



SOLUBILITY, CORRELATION AND THERMODYNAMIC ANALYSIS OF GLUTARIC ACID IN PURE AND BINARY SOLVENT SYSTEM

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ABSTRACT

The solubility of Glutaric acid in pure water, 1-propanol and binary solvent (water + 1-propanol) was investigated 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 Apelblat and van't Hoff model was used to correlate the obtained solubility data and these models provide better correlation in this study. The molecular solute-solvent interactions were studied from the calculation of activity coefficients. Molecular simulation (DFT) was carried out to correlate solubility in the present study. van't Hoff equation was used to determine thermodynamic parameters (ΔH_{soln}^0 , ΔS_{soln}^0 , ΔG_{soln}^0 , % ζ H, and % ζ TS) of solution.

Keywords: Solubility, Glutaric acid, Apelblat equation, DFT

1. INTRODUCTION

In the production of plastics, dyes, surfactants, polyamides, and polyurethanes, particularly for the manufacture of pharmaceuticals, agricultural chemicals, synthetic rubbers, Glutaric acid is widely used as a raw material [1-3]. High purity glutaric acid can be obtained via crystallization from mixed dibasic acids. Therefore, it is important to separate and recover glutaric acid from the byproducts (mixed dibasic acid) [4]. Pure glutaric acid can be obtained by the method of repeated recrystallization from some common solvents, such as cyclohexanol, cyclohexanone, water, acetone, and so on. It is well-known that solid-liquid phase equilibrium data play an important role in the development and operation of crystallization processes [5]. Solubility is an important basic property of solid-liquid equilibrium (SLE) in the chemical industry. Such data are required for the proper design and optimization of various chemical processes [6].

However, the solubilities of glutaric acid are rarely available. Therefore solubilities of glutaric acid in water, 1-propanol and water + 1-propanol binary mixtures over different composition is determined at various temperatures and correlated by Apelblat and van't Hoff models. The activity coefficients are calculated to evaluate molecular solute-solvent interaction.

2. MATERIAL AND METHODS

In this study, triple distilled water was used. Glutaric Acid of purity 99.5% and 1-propanol of purity 99.9 % was supplied by MERCK. The method of solubility measurement has been used earlier [7-9]. In this work; an excess amount of glutaric 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 3 h) so that equilibrium is attained 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. 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 mole fraction solubility (X_b), initial the mole fraction of 1-propanol (X_C^0), and initial the mole

fraction of water (X_a^0) were calculated using usual Eq. 1 and 2.

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

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

Where m_b , m_a , and m_c are the mass of solute, water, ethanol respectively, and M_b , M_a , and M_c are the molecular weight of the solute, water, and 1-propanol, respectively.

2.1. Molecular simulation

Density functional theory (DFT) calculations were carried out using Gaussian 03 method [10, 11] to correlate solubilities variation in pure solvents. Geometry optimizations for all structures carried out at the B3LYP/6-311+ G (d, p) levels. After the geometries of all involving molecules were optimized at this level, the interaction energy E_{inter} was calculated as [12]:

$$E_{\text{inter}} = E_{\text{glu-sol}} - E_{\text{glu}} - E_{\text{sol}} \quad (3)$$

Where E_{glu} , E_{sol} , and $E_{\text{glu-sol}}$ are the total energies of glutaric acid, solvent and glutaric acid with each solvent, respectively.

Table 2. Mole fraction solubility X_b of glutaric acid in water + 1-propanol binary mixtures for various initial mole fractions (X_c^0) of 1-propanol

X_c^0	X_b								
	293.15	296.15	298.15	300.15	303.15	305.15	308.15	310.15	313.15
0.0000	0.1305	0.1448	0.1544	0.1547	0.1845	0.1819	0.1976	0.2015	0.2118
0.0285	0.1432	0.1543	0.1613	0.1837	0.1962	0.2121	0.2382	0.2521	0.2671
0.0620	0.1711	0.1946	0.1963	0.2044	0.2160	0.2246	0.2319	0.2484	0.2651
0.1018	0.1915	0.2193	0.2180	0.2029	0.2079	0.2148	0.2447	0.2631	0.2613
0.1498	0.2228	0.2309	0.2429	0.2529	0.2644	0.2725	0.2845	0.2775	0.2842
0.2091	0.2276	0.2140	0.2102	0.2101	0.2596	0.2556	0.2609	0.2671	0.2658
0.2839	0.2366	0.2404	0.2389	0.2397	0.2731	0.2781	0.2939	0.3055	0.3047
0.3815	0.2338	0.2379	0.2431	0.2460	0.2790	0.2845	0.2993	0.3121	0.3181
0.5140	0.2434	0.2509	0.2615	0.2657	0.2823	0.2975	0.3086	0.3264	0.3213
0.7041	0.2449	0.2450	0.2513	0.2600	0.2761	0.2856	0.3070	0.3094	0.3348
1.0000	0.2004	0.2099	0.2257	0.2378	0.2584	0.2619	0.2819	0.2938	0.3059
X^{idl}	0.2081	0.2230	0.2335	0.2444	0.2615	0.2735	0.2923	0.3055	0.3262

In order to find the relationships between the solubility, temperature and solvent composition, the graphs of corresponding mole fraction solubility against

3. RESULTS AND DISCUSSION

3.1. Experimental Reliability

To verify the reliability and accuracy of the experimental apparatus and method, the solubilities of glutaric acid in pure water were measured and compared with the literature data [13, 14] respectively. Our results agree well with the published data. Table 1 indicates the experimental apparatus and method used in this work is reliable.

Table 1: Comparison of Experimental Solubility of glutaric acid with Literature

Solvent	T/K	X_b	
		Expt.	Lit.
Water	293.15	0.1305	0.1385 ^a
	298.15	0.1544	0.1600 ^a 0.1789 ^b
	308.15	0.1976	0.2161 ^a
	313.15	0.2118	0.2493 ^a 0.2665 ^b

Where $a = [11]$, $b = [12]$

3.2. Solubility results

The measured solubility (X_b) data of glutaric acid in pure water, 1-propanol and water + 1-propanol binary mixtures at the nine temperatures ranging from (293.15 to 313.15) K is presented in Table 2.

temperature and initial mole fraction (X_c^0) of 1-propanol are presented in Fig.1 and 2. The Fig.1 shows that solubility of glutaric acid in pure and binary solvent increases with increasing temperature which indicates the

process of dissolution is endothermic. In case of pure solvents, solubility is found to be higher in 1-propanol than water and for binary solvent systems, solubility increases with increasing content of 1-propanol up to $X_C^0 = 0.5140$ at each experimental temperature.

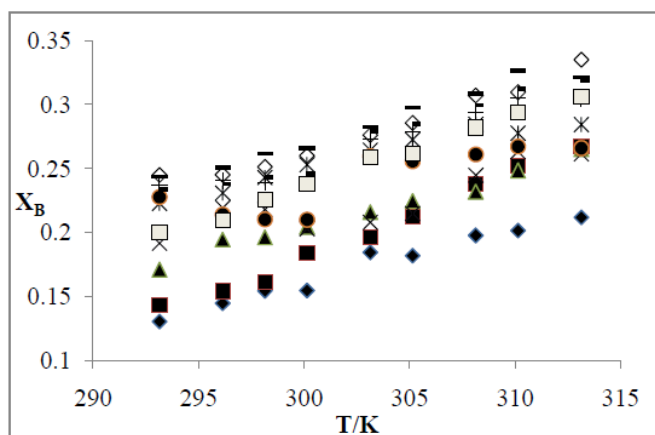


Fig.1: Mole fraction solubility (X_b) variation with Temperature at Initial mole fraction (X_C^0) of 1-propanol

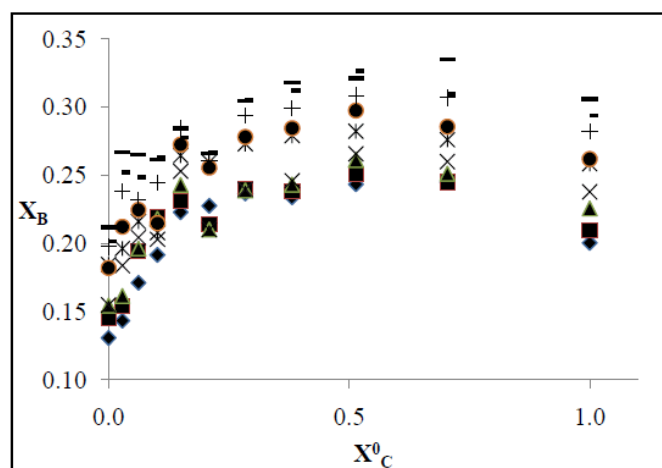
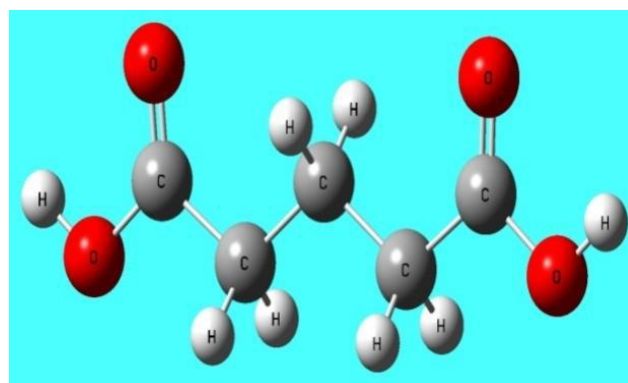
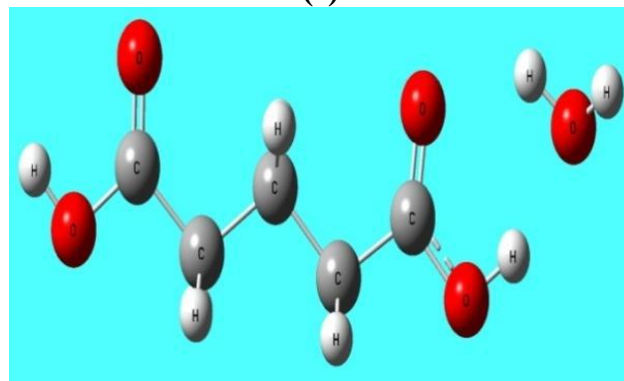


Fig.2: Mole fraction solubility (X_b) variation with Initial mole fraction (X_C^0) of 1- propanol at various temperatures.

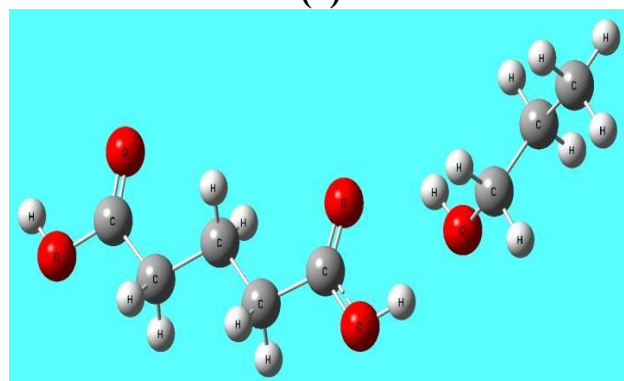
The minimum energy geometries of glutaric acid, glutaric acid + water, glutaric acid + 1-propanol are shown in Fig. 3. The order of absolute value of E_{inter} is 1-propanol (44.0947 KJ/mol) > water 43.3912). Means that larger the absolute value of interaction energy, stronger the interaction between solvent and solute molecule, and hence solute dissolve more easily in the corresponding solvents. This could be the one reason for higher solubility of glutaric acid in 1-propanol than pure water.



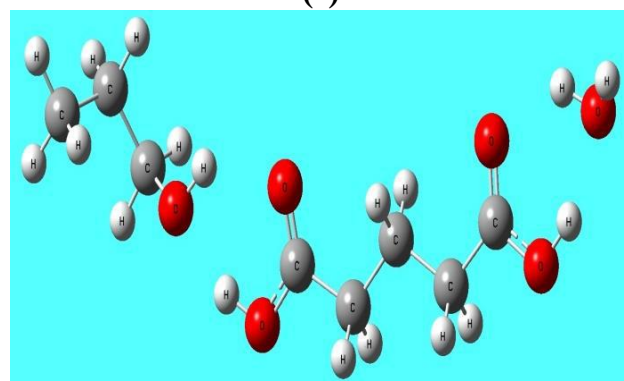
(a)



(b)



(c)



(d)

Fig. 3: Optimized structure of a) glutaric acid; b) glutaric acid + Water; c) glutaric acid + 1-propanol; d) glutaric acid +water + 1-propanol respectively.

3.3. Activity coefficients for Glutaric acid

Table 3 shows that the activity coefficients (γ) of glutaric acid at (293.15, 295.15, 298.15, 300.15, 303.15, 305.15, 308.15, and 313.15) K and in eleven cosolvent mixtures including pure solvents (water and 1-propanol). The (γ) values of glutaric acid in each solvent system are calculated using equation 4.

$$\gamma = \frac{X^{\text{idl}}}{X_b} \quad (4)$$

Where X^{idl} , the ideal solubility is calculated by using equation 5 and X_b is the experimental solubility.

$$\ln X^{\text{idl}} = \frac{-\Delta H_f(T_f - T)}{RT_f T} + \left(\frac{\Delta C_p}{R} \right) \left[\frac{T_f - T}{T} + \ln \left(\frac{T}{T_f} \right) \right] \quad (5)$$

Here R is universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and ΔC_p is difference in molar heat capacity of liquid state from that of crystalline state [15, 16]. The values of T_{fus} , ΔH_{fus} and ΔC_p for glutaric acid have reported in the

literature [17]. These values were used to calculate X^{idl} using equation 5 and results are listed in table 1.

The γ values for glutaric acid in each solvent system at $T = (293.15 \text{ to } 313.15) \text{ K}$ are summarized in Table 3.

It was observed a very little effect in the values of γ with temperature at each initial composition of 1-propanol. But the values of γ for glutaric acid were found to be decreases with the increase in concentration of 1-propanol in the solvent mixture at each experimental temperature. This trend of γ for glutaric acid were in good agreement with solubility results that the solubility of glutaric acid increases with mole fraction (X_C^0) of 1-propanol. Based on these results, for glutaric acid, higher solute-solvent molecular interactions were observed in water+ 1-propanol mixtures as compared to pure water as a solvent.

Table 3 Activity Coefficient (γ) of glutaric acid in water + ethanol binary mixtures at $T = (293.15 \text{ to } 313.15) \text{ K}$

X_C^0	T / K								
	293.15	296.15	298.15	300.15	303.15	305.15	308.15	310.15	313.15
0.0000	1.5940	1.5407	1.5121	1.5791	1.4175	1.5035	1.4792	1.5163	1.5400
0.0285	1.4532	1.4450	1.4471	1.3301	1.3329	1.2890	1.2271	1.2119	1.2213
0.0620	1.2165	1.1462	1.1897	1.1958	1.2104	1.2175	1.2605	1.2298	1.2306
0.1018	1.0865	1.0171	1.0710	1.2042	1.2576	1.2732	1.1947	1.1609	1.2480
0.1498	0.9341	0.9661	0.9613	0.9662	0.9890	1.0035	1.0276	1.1006	1.1475
0.2091	0.9141	1.0421	1.1110	1.1633	1.0071	1.0700	1.1203	1.1437	1.2269
0.2839	0.8795	0.9278	0.9774	1.0197	0.9574	0.9833	0.9947	1.0000	1.0705
0.3815	0.8899	0.9376	0.9606	0.9934	0.9371	0.9611	0.9765	0.9788	1.0252
0.5140	0.8549	0.8888	0.8930	0.9196	0.9263	0.9191	0.9473	0.9360	1.0152
0.7041	0.8496	0.9103	0.9292	0.9399	0.9473	0.9575	0.9522	0.9872	0.9741
1.0000	1.0385	1.0626	1.0346	1.0275	1.0120	1.0443	1.0370	1.0397	1.0663

3.4. Data Correlation

In pure and binary solvent system, experimental solubility data was correlated by Apelblat and van't Hoff model. The Modified Apelblat equation is a semi-empirical equation, which is widely used to correlate the solid-liquid equilibrium. In this work, the solubility of glutaric acid at different temperatures was described by the modified Apelblat equation [18]

$$\ln X_b = A + \frac{B}{T/K} + C \ln T/K \quad (6)$$

Where X_b and T are mole fraction of solute and absolute temperature, respectively and A, B, and C are empirical constants. The A and B reflecting the non-idealities of the real solution in terms of variation of activity coefficient in the solution, and C representing the effect of temperature on the fusion enthalpy [19, 20]. The experimental mole fraction solubility in Table 1 was correlated with equation 6 and the parameter values of A, B, and C is given in Table 4.

Table 4. Parameters of equation 6 for glutaric acid in water, ethanol and binary mixtures

X_c^0	A	B	C	R^2
0.0000	609.871	-29512.9	-89.9957	0.9770
0.0285	46.989	-4786.45	-5.74318	0.9907
0.0620	55.791	-4138.89	-7.64213	0.9785
0.1018	-833.20	36416.65	124.522	0.9857
0.1498	630.894	-29549.7	-93.5821	0.9792
0.2091	-306.732	12759.14	46.0621	0.9861
0.2839	-272.038	10995.46	41.0273	0.9181
0.3815	-158.824	5721.118	24.2630	0.9589
0.5140	77.748	-4807.57	-11.0508	0.9720
0.7041	-541.175	23063.71	81.1657	0.9870
1.0000	277.677	-14314.4	-40.5705	0.9933

The van't Hoff equation [21] is widely used to describe the relationship between solute and the temperature T/K considering the influence of the solvent as an ideal solution model, which can be described as:

$$\ln X_b = A + \frac{B}{T} \quad (7)$$

In this equation, the logarithm of solubility X_b is linear with the reciprocal of thermodynamic temperature. Where T represents the system temperature, and A and B are equation parameters. The values of correlation coefficient (R^2) for Apelblat equation (Table 4) and van't Hoff equation (Table 5) indicated that these equations fit quite well in pure and binary solvents.

Table 5. Parameters of equation 7 for glutaric acid in water, ethanol and binary mixtures

X_c^0	A	B	R^2
0.0000	5.6550	-2247	0.9640
0.0285	8.4300	-3046	0.9900
0.0620	4.4840	-1823	0.9780
0.1018	2.8250	-1309	0.7320
0.1498	2.5990	-1197	0.9330
0.2091	2.5210	-1196	0.6780
0.2839	3.4130	-1434	0.9120
0.3815	4.0740	-1629	0.9570
0.5140	3.5550	-1459	0.9710
0.7041	3.7590	-1526	0.9650
1.0000	5.2930	-2022	0.9900

3.5. Thermodynamic Analysis

To understand the thermodynamics involved in dissolution process of glutaric acid in pure and binary

solvents at temperature ranging from 293.15 to 313.15 K, the standard molar enthalpy change of solution ΔH_{soln}^0 , standard molar entropy change ΔS_{soln}^0 , and standard molar Gibbs energy change ΔG_{soln}^0 for the solution process are calculated according to van't Hoff equation [22, 23].

$$\Delta H_{sol}^0 = -R \left(\frac{\partial \ln x_b}{\partial (1/T)} \right) = -R \left[\frac{\partial \ln x_b}{\partial \left(\frac{1}{T} - \frac{1}{T_{mean}} \right)} \right] \quad (8)$$

$$\Delta G_{soln}^0 = -R \cdot T \times \text{intercept} \quad (9)$$

$$\Delta S_{soln}^0 = \frac{\Delta H_{soln}^0 - \Delta G_{soln}^0}{T_{mean}} \quad (10)$$

In equation 8, T_{mean} is the mean harmonic temperature i.e. $T_{mean} = 303.03$ K. The slope and the intercept of the plot $\ln X_b$ vs. $(1/T - 1/T_{mean})$ for each solvent and binary mixture are listed in Table 6 and the plots $\ln X_b$ vs. $(1/T - 1/T_{mean})$ for glutaric acid at studied temperature are linear as shown in Fig. 4. In addition, the values of % ζ H and % ζ TS are also calculated by using following equations 11.

$$\begin{aligned} \% \zeta H &= \frac{\Delta H_{soln}^0}{|\Delta H_{soln}^0| + |T \Delta G_{soln}^0|} \times 100 \\ \% \zeta TS &= \frac{|T \Delta G_{soln}^0|}{|\Delta H_{soln}^0| + |T \Delta G_{soln}^0|} \times 100 \end{aligned} \quad (11)$$

The values of % ζ H and % ζ TS could be used to evaluate the effect of enthalpy and entropy to Gibbs energy in solution process. The calculated thermodynamic parameters (ΔH_{soln}^0 , ΔS_{soln}^0 , ΔG_{soln}^0 , % ζ H, and % ζ TS) in pure and binary solvents mixtures are shown in Table 8. It is observed that the values of (ΔH_{soln}^0 , ΔS_{soln}^0 ,

ΔG_{soln}^0) are all positive which indicates that solution process is endothermic and entropy-driven. $\Delta H_{\text{soln}}^0 > \Delta S_{\text{soln}}^0$ suggest that more energy is required to overcome the forces between solvent and solute in solution process [24, 25]. Table 8 also shows that $\zeta H\% >$

$\zeta TS\%$, which indicates main contributor to the positive standard molar Gibbs energy ΔG_{soln}^0 of solution of glutaric acid is the enthalpy during dissolution.

Table 6. Thermodynamic parameters Relative to dissolution Process of glutaric acid at $T_{\text{mean}} = 303.15$ K

X_C^0	Slope	Intercept	R^2	$\Delta H_{\text{soln}}^0 /$ kJK ⁻¹ mol ⁻¹	$\Delta G_{\text{soln}}^0 /$ kJK ⁻¹ mol ⁻¹	$\Delta S_{\text{soln}}^0 /$ kJK ⁻¹ mol ⁻¹	$T\Delta S_{\text{soln}}^0 /$ kJK ⁻¹ mol ⁻¹	$\zeta H\%$	$\zeta TS\%$
0.0000	-2155.5	-1.7662	0.9472	17.9208	4.4499	0.0445	13.4709	57.0877	42.9123
0.0285	-3046.5	-1.6226	0.9908	25.3286	4.0881	0.0701	21.2405	54.3893	45.6107
0.0620	-1823.6	-1.5337	0.9785	15.1614	3.8641	0.0373	11.2973	57.3021	42.6979
0.1018	-1309.6	-1.4961	0.9321	10.8880	3.7694	0.0235	7.1186	60.4666	39.5334
0.1498	-1197.4	-1.3521	0.9331	9.9552	3.4066	0.0216	6.5486	60.3206	39.6794
0.2091	-1196.1	-1.4253	0.9678	9.9444	3.5910	0.0210	6.3534	61.0168	38.9832
0.2839	-1434.4	-1.3206	0.9121	11.9256	3.3272	0.0284	8.5984	58.1057	41.8943
0.3815	-1629.8	-1.3038	0.9573	13.5502	3.2849	0.0339	10.2653	56.8965	43.1035
0.5140	-1459.5	-1.2613	0.9716	12.1343	3.1778	0.0296	8.9565	57.5336	42.4664
0.7041	-1526.8	-1.2789	0.9650	12.6938	3.2221	0.0313	9.4717	57.2684	42.7316
1.0000	-2022.9	-1.3818	0.9901	16.8184	3.4814	0.0440	13.3370	55.7724	44.2276

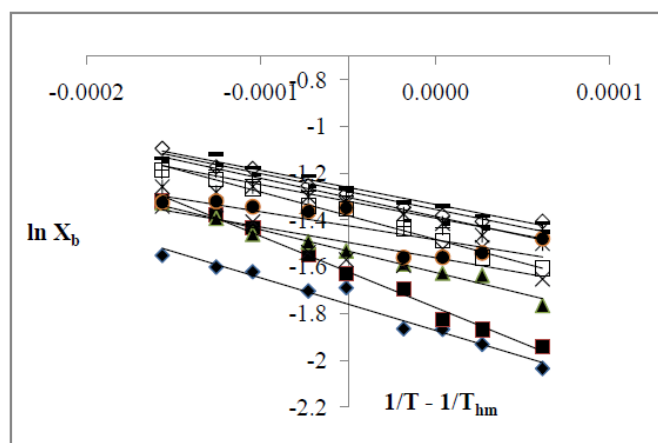


Fig. 4: Plot of $\ln X_B$ vs $(1/T - 1/T_{hm})$ for Glutaric acid + water + 1-propanol at various mole fractions

4. CONCLUSION

The solubility of Glutaric acid in pure water, 1-propanol and binary solvent (water + 1-propanol) was investigated 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 solubility of glutaric acid in pure and binary solvent is found to be increases with increasing temperature. In case of pure solvents, solubility is found to be higher in 1-

propanol than water and for binary solvent systems, solubility increases with increasing content of 1-propanol up to $X_C^0 = 0.5140$ at each experimental temperature. Based on γ values for glutaric acid, higher solute-solvent molecular interactions were observed in water+ 1-propanol mixtures as compared to pure water as a solvent. The values of correlation coefficient (R^2) for Apelblat equation and van't Hoff equation indicated that these equations fit quite well in pure and binary solvents. The values of (ΔH_{soln}^0 , ΔS_{soln}^0 , ΔG_{soln}^0) are all positive which indicates that solution process is endothermic and entropy-driven. $\zeta H\% > \zeta TS\%$, which indicates main contributor to the positive standard molar Gibbs energy ΔG_{soln}^0 of solution of glutaric acid is the enthalpy during dissolution.

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