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Full Paper

Association and thermodynamic Parameters for Succinic Acid in Binary Mixtures of Methanol and Water at Different Temperatures

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Abstract
By measuring the molal solubility and the mean activity coefficient for saturated succinic acid, we evaluated different association parameters in the binary mixtures of methanol-water at different temperatures. Different thermodynamic parameters, molar, Van der Waals, electrostriction, apparent molar volumes, dissociation constants, and association constants of succinic acid were estimated in order to indicate the contributions of solute-solvent interactions related to ion association and the results were discussed.

Keywords: Succinic acid; solubility; molar volumes; thermodynamic and association parameters.

1. Introduction

Succinic acid is a dicarboxylic acid that occurs in nature in such organisms as fungi and lichens [1] and known as “Spirit of Amber because it was first discovered and extracted from amber by pulverizing and distilling it using a sand bath. Succinic acid has been used in large scale applications including as a flavoring agent for food and beverages, it is used as an intermediate for the manufacture of lacquers, dyes, esters for perfumes, plasticizers, photographic chemicals, alkyd resins, metal treatment chemicals and coatings [2, 3]. In polymer research, succinic acid has been utilized to prepare biocompatible hybrid dendritic-linear polyester-ethers [4]. A study of the co-crystallization of cis-itraconazole with various 1,4-dicarboxylic acids, including succinic acid, has been reported [5]. Succinic acid has been used as a matrix in infrared (IR) MALDI analytical methods [6-8]. An analytical study of various low molecular weight organic acids, including succinic acid, using capillary zone electrophoresis-electrospray ionization mass spectrometry has been published [9],

it is also used in the manufacture of medicines.
The focus of this work is to evaluate the solubility of succinic acid in binary mixtures of methanol and water at different temperatures to study the effects of temperature and the addition of a methanol in the association, dissociation parameters of solvation and different molar volumes.

2. Experimental

2.1 Chemicals

The succinic acid and methanol used in the experiments were purchased from Merck, they are analytical grade reagents and were used without any further purification.

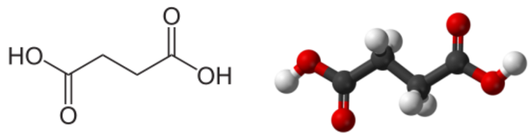

Fig. 1: The chemical structure of succinic acid

Some physical/chemical properties of succinic acid were listed in Table (1)

2.2. *Solubility measurement:*

The solubility of succinic acid in binary solvent mixtures of (methanol–water) was determined by using gravimetric method [12]. For each measurement, an excess mass of acid was added to about 30 mL binary solvent mixture.
The equilibrium cell was heated to a desired temperature with continuous stirring for about 12 hours by using a magnetic stirrer to fully mix the suspension and a condenser was used to prevent the evaporation of solvent during the experiments. The temperature of the cell was controlled by circulating water from a thermostat (CF41, Julabo, Germany) through the jacket of the vessel and measured by a thermometer with accuracy of ±0.02 K. After 12 hours, stirring was stopped, and the solution was kept for 3 hours to approach equilibrium and allow the undissolved solid to settle down in the lower portion of the glass vessel. About 3 mL upper clear saturated solution was withdrawn by a syringe (10 mL) and filtered quickly with a membrane filter (0.22 μm) and poured into a pre-weighed glass dish. The total weight of the solution and the glass dish was measured immediately using an analytical balance (Mettler Toledo AB204-S, Switzerland) with an accuracy of ±0.0001 g. When the mass of the residue reached at constant value, the final mass was recorded. At each temperature, the measurement was conducted three times, and the mean value was used to determine the molal solubility. The relative standard uncertainty of the solubility measurement based on the repeated observations is within 2%.
The pH readings of the saturated solutions were measured using a pH-meter of the type Tacussel/Minis 5000. The densities were measured by using a weighing bottle of 1ml and analytical balance (4 digits) of the type Mettler Toledo DA.

Table 1: Physical/Chemical Properties [10, 11]

Property	**Value**
Chemical name (IUPAC)	butanedioic acid
Molecular formula	$C_4H_6O_4$
Physical state	Odourless white crystal
Appearance	Colourless to white crystalline power
Density	1.56 g/cm^3
Molecular weight	118.088 g/mol
Melting Point	184 °C (363 °F; 457 K)
Boiling Point	235 °C (455 °F; 508 K)
Flash point	206 °C (403 °F; 479 K)
Magnetic susceptibility (χ)	$-57.9\cdot10^{-6}$ cm^3/mol
Acidity (pK_a)	pK_{a1} = 4.2, pK_{a2} = 5.6

3. Results and discussion

The solubility values for saturated succinic acid at different temperatures (298.15, 303.15, 308.15 and 313.15K) were listed in Table (2) and plotted graphically in Figure (2). The results show that the solubility of succinic acid increased by increasing the mole fraction of methanol (X_s) due to the increase in the solvation, and solute-solvent interaction and also the solubility increased by increasing of temperature with a given composition in all solvent mixtures, which indicates that the dissolving process of acids is endothermic [13].

The molar volumes (V_M) of succinic acid were obtained by dividing the molar mass by the densities. The packing density as reported by Kim et al. [14] and Gomaa et al. [15] was found to be a constant value and equal to 0.661. The Van der Waals (V_W) can be calculated from equation (1)

The electrostriction volume (V_e), which is the volume compressed by the solvent, was calculated using the following equation (2) (Gomaa et al. [16-17]).

The apparent molar volumes, V_ϕ , [18-19] were calculated using equation (3) [20].

The solvated radii (r) of succinic acid in (MeOH-H_2O) mixtures at different temperatures were calculated using equation (4) by considering the spherical form of the solvated molecules [21].

The values of V_M , V_W , V_e and V_ϕ for succinic acid are listed in Table (2). In comparing the data of solvation of succinic acid, it was observed that the values of V_M and V_W are increased by increasing the organic solvents content in the mixtures (Fig.2) due to the increase in the solubility and the volume of organic solvent compared to water.All the electrostriction volumes V_e calculated for succinic acid having negative values. The V_e increase in negativity on increasing the percentages of the organic solvent (Fig.2), indicating the more work (energy) is done by the solvent on the solvation sheaths of the acid. All succinic acid volumes V_M, V_w, V_e, and V_ϕ are increased by increase in temperature and MeOH percentage due to increase the solubility which favouring more solvation interactions.

Van der Waals radii, as tabulated by Bondi have been used for a wide range of applications. [22-

dissociation constant (i.e. K_1/K_2) for the dimmers of succinic acid which form a

27]. Bondi radii result from a refinement of the work of Pauling, [28] who determined standard values of atomic radii from contact distances between nonbonded atoms in molecular crystals. Van der Waals radii (r) are also increased by increase in temperature and MeOH percentage due to increase Van der Waals volume.

The activity coefficient was calculated using the relation [29].

K_{ass} values were calculated [30] from the ratios of association constant to

complex ion (HA_2^-) and hydrogen ion (H^+) and the values of K` (where K` is the dissociation constant of the associated acid complex, H_2A_2)) are given by the equations (6) ,(7), (8).The free energies of dissociation (ΔG_d), free energies of association (ΔG_A), difference free energies ($\Delta\Delta G$) and free en

ergies of solvation (ΔG_s) for succinic acid saturated solutions in various solvents were calculated by using the following equations and listed in Table (3) and plotted graphically in Figure (3).

$$\text{Packing density } (P) = \frac{V_w}{V_M} = 0.661 \pm 0.017 \qquad (1)$$

$$V_e = V_W - V_M \qquad (2)$$

$$V_\phi = M/d_o - (d\text{-}d_o/d.d_o)\, 1000/m \qquad (3)$$

where M is the molar mass of succinic acid, m is the solubility, d and d_0 are the densities of saturated solution and pure solvents, respectively.

$$V_M = \frac{1}{6}\pi N r^3 \qquad (4)$$

$$\log \gamma_\pm = -0.5062\sqrt{S} \qquad (5)$$

$$K` = a^2 H^+/m^2 \qquad (6)$$

$$pa_{H^+} = \frac{1}{2}\log\frac{K_1}{K_2} - \log m = pH - \log \gamma_\pm \qquad (7)$$

$$\frac{K_1}{K_2} = K` K_{ass} \qquad (8)$$

Where *a* is the activity. The values obtained *K`*, K_{ass} and $\frac{K_1}{K_2}$ are reported in Table (3).

$$\Delta G_d = -RT \ln K` \qquad (9)$$

$$\Delta G_A = -RT \ln K_{ass} \qquad (10)$$

$$\Delta\Delta G = \Delta G_{ass} - \Delta G_d \qquad (11)$$

$$\Delta G_s = -RT\, pK_{sp} \qquad (12)$$

$$pK_{sp} = -(\log 4S^3.\gamma_\pm^3) \qquad (13)$$

The Gibbs free energies (ΔG_s), (ΔG_A), and ($\Delta\Delta G$) for succinic acid are decreased in positivity with

The K' dissociation for succinic acid are decreased with increase of the mole fraction of increase of methanol content indicating more solvation process and less endothermic character reaction which increase its solvation behaviours.

methanol in the mixed ethanol – water mixtures at all the used temperatures while (K_{ass}) and (ΔG_d) are increased with rise of both the mole fraction of methanol in the mixtures and temperatures indicating more solvation by association.

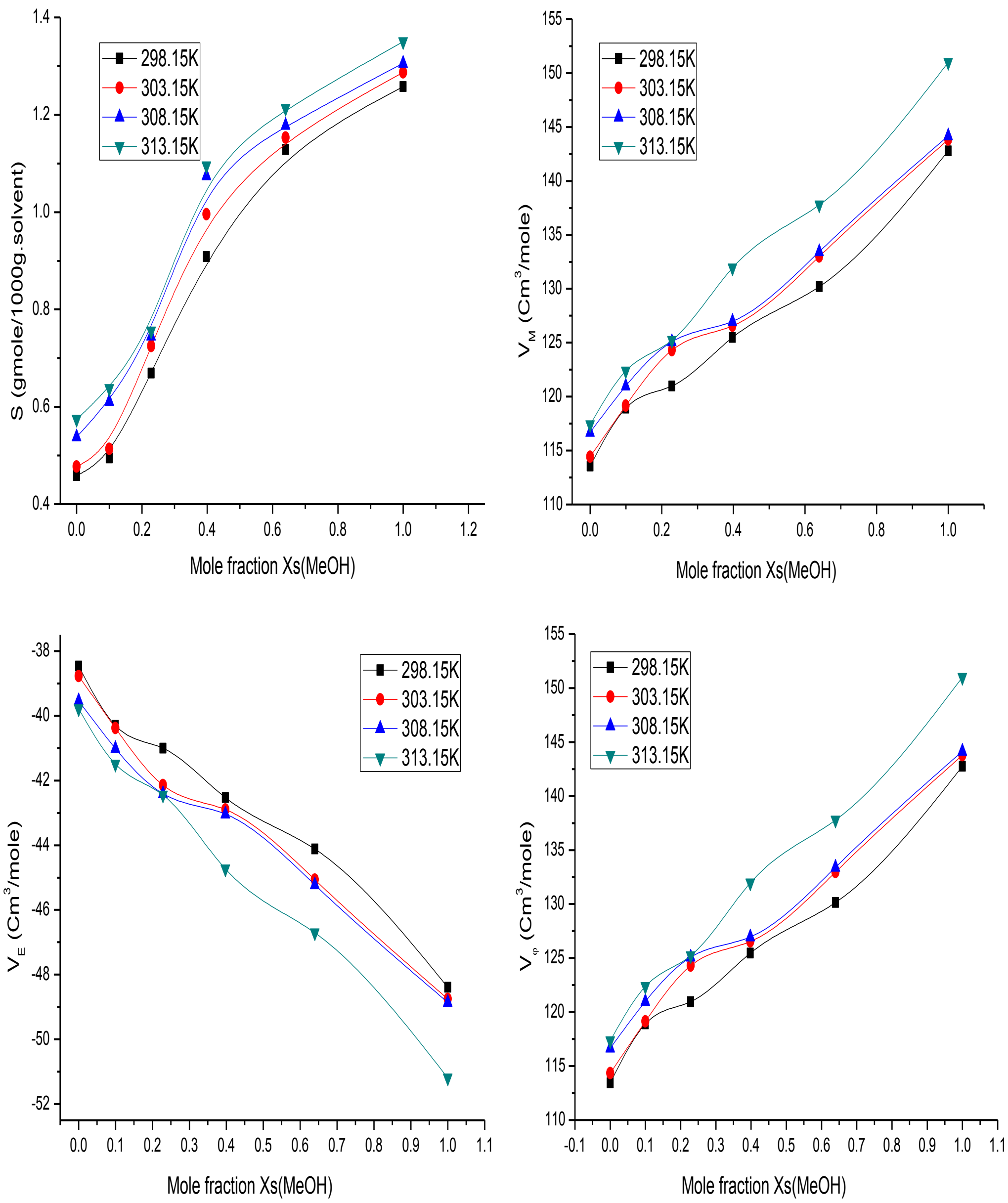

Fig. 2: Relation between S, V_M, V_W and V_ϕ of succinic acid and the mole fraction of MeOH (X_s) in (MeOH–H_2O) solvent mixtures at different temperatures.

Table 2: Molal solubility (S), Molar (V_M), Vandar waal (V_w), Electrostriction (V_e), Apparent (V_ϕ) volumes and Van der Waals radii of succinic acid in (MeOH–H_2O) mixed solvents at different temperatures.

MeOH vol. %	X_s	S molal solubility (mol/kg. solvent)				V_M (Cm^3/ mole)			
		298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
0	0	0.4587	0.4770	0.5382	0.5742	113.55	114.43	116.69	117.39
20	0.0999	0.4945	0.5134	0.6111	0.6378	118.92	119.16	120.99	122.37
40	0.2284	0.6691	0.7250	0.7455	0.7558	120.99	124.31	125.10	125.23
60	0.3976	0.9087	0.9958	1.0744	1.0953	125.49	126.57	126.98	131.94
80	0.6397	1.1283	1.153	1.1782	1.2136	130.2	132.98	133.44	137.79
100	1	1.2578	1.2868	1.3056	1.3502	142.79	143.84	144.19	151.01
MeOH vol. %	X_s	V_w (Cm^3/ mole)				V_e (Cm^3/ mole)			
0	0	74.996	75.586	77.106	77.571	-38.462	-38.77	-39.54	-39.78
20	0.0999	78.584	78.743	79.970	80.893	-40.303	-40.38	-41.01	-41.49
40	0.2284	79.948	82.162	82.687	82.774	-41.002	-42.14	-42.41	-42.45
60	0.3976	82.928	83.645	83.916	87.222	-42.53	-42.90	-43.04	-44.73
80	0.6397	86.028	87.881	88.179	91.078	-44.12	-45.07	-45.22	-46.71
100	1	94.355	95.046	95.276	99.809	-48.391	-48.75	-48.86	-51.19
MeOH vol. %	X_s	V_ϕ (Cm^3/ mole)				r^0in (Å)			
0	0	113.46	114.35	116.65	117.35	3.0040	3.0117	3.0314	3.0375
20	0.0999	118.89	119.13	120.98	122.38	3.0506	3.0527	3.0682	3.0798
40	0.2284	120.95	124.30	125.09	125.23	3.0682	3.0960	3.1026	3.1036
60	976 0.	125.46	26.54	126.95	131.95	3.1058	3.1147	3.1180	3.1581
80	0.6397	130.15	132.95	133.40	137.79	3.1442	3.1664	3.1700	3.2041
100	1	142.75	143.79	144.14	151.00	3.2424	3.2503	3.2530	3.3035

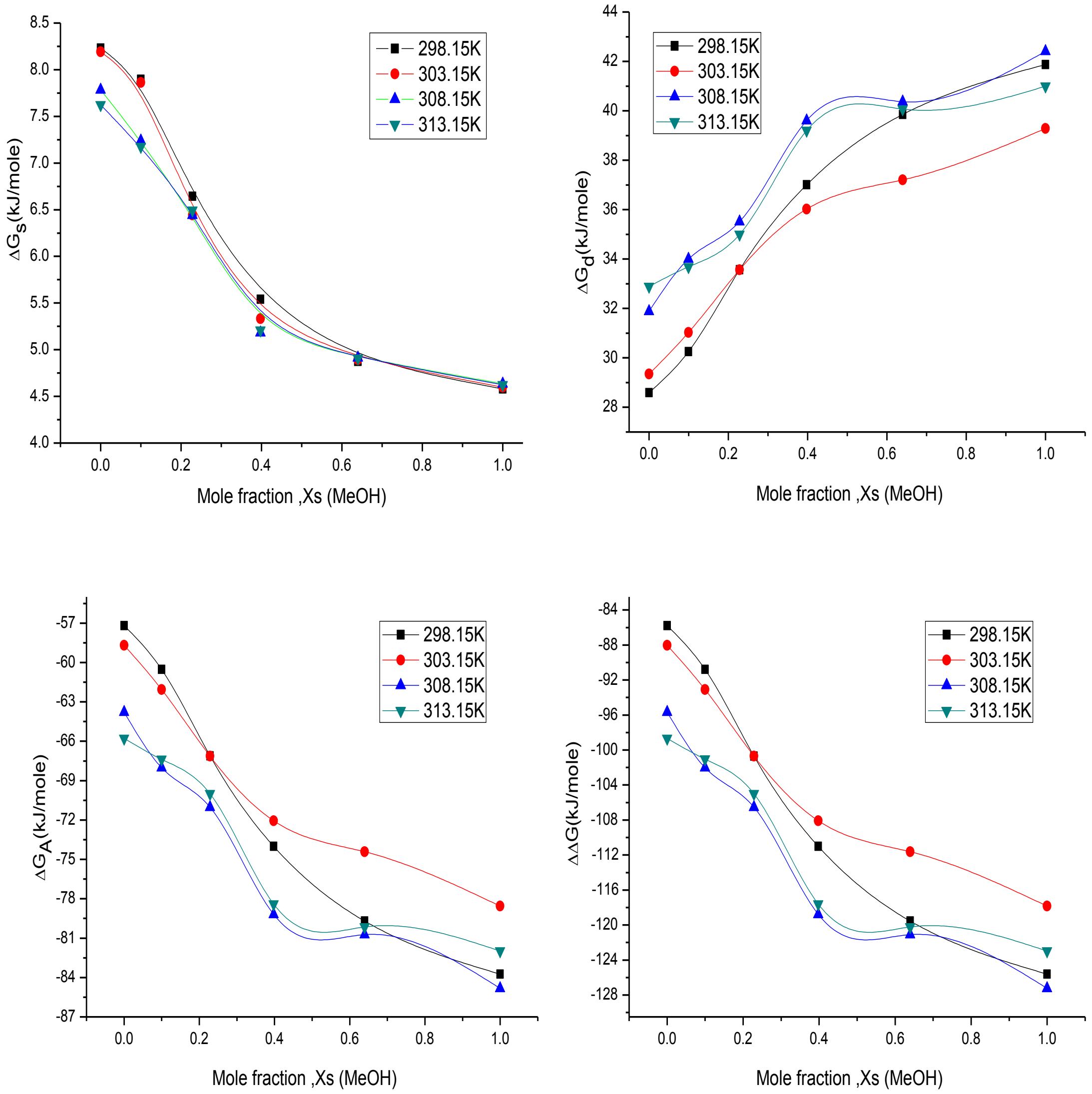

Fig. 3: Relation between ΔG_S, ΔG_d, ΔG_A, and $\Delta\Delta G$ of succinic acid and the mole fraction of MeOH (X_s) in ($MeOH–H_2O$) solvent mixtures at different temperatures.

Table 3: Dissociation constant (K′), association constant (K_{ass}), solvation free energies (ΔG_s), dissociation free energies (ΔG_d), association free energies (ΔG_A), and difference free energies ($\Delta\Delta G$) for succinic acid in (MeOH–H_2O) mixed solvents at different temperatures.

MeOH vol. %	X_s	K′ 298.15K	K′ 303.15K	K′ 308.15K	K′ 313.15K	K_{ass} 298.15K	K_{ass} 303.15K	K_{ass} 308.15K	K_{ass} 313.15K
0	0	$9.8x10^{-6}$	$8.79x10^{-6}$	$3.94x10^{-6}$	3.27x10-^{6}	$1.04x10^{10}$	$1.3x10^{10}$	$6.45x10^{10}$	$9.34x10^{10}$
20	0.0999	$5.01x10^{-6}$	$4.51x10^{-6}$	$1.72x10^{-6}$	$2.41x10^{-6}$	$3.99x10^{10}$	$4.93x10^{10}$	$3.37x10^{11}$	$1.72x10^{11}$
40	0.2284	$1.32x10^{-6}$	$1.65x10^{-6}$	$9.57x10^{-7}$	$1.45x10^{-6}$	$5.73x10^{11}$	$3.68x10^{11}$	$1.09x10^{12}$	$4.72x10^{11}$
60	0.3976	$3.3x10^{-7}$	$6.21x10^{-7}$	$1.94x10^{-7}$	$2.89x10^{-7}$	$9.2x10^{12}$	$2.59x10^{12}$	$2.65x10^{13}$	$1.19x10^{13}$
80	0.6397	$1.05x10^{-7}$	$3.88x10^{-7}$	$1.44x10^{-7}$	$2.07x10^{-7}$	$9.13x10^{13}$	$6.63x10^{12}$	$4.82x10^{13}$	$2.32x10^{13}$
100	1	$4.63x10^{-8}$	$1.71x10^{-7}$	$6.48x10^{-8}$	$1.45x10^{-7}$	$4.67x10^{14}$	$3.43x10^{13}$	$2.38x10^{14}$	$4.72x10^{13}$
MeOH vol. %	X_s	ΔG_S(kJ mol^{-1})				ΔG_d(kJ mol^{-1})			
0	0	8.231	8.191	7.783	7.623	28.592	29.348	31.888	32.889
20	0.0999	7.897	7.863	7.238	7.175	30.257	31.032	34.006	33.683
40	0.2284	6.643	6.442	6.441	6.493	33.562	33.565	35.513	34.998
60	0.3976	5.539	5.333	5.183	5.208	37.003	36.026	39.600	39.204
80	0.6397	4.873	4.893	4.912	4.908	39.848	37.210	40.365	40.073
100	1	4.579	4.597	4.635	4.624	41.871	39.281	42.413	40.995
MeOH vol. %	X_s	ΔG_A(kJ mol^{-1})				$\Delta\Delta G$(kJ mol^{-1})			
0	0	-57.185	-58.697	-63.777	-65.778	-85.778	-88.046	-95.666	-98.668
20	0.0999	-60.515	-62.064	-68.013	-67.3678	-90.773	-93.096	-102.020	-101.051
40	0.2284	-67.124	-67.130	-71.026	-69.996	-100.687	-100.696	-106.540	-104.995
60	0.3976	-74.006	-72.052	-79.200	-78.409	-111.009	-108.078	-118.801	-117.614
80	0.6397	-79.696	-74.421	-80.730	-80.146	-119.545	-111.633	-121.096	-120.219
100	1	-83.742	-78.563	-84.826	-81.990	-125.614	-117.845	-127.240	-122.985

4. Conclusions

The saturated solution of succinic acid in the (methanol–water) mixed solvents is found to increase with the increase the mole fraction of MeOH in the solution due to the ion association phenomenon. It was observed from the different volume values, that all volumes for succinic acid increased by increasing methanol content in the mixed solvent due mainly to the higher solvation. Also the electrostriction volumes increase in negativity confirming the increase in solvent effect by more adding methanol to the mixtures. It was concluded that the solute-solvent interaction increased by increasing $\Delta\Delta G$ and ΔG_s mainly due to the increase of the association parameters in the corresponding solvents. Increasing methanol percentage is achieved by increase in all the association parameters in the mixture used that favor more solute-solvent interactions.

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