7380	6.7441	6.7273
0.090565	6.7993	6.7589	6.7101	6.7036	6.7038	6.6925	6.6849	6.6817	6.6651
0.100733	6.7386	6.7039	6.6572	6.6475	6.6464	6.6321	6.6248	6.6301	6.6154
m	**20% EG**								
0.009726	8.6250	8.5399	8.4860	8.4449	8.4031	8.3926	8.3632	8.3485	8.3361
0.019472	8.1330	8.0539	7.9952	7.9618	7.9233	7.9200	7.8966	7.8773	7.8715
0.029238	7.8423	7.7675	7.7095	7.6734	7.6397	7.6353	7.6229	7.6089	7.5908
0.039023	7.6444	7.5712	7.5095	7.4872	7.4503	7.4457	7.4334	7.4240	7.4136
0.048829	7.5445	7.4752	7.4103	7.3884	7.3572	7.3462	7.3345	7.3287	7.3184
0.058654	7.4632	7.3853	7.3243	7.3027	7.2689	7.2716	7.2569	7.2433	7.2334
0.068499	7.3867	7.3110	7.2504	7.2240	7.1992	7.1955	7.1797	7.1712	7.1616
0.078365	7.3250	7.2441	7.1909	7.1613	7.1352	7.1252	7.1165	7.1082	7.0941
0.088250	7.2654	7.1884	7.1231	7.0974	7.0736	7.0622	7.0572	7.0460	7.0370
0.098156	7.2049	7.1283	7.0668	7.0415	7.0215	7.0103	7.0041	6.9931	6.9843
m	**30% EG**								
0.009608	9.0974	9.0477	8.9821	8.9546	8.9209	8.8937	8.8674	8.8249	8.8202
0.019236	8.5924	8.5650	8.5035	8.4700	8.4419	8.4242	8.3990	8.3668	8.3515
0.028882	8.3243	8.2885	8.2328	8.2000	8.1739	8.1620	8.1392	8.1060	8.0989
0.038548	8.1323	8.0982	8.0424	8.0146	7.9832	7.9730	7.9454	7.9235	7.9162
0.048234	8.0311	7.9885	7.9454	7.9216	7.8819	7.8723	7.8584	7.8255	7.8186
0.057939	7.9411	7.9025	7.8581	7.8296	7.8073	7.7947	7.7664	7.7454	7.7309
0.067663	7.8704	7.8267	7.7810	7.7581	7.7343	7.7222	7.6977	7.6754	7.6659
0.077407	7.8035	7.7620	7.7166	7.6957	7.6688	7.6538	7.6346	7.6127	7.6019
0.087171	7.7477	7.7101	7.6613	7.6304	7.6073	7.5928	7.5756	7.5492	7.5404
0.096954	7.6892	7.6572	7.6035	7.5782	7.5536	7.5411	7.5259	7.5030	7.4896

Table 7. Thermodynamic functions of the second dissociation constants $\mathbf{pK_2}$ at different temperatures obtained by (L.S.M.) with other constants in 10% Ethylene glycol-water mixtures.

10% EG							
$\mathbf{T/K}$	$\boldsymbol{\beta \pm \sigma_\beta}$			$\mathbf{pK_2 \pm \sigma_{pK_2}}$			$\mathbf{R^2}$
278.15	-2.7652	±	0.42689	7.9541	±	0.133296	0.8399
283.15	-2.7443	±	0.83932	7.9065	±	0.132554	0.8393
288.15	-2.7211	±	0.84071	7.8517	±	0.130759	0.8517
293.15	-2.6984	±	0.84124	7.8336	±	0.129415	0.8412
298.15	-2.6653	±	0.83986	7.8175	±	0.128486	0.8399
303.15	-2.6742	±	0.40388	7.8108	±	0.12611	0.8457

308.15	-2.6625	±	0.40298	7.7963	±	0.12583	0.8451
313.15	-2.6317	±	0.39337	7.7879	±	0.122827	0.8484
318.15	-2.6059	±	0.39172	7.76	±	0.122313	0.8469
20% EG							
278.15	-2.7420	±	0.42206	8.3822	±	0.128417	0.8407
283.15	-2.7366	±	0.84521	8.3038	±	0.125983	0.8452
288.15	-2.7468	±	0.84368	8.2467	±	0.127188	0.8437
293.15	-2.7203	±	0.84697	8.2112	±	0.124389	0.8470
298.15	-2.6747	±	0.84249	8.1678	±	0.124407	0.8425
303.15	-2.6838	±	0.40311	8.1636	±	0.122652	0.8471
308.15	-2.6417	±	0.39644	8.1382	±	0.120624	0.8473
313.15	-2.6278	±	0.39341	8.1229	±	0.119699	0.8480
318.15	-2.6236	±	0.39432	8.111	±	0.119977	0.8470
30% EG							
278.15	-2.7476	±	0.41965	8.8542	±	0.126123	0.8427
283.15	-2.7433	±	0.84534	8.8147	±	0.124685	0.8453
288.15	-2.7091	±	0.84843	8.7537	±	0.121673	0.8484
293.15	-2.6957	±	0.84696	8.7227	±	0.121761	0.8470
298.15	-2.6765	±	0.84476	8.6896	±	0.121916	0.8448
303.15	-2.6603	±	0.39526	8.6710	±	0.118793	0.8499
308.15	-2.6393	±	0.39654	8.6434	±	0.119178	0.8470
313.15	-2.6040	±	0.38858	8.6062	±	0.116786	0.8488
318.15	-2.6121	±	0.38942	8.5986	±	0.117037	0.8490

Table 8. $\Delta \mathbf{pK}$ and the ratio $\mathbf{K_1}/\mathbf{K_2}$ of malonic acid at different temperatures in 10,20,and 30% Ethylene glycol-water mixtures.

10% EG			**20% EG**			**30% EG**		
T/K	$\mathbf{pK_2 - pK_1}$	**K1/K2**	**T/K**	$\mathbf{pK_2 - pK_1}$	**K1/K2**	**T/K**	$\mathbf{pK_2 - pK_1}$	**K1/K2**
278.15	5.2751	188408	278.15	5.4839	304719.3	278.15	5.8392	690558
283.15	5.2540	179473	283.15	5.4292	268658.1	283.15	5.8168	655843
288.15	5.2400	173780	288.15	5.4150	260016.0	288.15	5.7829	606597
293.15	5.2254	168035	293.15	5.3940	247742.2	293.15	5.7631	579562
298.15	5.2102	162256	298.15	5.3718	235396.5	298.15	5.7347	542875
303.15	5.2052	160398	303.15	5.3704	234638.9	303.15	5.7171	521315
308.15	5.1920	155597	308.15	5.3479	222792.2	308.15	5.6918	491813
313.15	5.1848	153038	313.15	5.3335	215526.2	313.15	5.6578	454779
318.15	5.1574	143681	318.15	5.3222	209990.7	318.15	5.6467	443302

Thermodynamic Quantities of Dissociation

$$\mathrm{pK} = \frac{\mathrm{A_1}}{\mathrm{T}} - \mathrm{A_2} + \mathrm{A_3T} \qquad (7)$$

The values of the first and second thermodynamic dissociation constant, (pK_i) thus obtained at different temperatures were fitted to an equation of the type (7) by writing it in the form

$$\mathrm{T.pK} = \mathrm{A_1} - \mathrm{A_2T} + \mathrm{A_3T^2} \qquad (8)$$

By giving the data of $\mathrm{T.pK}$ and T for the computer and by the (L.S.M.) method as shown in figure 1, 2. The value of constant $(\mathrm{A_1},\ \mathrm{A_2} \text{and } \mathrm{A_3})$ that is used to calculate thermodynamic quantities for the first and second dissociation obtained as follows[9].

a) The standard change in free energy, $\Delta \mathrm{G_i^0} = 2.3026\mathrm{R}(\mathrm{A_1} - \mathrm{A_2T} + \mathrm{A_3T^2})$ (9)

b) The standard change in entropy , $\Delta \mathrm{S_i^0} = 2.3026\mathrm{R}(\mathrm{A_2} - 2\mathrm{A_3T})$ (10)

c) The standard change in Heat content, $\Delta \mathrm{H_i^0} = 2.3026\mathrm{R}(\mathrm{A_1} - \mathrm{A_3T^2})$ (11)

d) The standard change in Heat capacity, $\Delta \mathrm{Cp_i^0} = 2.3026\mathrm{R}(-2\mathrm{A_3T})$ (12)

The value of thermodynamic functions for the first and second dissociation are summarized in table (9) and (10) respectively. The negative value of $\Delta \mathrm{S_i^0}$ for both dissociation processes increase as temperature increase, also it becomes more negative in mixture with higher X% Ethylene glycol-water content, The value of $\Delta \mathrm{H^0}$ decreases as temperature increase and decreases with the increase of X% Ethylene glycol-water. This can be the fact that the reaction becomes more endothermic in mixture with high X% constants, The negative value of thermodynamic function standard heat capacity $\Delta \mathrm{Cp^0}$, increase with the increase of temperature and decreases with the increase of X% Ethylene glycol-water mixtures, this is due to points of electrostatic interaction with the charged which leads to the orientation of the solvent molecules.

Table 9. Thermodynamic functions for dissociation at different temperatures from first dissociation constant for malonic acid in 10% Ethylene glycol-water mixtures

10% EG				
T/K	$\mathbf{\Delta G_1^0}$ $(\mathbf{J.mol^{-1}})$	$\mathbf{\Delta S_1^0}$ $(\mathbf{J.mol^{-1}})$	$\mathbf{\Delta H_1^0}$ $(\mathbf{J.mol^{-1}})$	$\mathbf{\Delta Cp_1^0}$ $(\mathbf{J.mol^{-1}})$
278.15	14224.24	-21.5025	8243.314	-275.837
283.15	14344.15	-26.4610	6851.731	-280.796
288.15	14488.85	-31.4194	5435.356	-285.754
293.15	14658.35	-36.3778	3994.190	-290.713
298.15	14852.63	-41.3362	2528.230	-295.671
303.15	15071.71	-46.2947	1037.479	-300.629

308.15	15315.58	-51.2531	-478.064	-305.588
313.15	15584.24	-56.2115	-2018.40	-310.546
318.15	15877.69	-61.1700	-3583.53	-315.505
20% EG				
278.15	15401.39	-15.0413	11217.66	-329.088
283.15	15491.38	-20.9569	9557.432	-335.003
288.15	15610.96	-26.8726	7867.626	-340.919
293.15	15760.11	-32.7882	6148.241	-346.835
298.15	15938.84	-38.7039	4399.278	-352.75
303.15	16147.15	-44.6195	2620.737	-358.666
308.15	16385.03	-50.5352	812.6182	-364.582
313.15	16652.5	-56.4508	-1025.08	-370.497
318.15	16949.54	-62.3665	-2892.36	-376.413
30% EG				
278.15	16119.63	-33.5825	6778.65	-215.132
283.15	16297.21	-37.4497	5693.323	-218.999
288.15	16494.13	-41.3169	4588.66	-222.866
293.15	16710.38	-45.1841	3464.661	-226.733
298.15	16945.97	-49.0513	2321.326	-230.601
303.15	17200.89	-52.9185	1158.656	-234.468
308.15	17475.15	-56.7857	-23.3512	-238.335
313.15	17768.75	-60.6529	-1224.69	-242.202
318.15	18081.68	-64.5201	-2445.37	-246.069

Table 10. Thermodynamic functions for dissociation at different temperatures from second dissociation constant for malonic acid in 10, 20, and 30% Ethylene glycol-water mixtures

10% EG				
T/K	ΔG_2^0 $(J.mol^{-1})$	ΔS_2^0 $(J.mol^{-1})$	ΔH_2^0 $(J.mol^{-1})$	ΔCp_2^0 $(J.mol^{-1})$
278.15	42331.56	-106.805	12623.77	-272.642
283.15	42877.84	-111.706	11248.31	-277.543
288.15	43448.62	-116.607	9848.34	-282.444
293.15	44043.90	-121.508	8423.866	-287.345
298.15	44663.70	-126.409	6974.887	-292.246
303.15	45307.99	-131.31	5501.404	-297.147
308.15	45976.79	-136.211	4003.415	-302.048
313.15	46670.10	-141.112	2480.921	-306.949
318.15	47387.91	-146.013	933.9224	-311.85
20% EG				
278.15	44511.74	-86.8008	20368.09	-474.994
283.15	44967.09	-95.3393	17971.77	-483.532
288.15	45465.13	-103.878	15532.76	-492.071
293.15	46005.86	-112.416	13051.06	-500.609
298.15	46589.29	-120.955	10526.67	-509.148
303.15	47215.41	-129.493	7959.586	-517.686
308.15	47884.22	-138.032	5349.809	-526.225
313.15	48595.72	-146.57	2697.34	-534.763
318.15	49349.92	-155.108	2.177812	-543.302
30% EG				
278.15	47203	-116.355	14838.76	-200.222
283.15	47793.77	-119.955	13828.66	-203.821
288.15	48402.55	-123.554	12800.55	-207.42
293.15	49029.31	-127.153	11754.46	-211.019
298.15	49674.07	-130.752	10690.36	-214.618
303.15	50336.83	-134.351	9608.273	-218.218

308.15	51017.59	-137.95	8508.188	-221.817
313.15	51716.33	-141.55	7390.106	-225.416
318.15	52433.08	-145.149	6254.029	-229.015

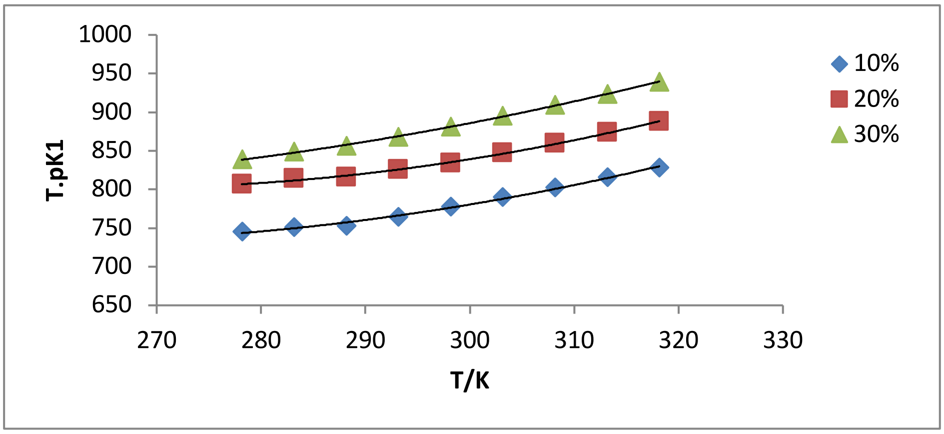

Fig. 1. change of T.pK1 with the temperature T/K in a different composition of Ethylene glycol-water mixtures

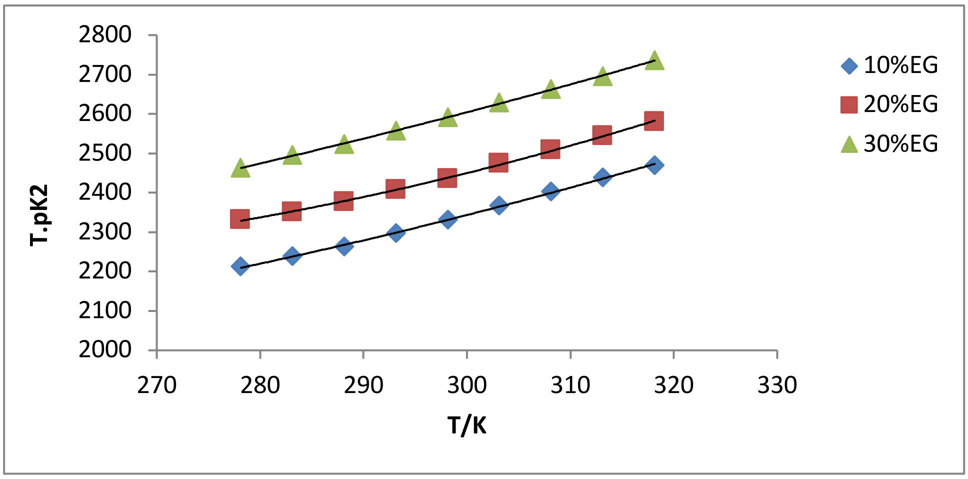

Fig. 2. change of T.pK2 with the temperature T/K in a different composition of Ethylene glycol-water mixtures

4. CONCLUSION

The ratio K_1/K_2 decreases with the increase of the temperature because the water is attached by strong hydrogen bond with the carboxylate and weak bond with the carboxyl group. Weakness is caused in the intra-hydrogen bonding that effect for the ratio K_1/K_2 when the X% Ethylene glycol is added to the water. The ethylene glycol molecule is attached by hydrogen bonding with the water and this causes decrease of water attached with the acid ion leading to increase intra-hydrogen bond force following the increase in the value of K_1/K_2.

The positive values of ΔG_i^0 and ΔH_i^0 indicate that nonspontaneous and endothermic cell reaction, and the negative values of ΔS_i^0 revealing that the entropy is not in favor of cell reaction.

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