

# SOLUBILITY, SOLUTION THERMODYNAMICS AND DFT STUDY OF GLUTARIC ACID IN WATER, METHANOL AND THEIR BINARY MIXTURES AT VARIOUS TEMPERATURES

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## ABSTRACT

The solubility of Glutaric acid in water, methanol and water + methanol binary solvent was measured over the different composition range between 0 to 1 weight fraction of methanol 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 Apelblat equation and the correlated solubilities data were in good accord with the experimental data. DFT study was carried out to correlate solubility in various solvents. Thermodynamic functions were calculated using van't Hoff equation.

**Key Words:** Solubility, Glutaric acid, Apelblat equation, DFT

## 1. INTRODUCTION

Glutaric acid is an important chemical raw material which is widely used in the production of plastics, dyes, surfactants, polyamides, and polyurethanes, particularly for the manufacture of pharmaceuticals, agricultural chemicals, synthetic rubbers, and so forth [1–3]. In industrial manufacturing processes, glutaric acid can be obtained via crystallization from mixed dibasic acids. So, it is difficult to obtain high purity glutaric acid. 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, methanol and water + methanol binary mixtures over different composition is determined at various temperatures and correlated by Apelblat equation

## 2. EXPERIMENTAL

### 2.1 Materials and Apparatus:

In all experiments, triple distilled water was used. Glutaric Acid was supplied by MERCK with purity 99.5% and Methanol 99.9 % was supplied by Jiangyin Huaxi International Trade Co. (China). The apparatus and procedures used for solubility and density measurement have been described earlier in detail [7–9]. Briefly 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  $\pm 0.1$  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 ( $\pm 0.1$ ) 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 ( $X_C^0$ ), and initial the mole fraction of water ( $X_A^0$ ) were calculated using usual Eq. 1 and 2:

$$X_b = (m_b / M_b) / (m_b / M_b + m_A / M_A + m_C / M_C) \quad (1)$$

$$X_C^0 = (m_C / M_C) / (m_A / M_A + m_C / M_C) \text{ and } X_A^0 = (m_A / M_A) / (m_A / M_A + m_C / M_C) \quad (2)$$

Where  $m_B$ ,  $m_A$ , and  $m_C$  are the mass of solute, water, methanol respectively, and  $M_b$ ,  $M_A$ , and  $M_C$  are the molecular weight of the solute, water, and methanol, respectively.

## 2.2 Computational Method:-

Density functional theory (DFT) calculations were carried out using Gaussian 03 method to correlate different solubilities. 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 defined as [10]:

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

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

## 3. RESULTS AND DISCUSSION

### 3.1 Solubility Data:

The experimental values of solubility ( $X_B$ ) of glutaric acid in water, methanol and water + methanol mixtures at (293.15, 296.15, 298.15, 300.15, 303.15, 305.15, 308.15, 310.15 and 313.15) K is listed in Table 1. The results shows that the solubility of glutaric acid in water, methanol and water + methanol mixtures increases with temperature at given initial compositions (Fig.1). But solvent composition has different effect on solubilities of glutaric acid (Fig. 2). The solubilities of the glutaric acid in water, methanol and water + methanol mixtures increases with increasing mole fraction ( $X_C^0$ ) of methanol upto ( $X_C^0 = 0.8349$ ). But solubility of glutaric acid in pure methanol was found to be less than the solubilities at ( $X_C^0 = 0.622$  and  $0.8349$ ). The solid-liquid equilibrium system of glutaric acid in water + methanol shows maximum solubility effect at ( $X_C^0 = 0.8349$ ). This means that solvent-solute interactions are higher at ( $X_C^0 = 0.8349$ ). The solubility of glutaric acid is higher in pure methanol than water indicates polarity of solvent has no effect on solubility. This can be explained from interaction energy  $E_{inter}$  between glutaric acid and pure solvents (Water and methanol) calculated by DFT.

The minimum energy geometries of glutaric acid, glutaric acid + water, glutaric acid + methanol are shown in Fig. 3 and Fig. 4. The order of absolute value of  $E_{inter}$  is methanol (44.457 KJ/mol) > water 43.3912). This result justifies the experimental solubility trend. 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.

Table 1. Mole fraction solubility  $X_b$  of glutaric acid in water + methanol binary mixtures for various initial mole fractions ( $X_C^0$ ) of methanol.

$X_C^0$	$X_b$								
	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	0.1915	0.2118
0.0588	0.1438	0.1627	0.1705	0.1630	0.1850	0.2167	0.2273	0.2664	0.2367
0.1232	0.1426	0.1640	0.1813	0.1973	0.2129	0.2267	0.2427	0.2549	0.2778
0.1942	0.1726	0.1904	0.1850	0.2107	0.2304	0.2384	0.2590	0.2737	0.2908
0.2726	0.1866	0.2042	0.2128	0.2248	0.2386	0.2505	0.2757	0.2825	0.3006
0.3599	0.2188	0.2095	0.2244	0.2328	0.2536	0.2650	0.2779	0.2898	0.3204
0.4575	0.2093	0.2293	0.2340	0.2464	0.2564	0.2747	0.2876	0.3057	0.3196
0.5675	0.2163	0.2302	0.2413	0.2438	0.2628	0.2743	0.2926	0.3070	0.3300
0.6922	0.2764	0.2815	0.2969	0.3094	0.3177	0.3263	0.3448	0.3494	0.3692
0.8350	0.2822	0.2905	0.3045	0.3109	0.3245	0.3372	0.3491	0.3589	0.3769
1.0000	0.2341	0.2459	0.2579	0.2666	0.2928	0.2961	0.3108	0.3251	0.3526

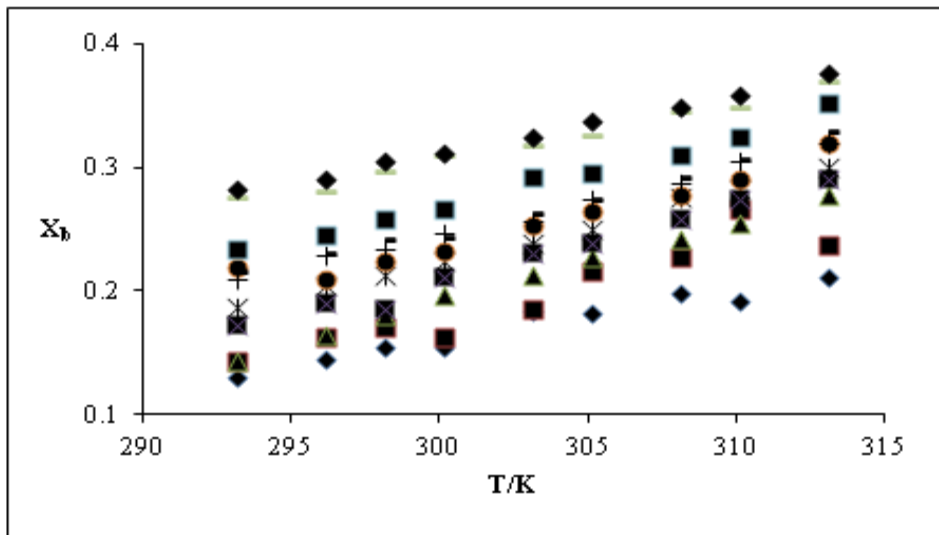


Fig.1 Mole fraction solubility ( $X_b$ ) variation with temperatures.

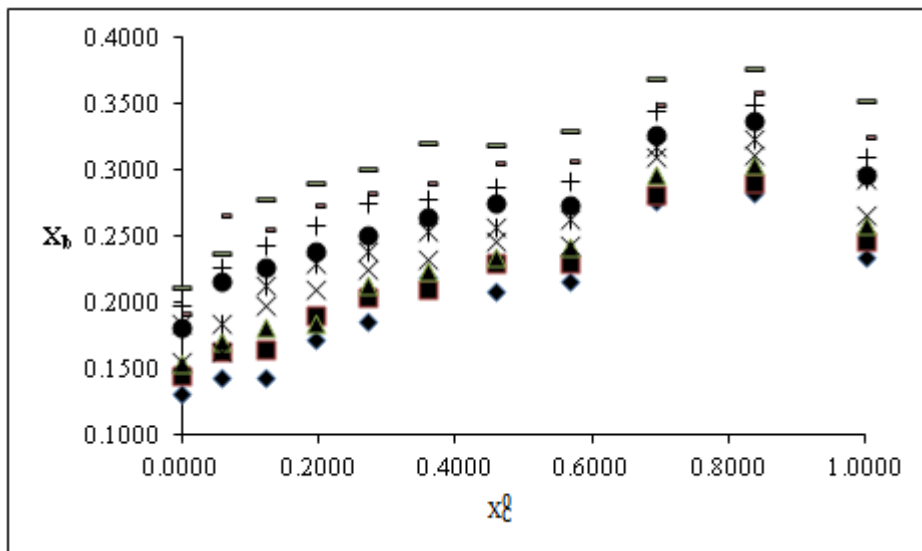


Fig.2 Mole fraction solubility ( $X_B$ ) variation with initial mole fraction ( $X_C^0$ ) of methanol at temperatures

### 3.2 Correlation of Experimental Data:

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 [11]

$$\ln X_b = A + \frac{B}{T/K} + C \ln T/K \tag{4}$$

Where  $X_b$  and  $T$  are mole fraction of solute and absolute temperature, respectively and  $A$ ,  $B$ , and  $C$  are empirical constants. The experimental mole fraction solubility in Table 1 was correlated with eq. 3 and the parameter values of  $A$ ,  $B$ , and  $C$  is given in Table 2.

Table 2. Parameters of equation 3 for glutaric acid in water, methanol and binary mixtures

$X_c^0$	A	B	C	$R^2$
0.0000	663.06	-31835	-97.964	0.9630
0.0588	126.72	-8092	-17.791	0.9002
0.1232	824.59	-39785	-121.60	0.9964
0.1942	-5.4233	-1933.3	1.8048	0.9805
0.2726	81.145	-5593.1	-11.220	0.9968
0.3599	-697.22	29782	104.57	0.9718
0.4575	-29.825	-349.36	5.1862	0.9931
0.5675	-310.97	12346	47.059	0.9971
0.6922	-31.112	207.87	5.1245	0.9892
0.8350	-59.057	1474.7	9.2871	0.9966
1.0000	-97.617	2777.6	15.260	0.9914

### 3.3 Solution Thermodynamics:-

Thermodynamics involved in the solution process of solute in various solvents can be understood from thermodynamics functions. In this work the thermodynamic functions in the process of solution of glutaric acid are calculated on the basis of the solubility of glutaric acid. According to the van't Hoff equation [12, 13], the standard molar enthalpy change of solution  $\Delta H_{soln}^0$  is generally obtained from the slope of the  $\ln X_b$  vs.  $1/T$  plot. In the present work,  $T_{mean} = 303.03$  K and a limited temperature range is 293.15 to 313.15 K in both pure solvents and binary solvent mixtures. The values of  $\Delta H_{soln}^0$  are derived using usual Eq 4:

$$\Delta H_{soln}^0 = -R \left( \frac{\partial \ln x_b}{\partial (1/T)} \right) = -R \left[ \frac{\partial \ln x_b}{\partial \left( \frac{1}{T} - \frac{1}{T_{mean}} \right)} \right] \quad (4)$$

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 3. The standard molar Gibbs energy change for the solution process  $\Delta G_{soln}^0$ , can be calculated by Eq. 5:

$$\Delta G_{soln}^0 = -R \cdot T \times \text{intercept} \quad (5)$$

The standard molar entropy change  $\Delta S_{soln}^0$  is obtained from Eq.6:

$$\Delta S_{soln}^0 = \frac{\Delta H_{soln}^0 - \Delta G_{soln}^0}{T_{mean}} \quad (6)$$

Both  $\Delta G_{soln}^0$  and  $\Delta S_{soln}^0$  pertain to the mean temperature  $T_{mean} = 303.03$  K. The results are shown in Table 3, together with  $\% \zeta_H$  and  $\% \zeta_{TS}$ . The  $\% \zeta_H$  and  $\% \zeta_{TS}$  represent the comparison of the relative contributions by enthalpy and entropy respectively, which are calculated by Eq. 7  $\% \zeta_H = \frac{\Delta H_{soln}^0}{|\Delta H_{soln}^0| + |T \Delta G_{soln}^0|} \times 100$  And

$$\% \zeta_{TS} = \frac{|T \Delta G_{soln}^0|}{|\Delta H_{soln}^0| + |T \Delta G_{soln}^0|} \times 100 \quad (7)$$

Table 3. Thermodynamic Functions Relative to Solution Process of glutaric acid at  $T_{\text{mean}} = 303.15 \text{ K}$ 

$X_C^0$	slope	intercept	$R^2$	$\Delta H_{\text{soln}}^0 / \text{kJK}^{-1}\text{mol}^{-1}$	$\Delta G_{\text{soln}}^0 / \text{kJK}^{-1}\text{mol}^{-1}$	$\Delta S_{\text{soln}}^0 / \text{kJK}^{-1}\text{mol}^{-1}$	$T\Delta S_{\text{soln}}^0 / \text{kJK}^{-1}\text{mol}^{-1}$	$\zeta_H\%$	$\zeta_{TS}\%$
0.0000	-2155	-1.7660	0.9470	17.9167	4.4494	0.0444	13.4673	57.0886	42.9114
0.0588	-2701	-1.6400	0.9890	22.4561	4.1319	0.0605	18.3242	55.0661	44.9339
0.1232	-2942	-1.5710	0.9820	24.4598	3.9581	0.0677	20.5017	54.4016	45.5984
0.1942	-2480	-1.4900	0.9800	20.6187	3.7540	0.0557	16.8647	55.0076	44.9924
0.2726	-2193	-1.4270	0.9960	18.2326	3.5953	0.0483	14.6373	55.4689	44.5311
0.3599	-1901	-1.3740	0.9480	15.8049	3.4617	0.0407	12.3432	56.1492	43.8508
0.4575	-1920	-1.3430	0.9930	15.9629	3.3836	0.0415	12.5792	55.9275	44.0725
0.5675	-1911	-1.3280	0.9920	15.8881	3.3459	0.0414	12.5422	55.8843	44.1157
0.6922	-1344	-1.1440	0.9890	11.1740	2.8823	0.0274	8.2917	57.4034	42.5966
0.8350	-1338	-1.1230	0.9960	11.1241	2.8294	0.0274	8.2948	57.2851	42.7149
1.0000	-1845	-1.2540	0.9900	15.3393	3.1594	0.0402	12.1799	55.7404	44.2596

Table 3 shows that the standard Gibbs free energy  $\Delta G_{\text{soln}}^0$  of glutaric acid is positive in the studied pure and binary solvents suggest spontaneous dissolution of compound. The positive enthalpy  $\Delta H_{\text{soln}}^0$  indicates dissolution of glutaric acid in water, methanol and binary mixture is endothermic process. In this work, the entropy of solution is positive for all mole fraction of methanol indicating the entropy as driving the solution process. It is observed that the main contributor to the positive standard molar Gibbs energy  $\Delta G_{\text{soln}}^0$  of solution of glutaric acid is the enthalpy during dissolution because the values of  $\% \zeta_H$  are greater than 50%.

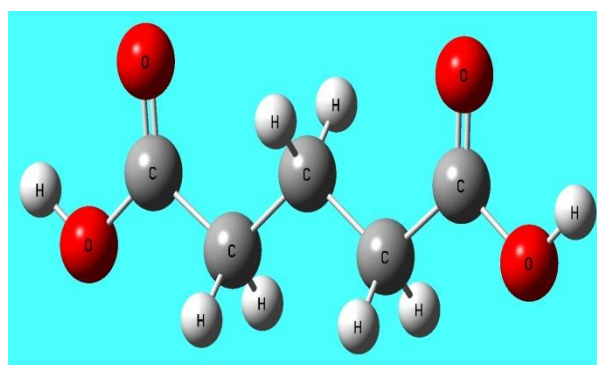
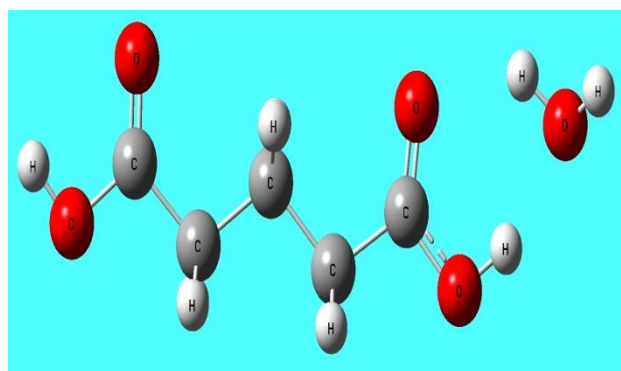
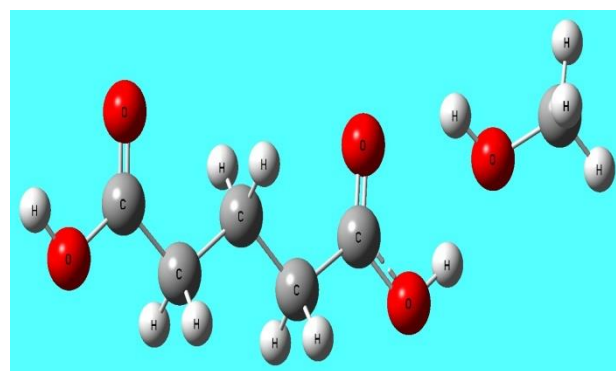


Fig. 3 Optimized structure of glutaric acid



a)



b)

Fig.4) Interaction between glutaric acid and water (a), methanol respectively

#### 4. Conclusions

Solubility of the glutaric acid in water, methanol and water + methanol mixture increases with increase in temperature at given initial composition. The solubilities of the glutaric acid in water, methanol and water + methanol mixtures increases with increasing mole fraction ( $X_C^0$ ) of methanol upto ( $X_C^0 = 0.8349$ ). The solid-liquid equilibrium system of glutaric acid in water + methanol shows maximum solubility effect at ( $X_C^0 = 0.8349$ ). This means that solvent-solute interactions are higher in water + methanol mixtures. The experimental data are very well correlated by the Apelblat equation. The positive enthalpy and Gibb's free energy of dissolution suggest endothermic and spontaneous dissolution of glutaric acid in all the studied solvents respectively. For all mole fractions ( $X_C^0$ ) of methanol, the main contributor to the positive standard molar Gibbs energy of solution of Glutaric acid is the enthalpy. Computational studies based on density functional theory (DFT) were used to explain the solubility between water and methanol.

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