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Research Article

SOLUBILITY, MOLECULAR INTERACTIONS THROUGH DFT STUDY OF MALONIC ACID IN WATER, 1-PROPANOL AND THEIR BINARY MIXTURES AT 293.15-313.15K TEMPERATURE

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ABSTRACT

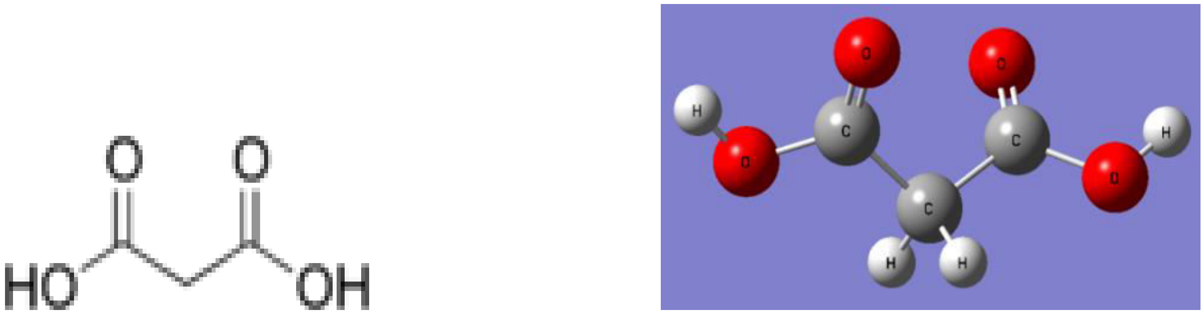
The measurement of solubilities of malonic acid in pure water, 1-propanol and water + 1-propanol binary solvent mixtures were carried out over the entire composition range between 0 to 1 weight fraction of 1-propanol at (293.15, 295.15, 298.15, 300.15, 303.15, 305.15, 308.15, and 313.15) K. The experimental solubility data were correlated by using Apelblat, van't Hoff equation and CNIBS/R-K model. These equations provide better correlation in these measurements. DFT was carried out to correlate solubility in various solvents system. Thermodynamic parameters (ΔH^{0}_{soln}, ΔS^{0}_{soln}, ΔG^{0}_{soln}, %ζH, %ζTS) of solution were calculated using van't Hoff equation.

Keywords: Solubility, Malonic acid, Apelblat equation, DFT.

1. INTRODUCTION

Malonic acid (MA) (fig. 1) is used as a building block chemical to produce numerous valuable compounds [1]. In food and drug applications, malonic acid can be used to control acidity, either as an excipient in pharmaceutical formulation or natural preservative additive for foods. The solubility data of such important organic compounds can be used in industrial, pharma-ceutical, separation, purification, and environmental applications [2]. It is well-known that solid-liquid phase equilibrium data play an important role in the development and operation of crystallization processes [3]. To determine proper solvents and to design an optimized production process, it is necessary to know the solubility in different solvents.

In these investigations, the solubilities of Malonic acid in pure water, 1-propanol and their binary mixtures over different composition were determined at various temperatures. The experimental solubility data were correlated by using Apelblat, van't Hoff and CNIBS/R-K model. Thermodynamic properties of the solutions were calculated by using van't Hoff equation.



(a) (b)

Fig. 1: Chemical Structure of (a) Malonic Acid (b) three dimensional structure

2. EXPERIMENTAL

2.1. Materials and Apparatus

Malonic Acid (99%) was obtained from sigma Aldrich. Methanol (99.8%) and 1-propanol (99.9%) were supplied by Merck. They were used without any further purification. Triple distilled water was used throughout of all these investigations. The method of solubility measurement has been used earlier [4-6].

In this work; an excess amount of malonic acid was added to the binary solvents mixtures prepared by weight (Shimadzu, Auxzzo) with an uncertainty of ±0.1 mg, in a specially designed 100 mL double jacketed flask. Water was circulated at constant temperature between the outer and inner walls of the flask. The temperature of the circulating water was controlled by thermostat to within (0.1) K. The solution was continuously stirred using a magnetic stirrer for long time (about 1 h) so that equilibrium is assured and the solution was allowed to stand for 1 h. Then a fixed quantity of the supernatant liquid was withdrawn from the flask in a weighing bottle with the help of pipette which is hotter than the solution. The weight of this sample was taken and the sample was kept in an oven at 343 K until the whole solvent was evaporated. This was confirmed by weighing two or three times until a constant weight was obtained. The solubility has been calculated using weight of solute and weight of solution. Each experimental value of solubility is an average of at least three different measurements. The saturated mole fraction solubility (X_b), initial the mole fraction of methanol/ethanol (X_c^0), and initial the mole fraction of water (X_a^0) were calculated using usual Eq. 1 and 2:

$$X_b = \frac{m_b/M_b}{m_a/M_a+m_b/M_b+m_c/M_c} \qquad (1)$$

$$X_c^0 = \frac{m_c/M_c}{m_a/M_a+m_c/M_c} \quad \text{and} \quad X_a^0 = \frac{m_a/M_a}{m_a/M_a+m_c/M_c} \qquad (2)$$

Where m_b, m_a, and m_c are the mass of solute, water, methanol/ethanol respectively, and M_b, M_a, and M_c are the molecular weight of the solute, water, and methanol/ethanol, respectively.

2.2. DFT Study

DFT study of experimental molecules and their combinations were optimized on Window-7, Intel core i7 with 16 GB RAM of system. Computational study using Gaussian 03 software [7, 8] DFT/ B3LYP method, 6-311(G) +d p as basis set was performed to understand the fundamental interactions between solvent- solvent and solute- solvent molecules.

From the results of geometry optimization, zero point vibrational energy, nuclear repulsion energy, I.R. frequency of carboxylic -OH group, carboxylic -OH bond distance in angstroms unit and distances of intermolecular hydrogen bonding present between MA with water and alcohols are determined.

3. RESULTS AND DISCUSSION

3.1. Solubility of Malonic Acid (MA)

The mole fraction solubility (X_b) data of MA in pure water and 1-propanol within the temperature range 293.15 K to 313.15 K is presented in table 1, and graphically shown in fig. 2. It can be seen that solubility of MA in pure solvents found to increase with the increase in experimental temperature. Solubility is found to be higher in 1-propanol than water.

Table 1: Experimental mole fraction solubility (X_b) of MA in pure water and 1-propanol

T/K	X_b	
	Water	1-propanol
293.15	0.1805	0.2705
296.15	0.2051	0.2745
298.15	0.2016	0.2915
300.15	0.2287	0.2985
303.15	0.2363	0.3108
305.15	0.2509	0.3302
308.15	0.2591	0.3382
310.15	0.2603	0.3513
313.15	0.2751	0.3568

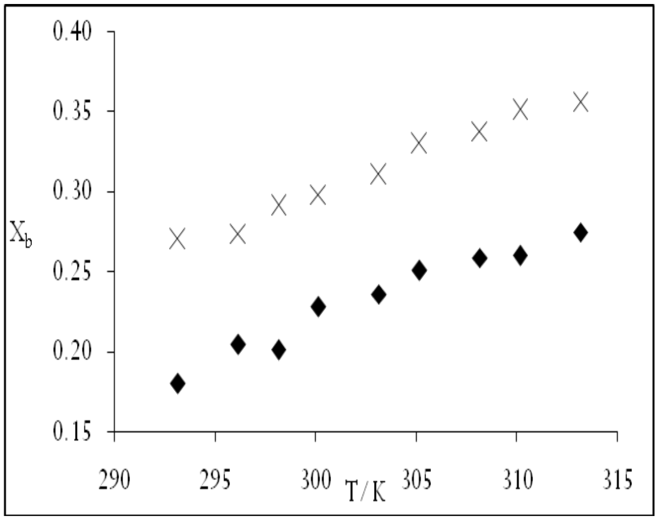


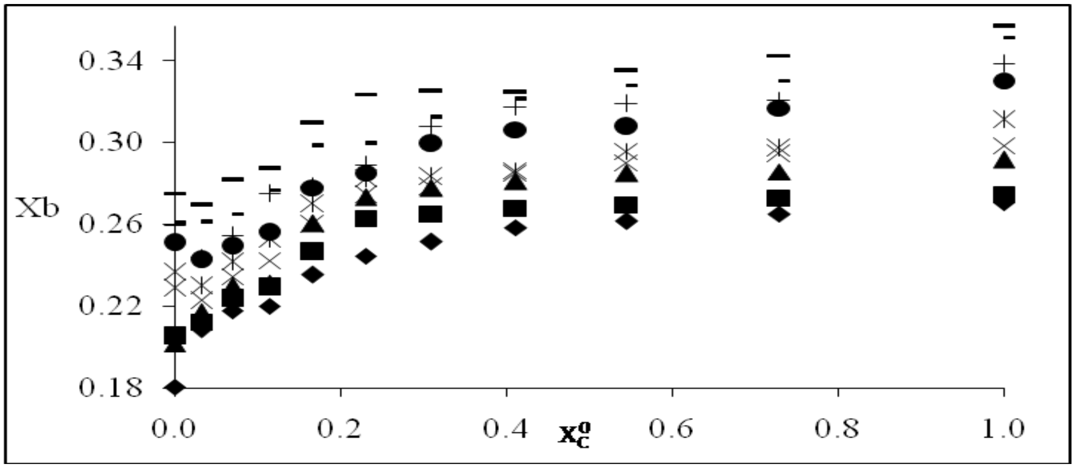
Fig. 2: Mole fraction solubility (X_b) variation with temperatures for water (♦) and 1-propanol (×)

The mole fraction solubilities (X_b) of MA in water + 1-propanol are also tabulated in table 2 along with calculated solubilities by using different correlating models. Also the variation of solubility of MA with initial mole fraction of 1-propanol (X_c^0) and temperature is shown in fig. 3 and 4 respectively. It is observed from tables 2 and fig. 3 and 4 that solubility of MA in studied binary system found to be increase with the initial mole fraction of 1-propanol (X_c^0) and temperature.

Table 2: Experimental (X_b) and calculated mole fraction solubility of MA in various initial mole fraction X_C^0 of 1-propanol at T= 293.15 to 313.15 K

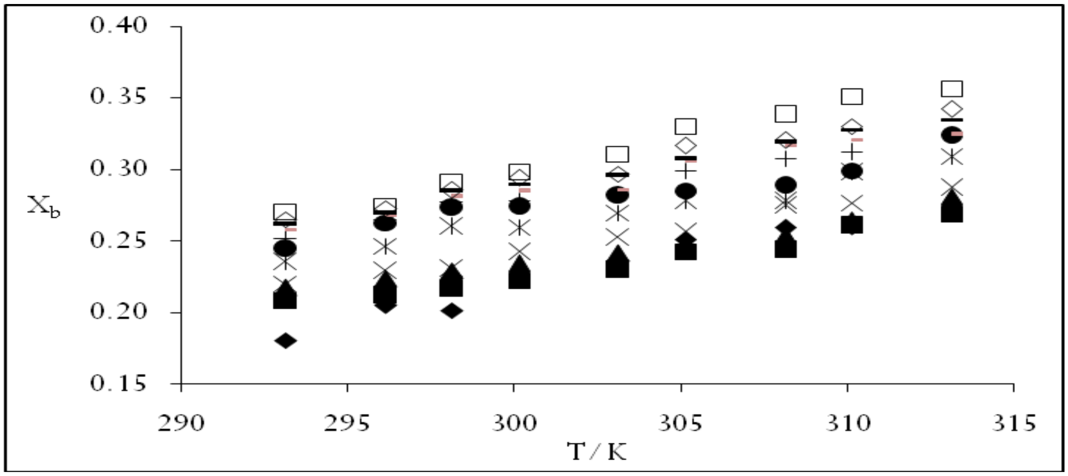
MA+ Water + 1-propanol					
T/K	X_C^0	X_b^{Expt}	X_b^{Apel}	$X_b^{van't}$	X_b^{CNIBS}
293.15	0.0000	0.1805	0.1812	0.1881	0.1874
	0.0322	0.2085	0.2075	0.2039	0.1998
	0.0697	0.2177	0.2184	0.2150	0.2125
	0.1139	0.2201	0.2190	0.2184	0.2250
	0.1666	0.2352	0.2378	0.2373	0.2365
	0.2307	0.2445	0.2507	0.2504	0.2460
	0.3102	0.2514	0.2535	0.2546	0.2528
	0.4116	0.2583	0.2577	0.2598	0.2566
	0.5453	0.2614	0.2609	0.2623	0.2594
	0.7296	0.2650	0.2642	0.2650	0.2666
	1.0000	0.2705	0.2664	0.2677	0.2703
296.15	0.0000	0.2051	0.1997	0.2007	0.2028
	0.0322	0.2121	0.2131	0.2126	0.2130
	0.0697	0.2235	0.2240	0.2235	0.2238
	0.1139	0.2291	0.2283	0.2282	0.2349
	0.1666	0.2464	0.2471	0.2470	0.2459
	0.2307	0.2628	0.2596	0.2595	0.2561
	0.3102	0.2651	0.2645	0.2646	0.2644
	0.4116	0.2678	0.2696	0.2699	0.2699
	0.5453	0.2695	0.2729	0.2731	0.2716
	0.7296	0.2729	0.2759	0.2760	0.2712
	1.0000	0.2745	0.2808	0.2810	0.2747
298.15	0.0000	0.2016	0.2115	0.2094	0.2017
	0.0322	0.2168	0.2176	0.2186	0.2144
	0.0697	0.2296	0.2283	0.2293	0.2279
	0.1139	0.2307	0.2347	0.2349	0.2418
	0.1666	0.2602	0.2535	0.2536	0.2554
	0.2307	0.2732	0.2657	0.2657	0.2679
	0.3102	0.2776	0.2717	0.2714	0.2777
	0.4116	0.2809	0.2773	0.2767	0.2836
	0.5453	0.2848	0.2807	0.2803	0.2851
	0.7296	0.2857	0.2837	0.2835	0.2850
	1.0000	0.2915	0.2904	0.2900	0.2917
300.15	0.0000	0.2287	0.2227	0.2183	0.2217
	0.0322	0.2224	0.2226	0.2247	0.2290
	0.0697	0.2344	0.2332	0.2351	0.2371
	0.1139	0.2422	0.2413	0.2416	0.2463
	0.1666	0.2598	0.2600	0.2603	0.2564
	0.2307	0.2741	0.2718	0.2720	0.2672
	0.3102	0.2782	0.2789	0.2783	0.2781
	0.4116	0.2850	0.2848	0.2836	0.2876
	0.5453	0.2900	0.2885	0.2877	0.2929
	0.7296	0.2943	0.2916	0.2911	0.2920
	1.0000	0.2985	0.3000	0.2992	0.2989
303.15	0.0000	0.2363	0.2380	0.2322	0.2288
	0.0322	0.2297	0.2312	0.2339	0.2369
	0.0697	0.2414	0.2415	0.2440	0.2457
	0.1139	0.2525	0.2515	0.2520	0.2552

	0.1666	0.2699	0.2701	0.2705	0.2650
	0.2307	0.2820	0.2813	0.2815	0.2749
	0.3102	0.2831	0.2896	0.2888	0.2841
	0.4116	0.2862	0.2956	0.2941	0.2913
	0.5453	0.2957	0.2999	0.2989	0.2951
	0.7296	0.2971	0.3033	0.3027	0.2961
	1.0000	0.3108	0.3143	0.3133	0.3110
305.15	0.0000	0.2509	0.2471	0.2418	0.2433
	0.0322	0.2426	0.2377	0.2401	0.2481
	0.0697	0.2493	0.2478	0.2500	0.2541
	0.1139	0.2560	0.2586	0.2590	0.2618
	0.1666	0.2778	0.2770	0.2773	0.2712
	0.2307	0.2852	0.2877	0.2879	0.2825
	0.3102	0.2993	0.2966	0.2958	0.2951
	0.4116	0.3061	0.3026	0.3012	0.3072
	0.5453	0.3076	0.3074	0.3065	0.3145
	0.7296	0.3169	0.3110	0.3105	0.3128
	1.0000	0.3302	0.3238	0.3229	0.3308
308.15	0.0000	0.2591	0.2589	0.2567	0.2502
	0.0322	0.2440	0.2487	0.2497	0.2543
	0.0697	0.2543	0.2583	0.2592	0.2599
	0.1139	0.2747	0.2696	0.2698	0.2676
	0.1666	0.2780	0.2877	0.2878	0.2775
	0.2307	0.2887	0.2975	0.2976	0.2898
	0.3102	0.3077	0.3069	0.3066	0.3038
	0.4116	0.3172	0.3125	0.3119	0.3171
	0.5453	0.3188	0.3184	0.3181	0.3238
	0.7296	0.3207	0.3227	0.3225	0.3180
	1.0000	0.3382	0.3380	0.3376	0.3386
310.15	0.0000	0.2603	0.2653	0.2670	0.2564
	0.0322	0.2608	0.2569	0.2562	0.2629
	0.0697	0.2651	0.2660	0.2654	0.2705
	0.1139	0.2768	0.2772	0.2770	0.2793
	0.1666	0.2981	0.2950	0.2949	0.2893
	0.2307	0.2994	0.3042	0.3042	0.3004
	0.3102	0.3120	0.3137	0.3139	0.3120
	0.4116	0.3210	0.3188	0.3192	0.3223
	0.5453	0.3278	0.3256	0.3259	0.3286
	0.7296	0.3301	0.3304	0.3305	0.3292
	1.0000	0.3513	0.3473	0.3476	0.3514
313.15	0.0000	0.2751	0.2727	0.2828	0.2672
	0.0322	0.2691	0.2706	0.2660	0.2757
	0.0697	0.2813	0.2790	0.2748	0.2848
	0.1139	0.2871	0.2890	0.2882	0.2944
	0.1666	0.3093	0.3063	0.3057	0.3043
	0.2307	0.3235	0.3145	0.3141	0.3142
	0.3102	0.3249	0.3236	0.3249	0.3233
	0.4116	0.3244	0.3277	0.3303	0.3309
	0.5453	0.3349	0.3360	0.3378	0.3360
	0.7296	0.3423	0.3419	0.3428	0.3402
	1.0000	0.3568	0.3611	0.3629	0.3571



(◆T=293.15 K, ■T=296.15 K; ▲T=298.15 K; ×T=300.15 K; ×T=303.15K; ●T=305.15 K; +T=308.15 K; -T=310.15 K and ▬T=313.15 K)

Fig. 3: Mole fraction solubility (X_b) variation with Initial mole fraction (X_c^0) of 1-propanol at various temperatures



(◆=wt. fraction 0.0; ■ = 0.1; ▲= 0.2; ×=0.3; × =0.4; ●=0.5; + = 0.6; - = 0.7; ▬ = 0.8 and ◇= 0.9; □ =1).

Fig. 4: Mole fraction solubility (X_b) variation with Temperature at Initial mole fraction (X_c^0) of 1-propanol

3.2. Solubility Correlation

3.2.1. Apelblat model

Among the different methods, the modified semi-empirical Apelblat model [9], Eq. 3, is a suitable way to correlate solubility data against temperature. The equation is based on solid-liquid equilibrium theory provide excellent agreement between experimental and calculated values of solubility.

$$\ln X_b = A + \frac{B}{T/K} + C \ln T/K \qquad (3)$$

A, B, and C are the model parameters and T is temperature in Kelvin. A and B reflects non-idealities of solutions, C represents temperature influence on fusion enthalpy [10, 11]. A, B, and C parameters are obtained from non-linear least square fitting. Solubility values of solute in water, and 1-propanol and their binary mixtures were calculated by Eq.3. The experimental mole fraction solubility in table 2 was correlated with equation 3 and the parameter values of A, B, and C is given in table 3.

3.2.2. The van't Hoff equation [12]

It is widely used to relate solubility with temperature T/K considering the influence of the solvent as an ideal solution model, which can be described as

$$\ln X_b = A + \frac{B}{T} \quad (4)$$

In Eq. 4, the ln X_b is linear with the reciprocal of experimental temperature. Where T is the temperature, and A and B are equation parameters. The values of correlation coefficient (R^2) for Apelblat equation (table 3) and van't Hoff equation (table 4) indicated that these equations fit quite well in pure and binary solvents.

3.2.3. CNIBS/Redlich-Kister model

The CNIBS/R-K model is also employed to fit the experimental data and describe the influence of binary solvent compositions on solubility. The model that relies on the solvent composition is defined as follows [13]:

$$\ln X_b = X_c^0 \ln X_1 + X_a^0 \ln X_2 + X_c^0 X_a^0 \sum_{i=0}^{n} M_i \left(X_c^0 - X_a^0\right)^i \quad (5)$$

Where X_a^0 is initial mole fraction of water and X_1 and X_2 are solubilities of solutes in pure 1-propanol and water, respectively. M_i is curve fit parameters and n is the number of solvents which equals 2 in this work. Substituting (1-X_c^0) forX_a^0, the above equation can be simplified as

$$\ln X_b = M_0 + M_1 X_c^0 + M_2 X_c^{0^2} + M_3 X_c^{0^3} + M_4 X_c^{0^4} \quad (6)$$

All values of M_i are the curve fit parameters. The values of R^2 are close to unity shows that CNIBS/Redlich-Kister model is very well appropriate for this solubility data. This model describes the effect of binary solvent compositon on MA solubility. The M_0, M_1, M_2, M_3, M_4 are the model parameters presented in Table 5 along with their correlation coefficient (R^2). The values of R^2 are close to unity for all compositions shows that CNIBS/R-K model fits the solubility data of MA in studied binary solvent mixtures.

Table 3: Model parameters and correlation coefficient of the Apelblat equation

X_c^0	Parameters			R^2	100RAD	100RMSD
	A	B	C			
0.0000	765.450	-36201	-113.308	0.9718	1.7430	0.4859
0.0322	-353.86	14863	53.0897	0.9826	0.8988	0.2760
0.0697	-317.051	13285	47.5664	0.9921	0.5596	0.1783
0.1139	-58.1426	1478.0	9.0802	0.9878	0.7779	0.2494
0.1666	-39.539	734.81	6.2661	0.9633	1.0980	0.4293
0.2307	-21.7242	37.2563	3.5582	0.9262	1.7761	0.5790
0.3102	90.3859	-5087.8	-13.0975	0.9785	0.8647	0.3229
0.4116	164.906	-8434.8	-24.203	0.9670	1.0955	0.4161
0.5453	109.448	-5981.1	-15.9116	0.9886	0.6711	0.2478
0.7296	60.4486	-3788.2	-8.6005	0.9823	0.8656	0.3295
1.0000	107.560	-6094.6	-15.5076	0.9815	1.1323	0.4050

Table 4: Model parameters and correlation coefficient of the van't Hoff equation

X_c^0	Parameters			100RAD	100RMSD
	A	B	R^2		
0.0000	4.7165	-1872.44	0.9439	2.9334	0.7107
0.0322	2.5761	-1221.39	0.9678	1.3873	0.3624
0.0697	2.3022	-1125.48	0.9779	0.8268	0.3037
0.1139	2.8208	-1272.98	0.9873	0.7590	0.2500
0.1666	2.5308	-1163.61	0.9631	1.1111	0.4334
0.2307	2.1656	-1040.79	0.9261	1.7664	0.5818
0.3102	2.4517	-1119.78	0.9774	0.8668	0.3281
0.4116	2.4116	-1102.12	0.9633	1.3014	0.4446
0.5453	2.6203	-1160.43	0.9871	0.7977	0.2655
0.7296	2.7057	-1182.52	0.9819	0.8594	0.3336
1.0000	3.4453	-1396.32	0.9805	1.1233	0.4268

Table 5: Model parameters and correlation coefficient of the CNIBS/R-K model

T/K	M_0	M_1	M_2	M_3	M_4	R^2
293.15	-1.6747	2.1699	-5.6575	6.5604	-2.7065	0.9708
296.15	-1.5955	1.6316	-3.2982	2.8356	-0.8655	0.9860
298.15	-1.6010	2.0406	-4.3605	3.9620	-1.2732	0.9806
300.15	-1.5063	1.0252	-0.8491	-0.5280	0.6505	0.9720
303.15	-1.4748	1.1329	-1.6198	0.6520	0.1419	0.9647
305.15	-1.4134	0.5725	0.9368	-3.0895	1.8872	0.9672
308.15	-1.3854	0.4485	1.7160	-4.5089	2.6468	0.9612
310.15	-1.3611	0.7890	-0.1739	-1.4089	1.1091	0.9842
313.15	-1.3197	1.0233	-1.6179	1.0041	-0.1194	0.9583

3.3. Thermodynamic parameters of dissolution

The thermodynamics involved in dissolution process of malonic acid in pure and binary solvents at temperature ranging from 293.15 to 313.15 K is studied by using van't Hoff analysis. The standard molar enthalpy change of solution ΔH^0_{soln}, standard molar entropy change ΔS^0_{soln}, and standard molar Gibbs energy change ΔG^0_{soln} for the solution process are calculated according to van't Hoff equation [14, 15].

$$\Delta H^0_{sol} = -R\left(\frac{\partial \ln x_b}{\partial (1/T)}\right) = -R\left[\frac{\partial \ln x_b}{\partial\left(\frac{1}{T} - \frac{1}{T_{mean}}\right)}\right] \quad (7)$$

$$\Delta G^0_{soln} = -R.T \times \text{intercept} \quad (8)$$

$$\Delta S^0_{soln} = \frac{\Delta H^0_{soln} - \Delta G^0_{soln}}{T_{mean}} \quad (9)$$

In Eq. 7, T_{mean} is the mean harmonic temperature *i.e.* T_{mean} = 303.03 K.

The plots ln X_b vs. (1/T - 1/ T_{mean}) for malonic acid at studied temperature are linear as shown in fig. 5.

In addition, the relative contribution of enthalpy (%ζH) and entropy (%ζTS) were calculated by using following Eq. 10. The values of %ζH and %ζTS could be used to evaluate the effect of enthalpy and entropy to Gibbs energy in solution process

$$\%\zeta H = \frac{\Delta H^0_{soln}}{|\Delta H^0_{soln}| + |T\Delta G^0_{soln}|} \times 100 \quad \text{and}$$

$$\%\zeta TS = \frac{|T\Delta G^0_{soln}|}{|\Delta H^0_{soln}| + |T\Delta G^0_{soln}|} \times 100 \quad (10)$$

The thermodynamic parameters (ΔH^0_{soln}, ΔS^0_{soln}, ΔG^0_{soln}, %ζH, and % ζTS) in pure and binary solvents mixtures are given in Table 6.

The ΔH^0_{soln} values for dissolution of MA in all mixtures are all positive indicating that dissolution process of MA in all mixtures is endothermic. The ΔH^0_{soln} value in pure water is 15.5671 $KJK^{-1}mol^{-1}$ and in 1-propanol is 11.6063 $KJK^{-1}mol^{-1}$. This indicates that more energy is required for the dissolution of MA in water as compared to dissolution of MA in 1-propanol. The value of ΔG°_{soln} and ΔS°_{soln} are positive, which means the dissolution process occurs with an increase of entropy and process is non-spontaneous. Table 6 shows that the values of %ζH are greater than the values of %ζTS for all studied mixtures which suggest that enthalpy is the main contributing force to the Gibbs free energy for the dissolution of MA. Overall the dissolution of MA in all binary solvent mixtures is enthalpy driven endothermic process.

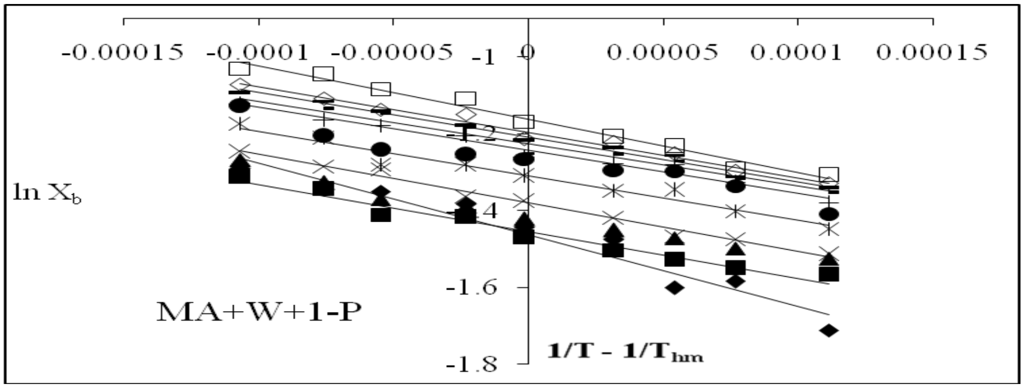
Table 6: Thermodynamic function relative to solution process of MA at T_{hm}= 303.15K

X^0_C	ΔH°_{sol} KJK^{-1} mol^{-1}	ΔG°_{sol} K J $K^{-1}mol^{-1}$	ΔS°_{sol} KJ $K^{-1}mol^{-1}$	ΔS°_{sol} JK^{-1} mol^{-1}	$T\Delta S^\circ_{sol}$ KJ K^{-1} mol^{-1}	ζH%	ζTS%
			MA + Water + 1-propanol				
0.0000	15.5671	3.6835	0.0392	39.2040	11.8803	56.7108	43.2892
0.0285	10.1514	3.6633	0.0214	21.4101	6.4881	61.0079	38.9921
0.0620	9.3533	3.5550	0.0191	19.1338	5.7983	61.7314	38.2686
0.1018	10.5837	3.4743	0.0235	23.4603	7.1094	59.8184	40.1816
0.1498	9.6692	3.2980	0.0210	21.0244	6.3712	60.2802	39.7198
0.2091	8.6466	3.1947	0.0180	17.9907	5.4519	61.3299	38.6701
0.2839	9.3034	3.1317	0.0204	20.3659	6.1717	60.1185	39.8815
0.3815	9.1620	3.0863	0.0200	20.0492	6.0757	60.1273	39.8727
0.5140	9.6442	3.0460	0.0218	21.7735	6.5982	59.3768	40.6232
0.7041	9.8271	3.0133	0.0225	22.4851	6.8139	59.0538	40.9462
1.0000	11.6063	2.9276	0.0286	28.6390	8.6787	57.2162	42.7838

3.4. DFT study

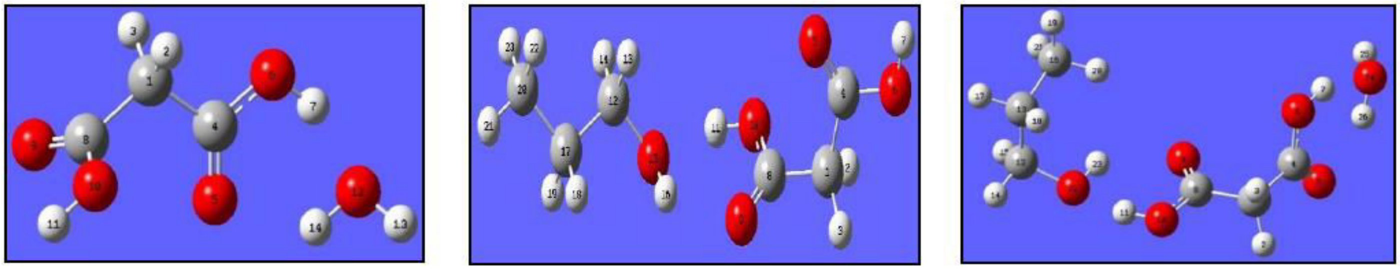
The optimized structures and theoretical IR of MA + water and MA + 1-propanol are shown in figure 6 and 7-9 respectively. From the results of geometry optimization, zero point vibrational energy, nuclear repulsion energy, I.R. frequency of carboxylic -OH group, carboxylic -OH bond distance in angstroms unit and distances of intermolecular hydrogen bonding present between MA with water and 1-propanol are determined. These properties are listed in table 7.

Table 7 shows that the bond distance of carboxylic -OH group of MA increases when the molecule combines with water and 1-propanol. The trend for carboxylic (-OH) bond distance of MA in pure solvents is: MAP (0.99405 Å) > MAW (0.98924 Å) which correlates the solubility order of MA in pure solvents. Fig. 6 shows that intermolecular interactions and H-bonding between MA and solvent molcules. H-bonding is formed in all cases with different intermolecular distances. For MAW and MAP complexs, carboxylic acid group in MA interacts with alcoholic -OH group of solvents producing two strong H-bonds with different intermolecular H-bond distances. The order for first intermolecular H-bond distance (Å) between one H atom of carboxylic group of MA and one O atom from solvent (-H---O-) is MAP (1.7272 Å) < MAW (1.7712 Å). The order for second intermolecular H-bond distance (Å) between one O atom of carboxylic group of MA and one H atom from solvent (-O---H-) is MAP (2.0781 Å) < MAW (2.1363 Å).



(◆=0.0; ■ = 0.1; ▲= 0.2; ×=0.3; × =0.4; ●=0.5; + = 0.6; - = 0.7; ▬ = 0.8 and ◇ = 0.9; □ =1)

Fig. 5: Plot of ln X_b vs ($1/T - 1/T_{hm}$) for MA + Water + 1-propanol at various mole/wt. fractions



(a) (b) (c)

Fig. 6: Optimized structure of a) MA + Water b) MA + 1-propanol and c) MA + water + 1-propanol

Table 7: Calculated υ-OH (-OH str. freq.), -OH bond distance, intermolecular H-bond distance for pure substance, binary solvents and ternary solution by DFT/B3LYP method at 6-311G +(d p) basis set

System (Gas)	Carboxylic υ-OH cm^{-1}	Carboxylic (-OH) Bond Dist. (Å)	Intermolecular H-Bond Dist. (Å) O-H	Intermolecular H-Bond Dist. (Å) C=O-H	Zero point vibration energy Kcal/mol	Nuclear Repulsion Energy Hartrees
MA	3750.79	0.9699	-	-	48.4546	299.128
MAW	3370.02	0.98924	1.7712	2.1363	64.1217	382.626
MAP	3274.03	0.99405	1.7272	2.0781	117.721	617.720
MAWP	3383.23 3307.95	0.98858 0.99357	1.7802 1.7357	2.04348 2.07434	133.546	724.905

Similarly solubility trend of MA in pure solvents can be explained by using theoretically computed stretching fequency of -OH in carboxylic group of MA as presented in Table 7 and graphically shown in Fig. 7-9. From these data, it is seen that υ-OH of MA is 3750.79 cm^{-1} which is very large as compared to υ-OH of MA with its solvent combinations. Higher value υ-OH means -OH group is free or less associated. The υ-OH of MA in MAW combination is 3370.02 cm^{-1} which slighlty higher than υ-OH of MA in MAP (3274.03cm^{-1}) combination. This confirms the effect of H-bonding on the υ-OH of MA which explains that solubility of MA in water is low as compared to that of in 1-propanol.

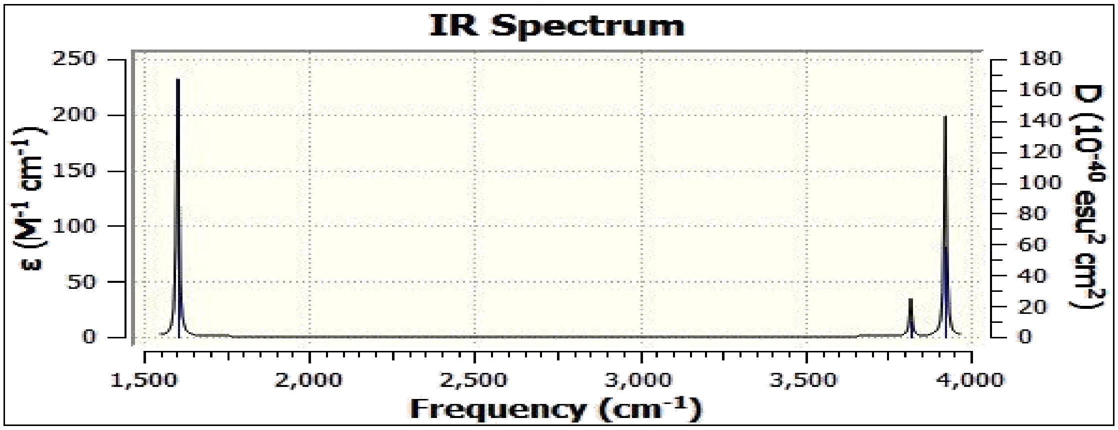


Fig. 7: Theoretical I.R. spectra of MA + Water in gas phase by DFT/B3LYP at 6-311G (+d p) basis set

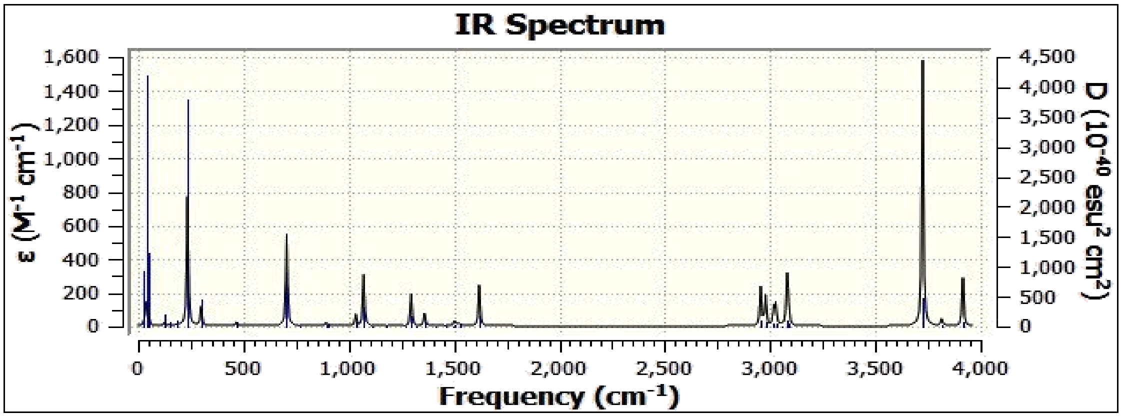


Fig. 8: Theoretical I.R. spectra of MA+1-propanol in gas phase by DFT/B3LYP at 6-311G (+d p) basis set

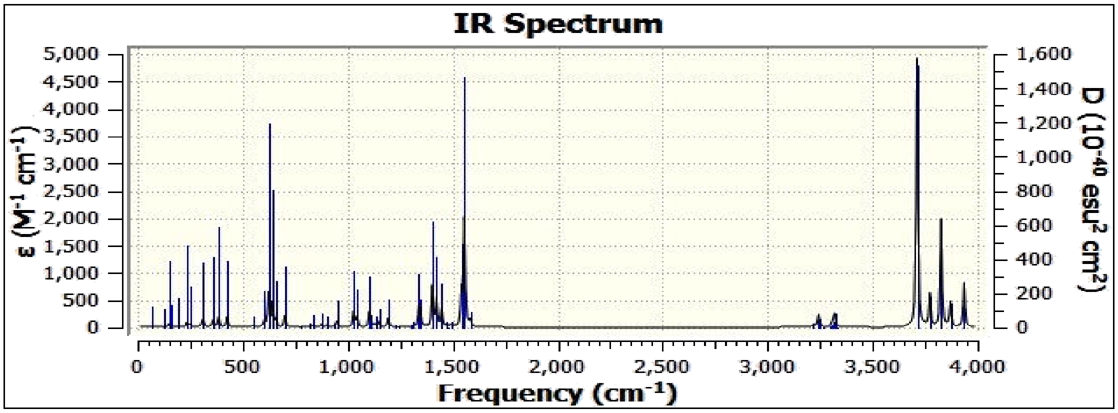


Fig. 9: Theoretical I.R. spectra of MA+Water+1-propanol in gas phase by DFT/B3LYP at 6-311G (+d p) basis set

4. CONCLUSION

Solubility of MA in pure solvents found to increase with the increase in experimental temperature. Solubility is found to be higher in 1-propanol than water. Solubilities of MA in all studied binary system increase with the initial mole fraction of 1-propanol (X_C^0) and temperature. The measured solubilities of MA are well correlated with temperature by Apelblat, van't Hoff and with composition by CNIBS/R-K model. Thermodynamic study from measured solubilities of MA indicates that dissolution of MA in all binary solvent mixtures is enthalpy driven endothermic process. The results of ζH suggest that enthalpy is the main contributing force to the Gibbs free energy for the dissolution of MA. In addition, DFT study provides important data which indicates that solubility of MA is also depends on H-bonding between solute and solvent. The theoretical IR study is useful to explain the solubility of MA in pure and binary solvent mixtures.

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Conflict of interest

None declared

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