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Studying the Thermodynamic Properties of DL-Malic Acid Acids in a Binary Mixture of Water and Tetrahydrofuran

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Abstract

In This Research Studied The solubility of DL-Malic acid in Water + THF mixtures by astatic analytical technique using the acid–base titration method at temperatures ranging from 298.15 to 323.15 K and atmospheric pressure 101.3 kPa. The effects of mass fraction Tetrahydrofuran in the solvent mixtures at (0.1 to 0.95) on the solubility were studied and stirring plus settled in different times.The experimental results indicated that the solubility of DL-Malic acid in the binary solvent mixtures increases with increasing temperature and mass fraction of THF. While stirring or settling times were investigated it has no effect on the solubility in Binary solvent.The equilibrium results consisted of solubility data and tie-lines were presented in ternary phase diagrams by Matlab program. The thermodynamic properties of solution enthalpy, entropy and Gibbs free energy change of solution is calculated by using the van't Hoff equation and Gibbs equation. The values of both the enthalpy change and the molar Gibbs free energy change of solution were positive which meaning that the dissolution of DL-malic acid into THF + water solvent mixtures is endothermic and non-spontaneous.

Keywords: Solubility, DL-Malic acid, Thermodynamic properties, Binary mixtures, Ternary system, Tetrahydrofuran, Solid–Liquid equilibrium (SLE).

1. Introduction

The physical properties and the thermodynamic behavior of binary mixtures have been studied for many reasons, one of the most important of which is that these properties may provide information about molecular interaction and development of solution models that describe the thermodynamic properties of DL-malic acid solutions, and can contribute to the elucidation of the nature of interactions between non-polar and polar groups [1.10], All systems seek thermodynamic equilibrium. The thermodynamic stability criterion provides that must be satisfied by providing that at a constant temperature and pressure, a steady state is that in which present a minimum of the Gibbs free energy

$$dG_{T,P} \leq 0 \quad (1)$$

When two or more substances are mixed, $dG_{T,P}$ is defined as the difference between the Gibbs free energy of the solution and the pure compounds. If $dG_{T,P} \leq 0$, forms a stable single phase solution, but if $dG_{T,P} \geq 0$, the homogeneous solution is unstable and the system is forced to split into two or more phases in order to minimize the Gibbs free energy. This way or two-phase systems are formed by multiphasic. [2]

Carboxylic acids such as DL- Malic acid is examples of compounds with wide industrial applications and high potential components which wide use in food and medicine applications. [3]

DL-Malic acid (shown in figure 1), a white crystalline powder, is widely used as an important intermediate in the process of tricarboxylic acid cycle, which can be used as food additives, pharmaceutical intermediates, cosmetics, rinses, metal cleaners, buffering agents, retarders in the textile industry and fluorescent whitening agent of polyester fiber., In industrial mass production, DL-malic acid is chemically synthesized by hydration of either maleic or fumaric acid at high temperature and pressure. [4]

To the best of our knowledge, the solubility of dl-malic acid in binary solvent mixtures has not been reported yet. The studies on the solubility and thermodynamic properties in binary solvent mixtures have received considerable attention by researchers during last decades. Moreover, it has become a common view that the use of binary solvent mixtures plays a significant role in the SLE system. In some cases, solubility in mixed solvents is higher at some compositions than in either of the pure solvents, which is called the synergistic effect. [5], reported in many literature, Authors using different method such as the solubility of Gallic acid in aqueous solutions has been reported in many literatures using a thermostatic reactor and UV/vis spectrophotometer analysis, [11] The solubility of daidzin in different organic solvents and (ethyl alcohol + water) mixed solvents was measured by high performance liquid chromatography (HPLC) analysis method.[12] Previous works about malic acid extraction by different solvents such as methanol plus (acetonitrile, N,N-dimethyl form amide, isopropyl alcohol) [3], And mixtures of ethanol + water [4], And for derivatives of this acid studies Such Solubility's of L-malic acid in pure organic solvents(acetonitrile, 1-butanol,acetone,ethyl acetate, 1-propanol,ethanol, iso -propanol)[6],

In this work, the solubility of DL-malic acid in Water plus THF binary solvent mixtures was measured at temperatures ranging from (293.15 to 323.15) K under atmosphere pressure (101.3 kPa) investigated by astatic analytical technique using the acid–base titration method, Then The thermodynamic properties of the dissolution process, including enthalpy, entropy and Gibbs free energy, were calculated by means of the van't Hoff analysis and Gibbs equation.

2. Experimental

2-1: Materials

DL-Malic acid (molecular weight 134.08, mass fraction >99.5%)was obtained from Merck Co. USA, and was kept in a desiccator with dry silica gel. Tetrahydrofuran, THF (0.995 in mass fraction) obtained from

POCH Co USA. Distilled and deionized water was used as a part of the solvent which was prepared in our laboratory, (Table 1).

Table 1. Provenance and mass fraction purity for materials used in the experiment

Chemical name	Formula	Initial mass fraction purity	Source
DL-Malic acid	$C_4H_6O_5$	99.5 %	Merck
THF	C_4H_8O	99.5 %	POCH
Water	H_2O	Deionized and redistilled water	Our laboratory
Sodium hydroxide	NaOH	99.99 %	Merck

L-Malic acid.

D-Malic acid.

Figure 1. Chemical structure of DL-Malic acid.

2-2: Apparatus and procedure

An amount of solute and weighed solvent were put into a jacketed glass flask (Sci Labware Pyrex) and the mixture was maintained under stirring at the desired temperature by circulating water from a thermostat (Haake P5 Sigma-Aldrich Co., Germany), with an uncertainty of ±0.01 K. Continuous stirring was kept for at least 3 h using a magnetic stirrer to reach the solid–liquid equilibrium(SLE) First experimental and 2 h second experimental and then gravitationally settled down for 1 h and 4 h, The experimental apparatus for the solubility determination is(shown in Figure 2)[2.8]. After that weighed sample was diluted with 50.0 g of distilled and deionized water. This solution was titrated with standardized solutions of NaOH using phenolphthalein as an indicator. Phenolphthalein was demonstrated to be an appropriate indicator for the titration of DL-Malic acid, the titrations have been carried out to the second endpoint for malic acid. The pH was around 8.3 at the end of titration and the color change of phenolphthalein was from colorless to reddish, which was operated at room temperature, three independent determinations were used to calculate an average solubility value at each temperature. An analytical balance (Sartorius, Switzerland) with a deviation of ±0.0001 g, the mass fraction of THF(W_2) prepared varied from 0.1 to 0.9 to cover all compositions range with the increment of 0.1. The mole fraction of DL-Malic acid in saturated solution (X_3), the mole fraction of THF in solvent mixtures (X_2) and the mole fraction of Water (X_1) were calculated by the following equations: [5.7]

$$W_2 = \frac{m_2}{m_1 + m_2} = \frac{\rho_2 * v_2}{\rho_1 * v_1 + \rho_2 * v_2} \qquad (2)$$

$$X_3 = \frac{n_3}{n_1 + n_2 + n_3} = \frac{\frac{m_3}{M_3}}{\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3}} \qquad (3)$$

$$X_2 = \frac{n_2}{n_1 + n_2 + n_3} = \frac{\frac{m_2}{M_2}}{\frac{m_1}{M_1} + \frac{m_2}{M_2} + \frac{m_3}{M_3}} \qquad (4)$$

$$X_1 = 1 - (X_3 + X_2) \qquad (5)$$

Where:

$m_{1.2.3}$: represent the mass of, water, THF, and, DL-Malic acid respectively.
$n_{1.2.3}$: are the mole of water, THF, and, DL-Malic acid respectively.
$M_{1.2.3}$: the molecular weights of water, THF, and, DL-Malic acid respectively.
$\rho_{1.2}$: water and THF density in order obtained from the Dortmund Information Bank. [9]

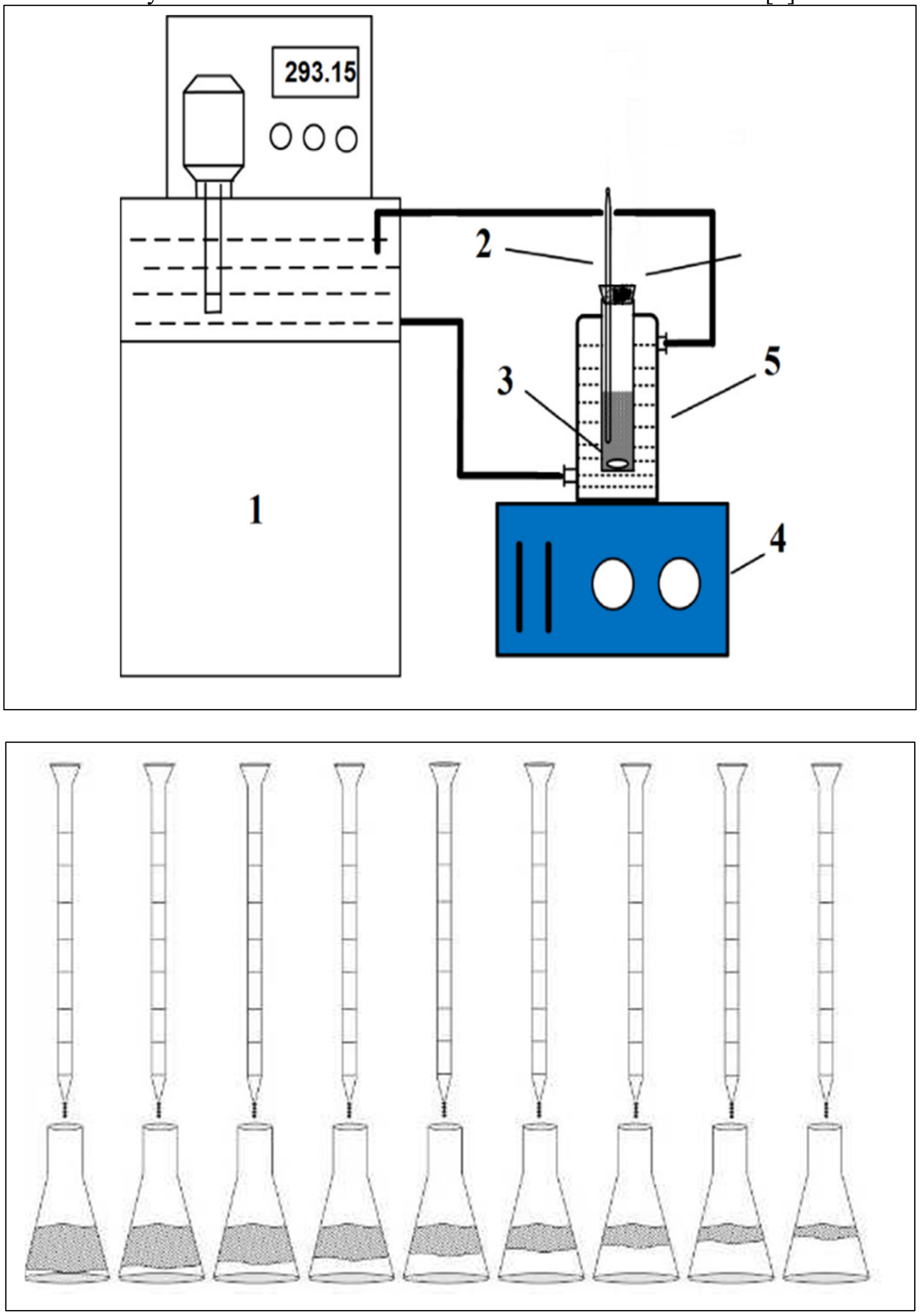

Fig. 2. Schematic diagram of experimental apparatus: 1-smart thermostatic water bath, 2- mercury-in-glass thermometer, 3-magnetic stirrer, 4-stirrer controller, 5-jacketed glass vessel.

3. Results and discussion

3.1: Solubility data

The solubility of DL-malic acid (X_3) in Water plus THF binary solvent mixtures with the temperature ranging from (293.15 to 323.15) K are presented in tables 2–5, and graphically showed in figures 3,4 by Matlab program.

Table 2. Mole fraction solubility of DL-malic acid and (Water + THF) binary solution mixtures at temperatures from (293.15) K

W2	V_{NaOH} ml (1N)	X1%	X2%	X3%
0.100	4.000	84.713	2.548	12.739
0.154	4.100	82.736	3.909	13.355
0.201	5.900	76.489	5.016	18.495
0.251	6.000	74.359	6.410	19.231
0.305	6.800	70.701	7.643	21.656
0.351	7.400	67.308	8.974	23.718
0.402	8.000	63.694	10.828	25.478
0.508	8.600	58.385	14.907	26.708
0.551	9.400	54.601	16.565	28.834
0.601	9.400	51.502	19.305	29.193
0.655	9.800	47.561	22.561	29.878
0.704	10.200	43.373	25.904	30.723
0.754	10.600	38.824	30.000	31.176
0.800	10.800	34.659	34.659	30.682
0.85	11.100	29.178	41.379	29.443
0.881	12.100	24.570	45.700	29.730
0.872	10.100	25.958	44.248	29.794
0.909	8.600	20.000	49.286	30.714
0.945	6.500	13.992	59.259	26.749

Table 3. Mole fraction solubility of DL-malic acid and (Water + THF) binary solution mixtures at temperatures from (303.15) K

W2	V_{NaOH} ml (1N)	X1%	X2%	X3%
0.114	4.700	82.758	2.508	14.734
0.169	4.800	80.891	3.822	15.287
0.231	6.600	74.390	5.488	20.122
0.283	6.700	72.274	6.854	20.872
0.336	7.500	68.308	8.615	23.077
0.385	8.200	64.814	9.877	25.309
0.439	9.000	60.976	11.585	27.439
0.489	9.600	57.317	13.415	29.268
0.536	10.400	53.293	15.569	31.138
0.585	10.400	50.600	17.700	31.700
0.638	10.800	46.988	20.482	32.530
0.684	11.200	43.114	23.353	33.533
0.731	11.600	39.053	26.627	34.320
0.779	11.800	35.057	31.035	33.908
0.824	12.100	30.641	35.654	33.705
0.873	12.800	25.126	42.713	32.161
0.877	10.800	24.859	44.633	30.508
0.914	9.300	18.983	49.492	31.525
0.946	7.200	13.492	57.937	28.571

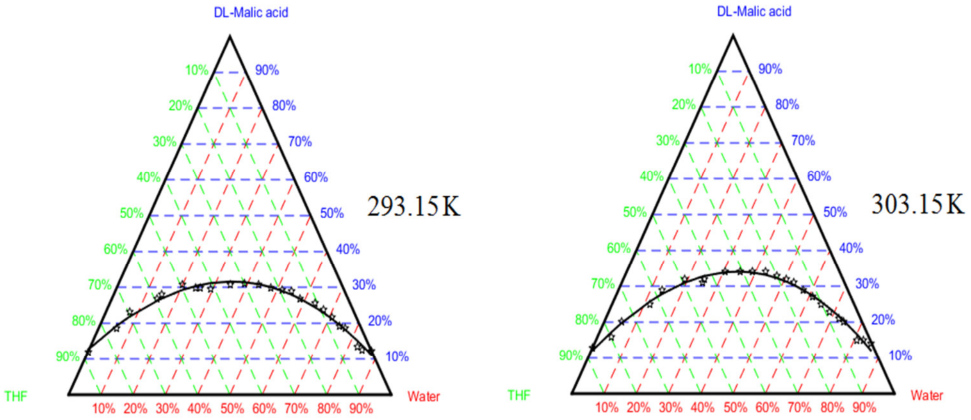

Fig. 3. Water + DL-Malic acid + THF phase diagram with tie lines at (293.15 & 303.15) K.

Table 4. Mole fraction solubility of DL-malic acid and (Water + THF) binary solution mixtures at temperatures from (313.15) K

W2	V $_{NaOH}$ ml (1N)	X1%	X2%	X3%
0.113	5.800	80.000	2.424	17.576
0.167	5.900	78.154	3.692	18.154
0.229	7.700	71.976	5.31	22.714
0.281	7.900	69.669	6.607	23.724
0.334	8.700	65.875	8.309	25.816
0.383	9.400	62.500	9.524	27.976
0.437	10.000	59.171	11.243	29.586
0.487	10.600	55.621	13.018	31.361
0.534	11.400	52.047	14.620	33.333
0.583	11.200	49.401	17.301	33.298
0.636	11.600	45.882	20.000	34.118
0.682	12.000	42.105	22.807	35.088
0.729	12.400	40.882	28.307	30.811
0.777	12.600	34.463	29.944	35.593
0.822	12.900	31.101	41.307	27.592
0.872	13.700	24.691	41.482	33.827
0.876	11.700	24.377	43.213	32.41
0.913	10.400	18.421	47.368	34.211
0.946	8.300	13.027	55.172	31.801

Table 5. Mole fraction solubility of DL-malic acid and (Water + THF) binary solution mixtures at temperatures from (323.15) K

W2	V_{NaOH} ml (1N)	X1%	X2%	X3%
0.112	7.400	76.162	2.326	21.512
0.167	7.500	74.487	3.519	21.994
0.228	9.300	68.733	5.070	26.197
0.28	9.400	66.667	6.322	27.011
0.333	10.200	63.068	7.955	28.977
0.381	10.700	60.172	9.169	30.659
0.435	11.300	56.980	10.826	32.194
0.485	11.900	53.561	12.536	33.903
0.532	12.700	50.140	14.085	35.775
0.581	12.700	47.564	16.052	36.384
0.634	13.100	44.193	18.697	37.110
0.681	13.500	40.564	21.408	38.028
0.728	13.900	36.768	24.513	38.719
0.776	14.100	33.242	28.338	38.420
0.821	14.300	29.024	33.245	37.731
0.871	15.100	23.981	39.808	36.211
0.876	13.100	23.592	41.287	35.121
0.912	11.600	17.834	45.223	36.943
0.946	9.500	12.546	52.399	35.055

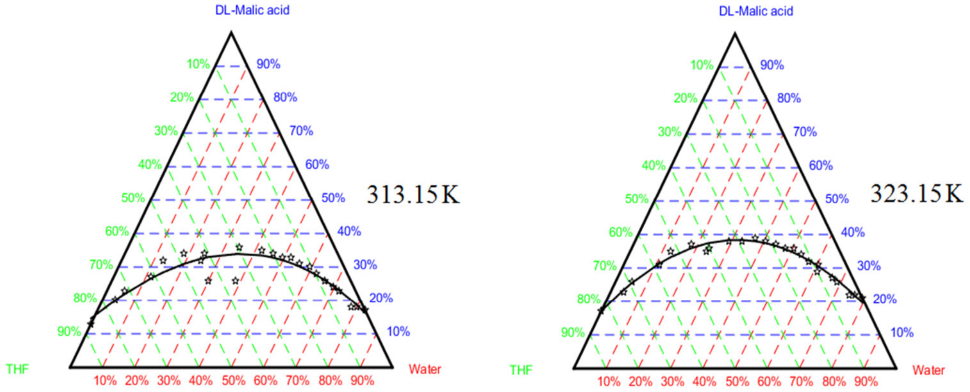

Fig. 4. Water + DL-Malic acid + THF phase diagram with tie lines at (313.15 & 323.15) K.

It can be seen that the solubility of DL-Malic acid in Binary solvents (Water + THF) is significantly higher than water only solvent. [5]. the solubility of DL-Malic acid increases with the increasing mass fraction of THF in solvents at a constant temperature, and it also increases with the increasing temperature at a constant solvent composition. The highly polar water molecules interact with the polar groups of the dl-malic acid, and THF is assumed to have highly polarity to interact with the polar groups of the dl-malic acid molecules than water. but they're together a very polar place. it is supposed that the hydroxyl (OH) and carboxyl (COOH) groups existing in dl-malic acid, would have a greater opportunity to form intermolecular hydrogen. It causes the increase of acid solubility with the increasing mass fraction of THF until reach the saturated solution. Hence, we can draw a conclusion that the polarity of solvents and the inter molecular hydrogen bonds could be the dominant factors to determine the solubility of dl-malic acid in THF + water system.

Table 6 Parameters of experimental values for DL-Malic acid in binary Water + THF solvent mixtures.

Form experimental solubility ternary phase diagrams equation			$f(X_3) = aX_3^3 + bX_3^2 + cX_3 + d$	
T\K	a	b	c	d
293.15	- 0.00839	- 0.00697	+0.79794	+6.41110
303.15	- 0.13300	- 0.00726	+ 0.90184	+4.98900
313.15	- 0.18640	- 0.00477	+0.73244	+8.0995
323.15	-0.01151	- 0.00989	+1.03700	+6.6853

3.2: Thermodynamic properties for the solution

For an ideal solution, the van't Hoff equation describes the relationship between the mole fraction of a DL-Malic acid and the absolute temperature, as shown in equation

$$\Delta H = -R\left(\frac{\partial lnX_3}{\partial\left(\frac{1}{T}\right)}\right)_P \quad (6)$$

Where

X_3: mole fraction of DL − Malic acid in saturated solution.

ΔH: the molar enthalpy of DL − Malic acid in saturated solution.

R: the gas constant (8.314 $Joul.mol^{-1}. K^{-1}$)

T: absolute temperature of solution.

By plotting ln x_3 versus 1/T, the dissolution enthalpy and entropy of DL-Malic acid in (Water + THF) binary mixtures could be obtained by linear fitting. The slope represents $\Delta H/RT$. The plot is shown in figure 5-7. and all the linear correlation coefficients are >0.95. This indicates that the dissolution enthalpy obtained could be considered as temperature independent within the temperature range studied.

While The Gibbs free energy of dissolution can be calculated by the following equation (7) and entropy from equation (8).[13.14] .The values of ΔH, ΔS and ΔG are given in table 7,8.

$$\Delta G = -RT\ln(X_3)_p \quad (7)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (8)$$

ΔS: the molar entropy of DL − Malic acid in saturated solution

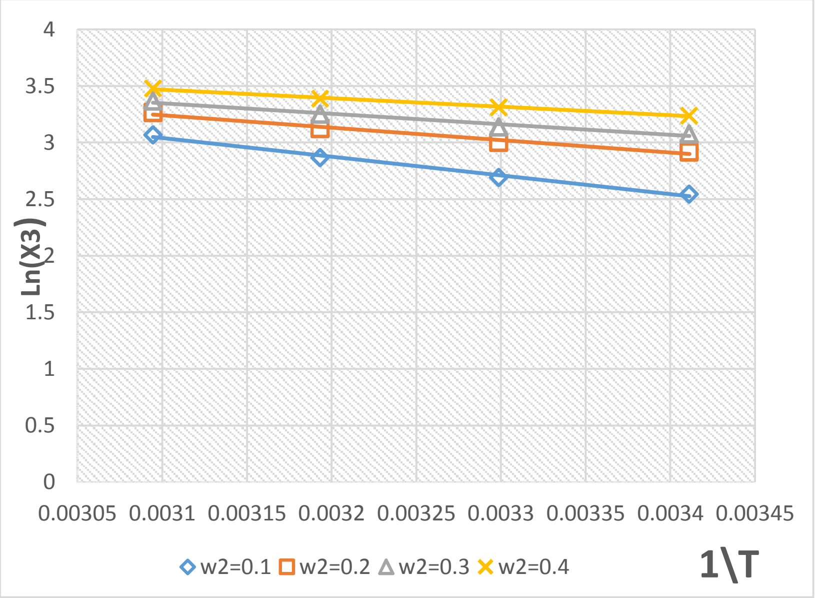

Fig. 5. A van't Hoff plot of the mole fraction solubility (ln X_3) of DL-Malic acid in binary (Water + THF) mixed solvent against (1/T)
w_2=0.1, w_2= 0.2, w_2=0.3, w_2=0.4

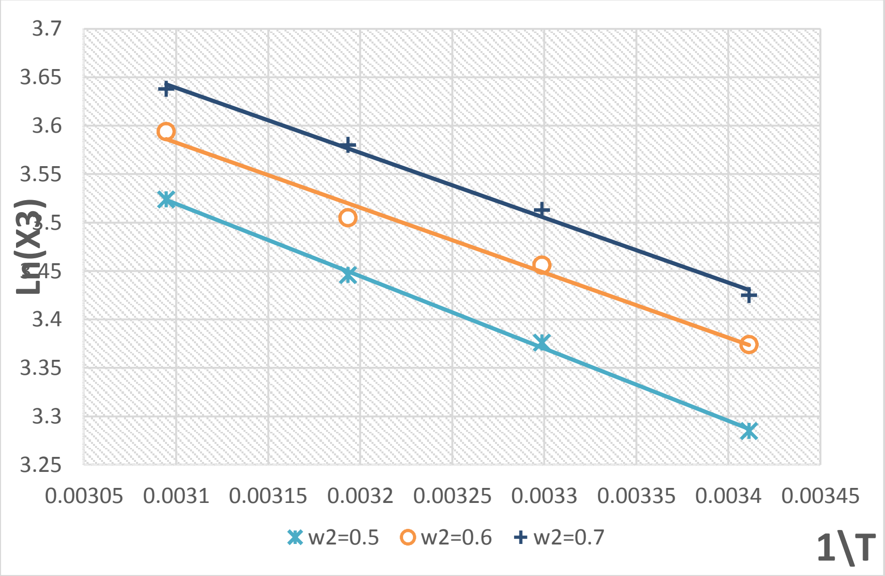

Fig. 6. A van't Hoff plot of the mole fraction solubility (ln X_3) of DL-Malic acid in binary (Water + THF) mixed solvent against (1/T)
w_2=0.5, w_2= 0.6, w_2=0.3, w_2=0.7

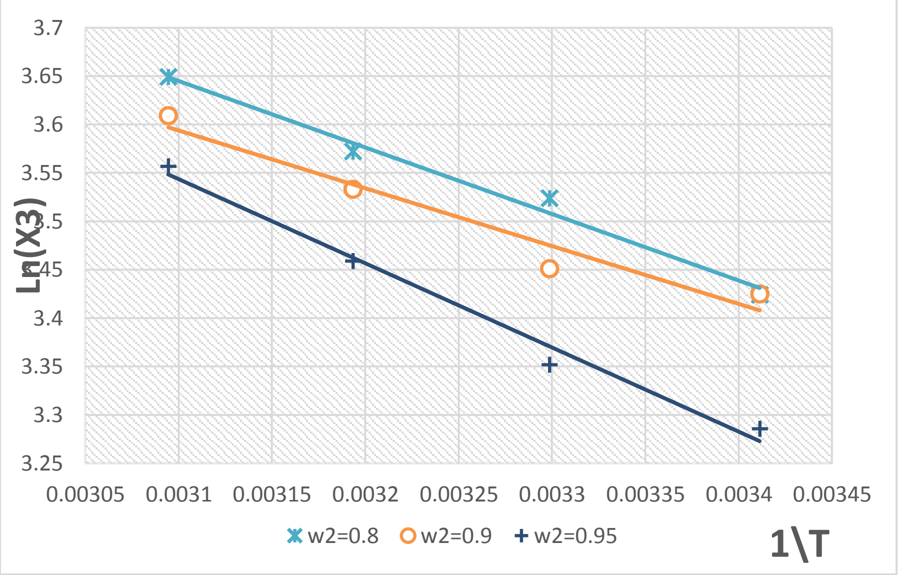

Fig. 7. A van't Hoff plot of the mole fraction solubility (ln X_3) of DL-Malic acid in binary (Water + THF) mixed solvent against (1/T)
w_2=0.8, w_2= 0.9, w_2=0.3, w_2=0.95

Table 7 Thermodynamic properties $(\Delta H, \Delta G)$ of the dissolution of {DL-Malic acid + Water+ THF} solvent mixtures

W_2	ΔH $(KJ.mol^{-1})$	$\Delta G_{293.15\,K}$ $(KJ.mol^{-1})$	$\Delta G_{303.15\,K}$ $(KJ.mol^{-1})$	$\Delta G_{313.15\,K}$ $(KJ.mol^{-1})$	$\Delta G_{323.15\,K}$ $(KJ.mol^{-1})$	R^2
0.1	13.737	5.022	4.827	4.527	4.128	0.989
0.2	9.14	4.113	4.041	3.859	3.599	0.979
0.3	7.75	3.729	3.696	3.526	3.328	0.977
0.4	6.249	3.333	3.259	3.171	3.045	0.993
0.5	6.201	3.218	3.097	3.019	2.906	0.998
0.6	5.577	3.001	2.896	2.863	2.716	0.987
0.7	5.572	2.876	2.754	2.727	2.598	0.995
0.8	5.703	2.88	2.726	2.69	2.57	0.986
0.9	4.964	2.877	2.91	2.793	2.675	0.950
0.95	7.225	3.214	3.157	2.983	2.816	0.986

Table 8 Thermodynamic properties (ΔS) of the dissolution of {DL-Malic acid + Water+ THF} solvent mixtures

W_2	$\Delta S_{293.15\ K}$ $(J.mol^{-1}.K^{-1})$	$\Delta S_{303.15\ K}$ $(J.mol^{-1}.K^{-1})$	$\Delta S_{313.15\ K}$ $(J.mol^{-1}.K^{-1})$	$\Delta S_{323.15\ K}$ $(J.mol^{-1}.K^{-1})$
0.1	29.729	29.391	29.411	29.735
0.2	17.148	16.820	16.864	17.147
0.3	13.717	13.373	13.489	13.684
0.4	9.947	9.863	9.829	9.915
0.5	10.176	10.239	10.161	10.197
0.6	8.787	8.844	8.667	8.853
0.7	9.197	9.296	9.085	9.203
0.8	9.63	9.820	9.622	9.695
0.9	7.119	6.776	6.933	7.083
0.95	13.682	13.419	13.546	13.644

Gibbs free energy shows a smooth change with increasing the mass fraction of THF in binary solvent mixtures. The positive entropy is usually observed for polar solutes and this is also observed in our case with dl-malic acid. According to the van't Hoff equation and the Gibbs equation, the thermodynamic properties for the solution process including Gibbs free energy, enthalpy, and entropy were obtained. Endothermic, and non-spontaneous, and entropy-driving were found overall to be the solution process for all the mixture selected.

4. Conclusion

Solubility data of DL-Malic acid in Water and + water were obtained at temperatures from 298.15 to 323.15 K by the acid–base titration method. The mass fraction solubility of DL-Malic acid in solvents increases with the increase of temperature and concentration of THF. Different dissolution and settling times were investigated and it was found that a much longer time has no effect on the solubility's in solvents. The equilibrium results consisted of solubility data and tie-lines were presented in ternary phase diagrams by Matlab program. The thermodynamic properties of solution enthalpy, entropy and Gibbs free energy change of solution is calculated by using the van't Hoff equation and Gibbs equation. The values of both the enthalpy change and the molar Gibbs free energy change of solution were positive which meaning that the dissolution of DL-malic acid into THF + water solvent mixtures is endothermic and non-spontaneous.

References

[1] Toumi A., Bouanz M., (2008)"**Volumetric and refractive index properties of iso butyric acid — water binary mixtures at temperatures ranging from 300.15 to 313.15 K**", Journal of Molecular Liquids, Tunisia 139 pp 55–60.

[2] Lima de Moura S., Aroldo Viana dos Santos J., Carlos Marques da Silva F.,(2013)"**Thermodynamic study of the liquid-liquid equilibrium water-chloroform-acetic acid**", Journal of Physical Chemistry, Brazil, pp 117-121.

[3] Daneshfar A., Baghlani M., Sadeghi Sarabi R., Sahraei R., Abassi S., (2012)" **Solubility of citric, malonic, and malic acids in different solvents from 303.2 to 333.2 K** "Journal of Fluid Phase Equilibria, Iran pp11-15.

[4] Zhang Q., Yang Y., Cheng L., Cao C., Ding Z., Wang C., Wenge Y., (2015)" **Thermodynamic models for determination of the solubility of DL-malic acid in methanol plus (acetonitrile, N, N-dimethyl form amide, isopropyl alcohol) binary solvent mixtures** "Journal of Chemical Thermodynamics 85 pp 148–154.

[5] Yuan Y., Leng Y., Wang J., Shao H., Huang C.,(2014)" **Solubility of dl-malic acid in water, ethanol and in mixtures of ethanol + water**" Journal of Fluid Phase Equilibria, China 377 pp 27-32.

[6] Kai Y., Hu Y., Cao Z., Liu X., Yang W.,(2013)" **Measurement and correlation solubility and mixing properties of l-malic acid in pure and mixed organic solvents**" Journal of Fluid Phase Equilibria, China 360 pp 466-471.

[7] Li Y.,Li C., Liu Y., Han S., Zhao H., (2017)"**Binary and ternary solid-liquid phase equilibrium for the systems formed by succinic acid, urea and diethylene glycol: determination and modelling",** Journal of Chemical Thermodynamics, China pp 1– 36.

[8] Li X., Wang M., Du C., Cong Y., Zhao H., (2017)" **Determination and correlation of solid-liquid phase equilibrium and phase diagram for multicomponent system of mixed dibasic acids. (IV)Quaternary system of (adipic acid + succinic acid + glutaric acid+ ethanol)**" Journal of Chemical Thermodynamics, China 110 pp 243– 251.

[9] http://www.ddbst.com/ddb.html.

[10] We D., Li, H., Nan Li Y., Cong Y., Zhu J., (2012)" **Effect of temperature on the solubility of 3-aminopyridine in binary ethanol + toluene solvent mixtures**" Journal of Fluid Phase Equilibria, China pp 132– 134.

[11] Noubigh A., jeribi C., Mgaidi A., Abderrabba M.,(2012)" ***Solubility of gallic acid in liquid mixtures of (ethanol + water) from (293.15 to 318.15) K***" Journal of Chemical Thermodynamics, Tunisia (2012) pp 75– 78.

[12] Ping Fan J., Yang D., Xu K._X., Guo X._J.,(2015)" ***Solubility of daidzin in different organic solvents and (ethyl alcohol + water) mixed solvents***" Journal of Chemical Thermodynamics, China pp 85– 89.

[13] Guo Q., Hu Y., Yang W. and et all. (2015)" Thermodynamic models for determination of the solubility of Omeprazole Sulfide in (ethanol + ethyl acetate) binary solvent mixtures" Journal of Fluid Phase Equilibria, China pp 1– 42.

[14] Wang H., Wang Q., Xiong Z., Chen C., Chen B., (2015)"***Solubility of benzoic acid in binary (benzyl alcohol + benzaldehyde) solvent mixtures***", Journal of Chemical Thermodynamics, China 83 pp 61– 66.