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Pimelic Acid Solubility in Pure and Mixed Solvent (Water + Methanol): Experimental Data, Correlation and Thermodynamic Analysis

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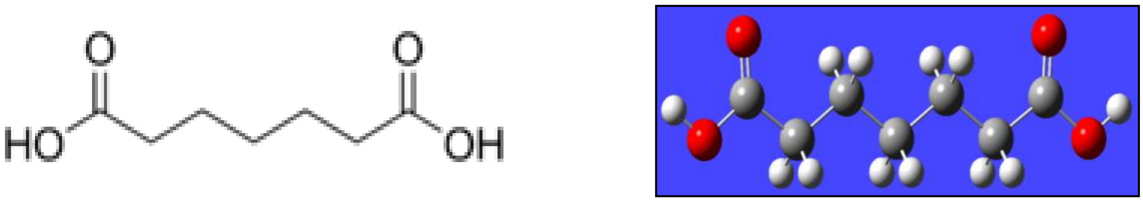
ABSTRACT

In this study, mole fraction solubility of pimelic acid (PA) in pure water, methanol and their binary solvent mixture at atmosperic pressure from T = (293.15 – 313.15) K was determined by gravimteric method. The correlation of solubility data was performed with van't Hoff and modified Apelblat model. Likewise, the thermodynamic parameters of pimelic acid in the corresponding solvent systems were determined and the results demonstrated that the procedure for the dissolution in the pure and mixed solvent is endothermic. DFT was carried out to correlate solubility in various solvents system. The experimental solubility and calculated solubility can be usefully applied to the final crystallization and/or purification process of PA synthesis and to pharmaceutical formulation development of PA.

KEYWORDS: Solubility, Pimelic acid, Apelblat equation, DFT.

INTRODUCTION

Pimelic acid (PA) [1,7-heptanedioic acid, $(CH_2)_5(COOH)_2$, molar mass: 160.17 g mol^{-1}, CAS:11-16-0 as shown in Fig.1)] is an important raw material in chemical and pharmaceutical industry. It is also used as intermediate for manufacturing medicines[1]. It is always used for biochemical studies; some of them have a variety of uses in synthesis[2]. Pimelic acid is also used as a raw material for the synthesis of 1,7-Heptanediol which is an important chemical widely used in the synthesis pharmaceuticals, surfactants, flavors, and cosmetics[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 pimelic acid in pure water, methanol and their binary mixtures over different composition were determined at various temperatures. The experimental solubility data were correlated by using Apelblat and van't Hoff model. Thermodynamic properties (ΔH^0_{soln}, ΔS^0_{soln}, ΔG^0_{soln}, %ζH, %ζTS) of the solutions were calculated by using van't Hoff equation.



(a) (b)

Fig.1 Chemical Structure of pimelic acid (PA) (a) three dimensional structure (b)

EXPERIMENTAL

Pimelic Acid (99%) was obtained from sigma Aldrich. Methanol (99.8%) was 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 pimelic 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:

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

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

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

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 PA with water and alcohols are determined.

RESULTS AND DISCUSSION

Solubility of Pimelic Acid (PA): The results of mole fraction solubility (X_b) of PA in pure water and methanol within the temperature range 293.15 K to 313.15 K are listed in Table 1 and shown graphically in Figure 2. It can be seen that solubility of PA in pure solvents found to increase with the increase in temperature. Solubility is found to be higher in methanol than water.

The values of measured mole fraction solubilities (X_b) of PA in water + methanol are also summerized in Table 2 along with calculated solubilities by using different correlating models. Also the variation of solubility of PA with initial mole fraction of methanol (X_C^0) and temperature is shown in Fig. 3 and 4 respectively. As a results from Tables 2 and Fig. 3 and 4 that solubility of PA in studied binary system found to be increase with the initial mole fraction of methanol (X_C^0) and temperature.

Solubility Correlation

i) Modified Apelblat model: Among the different methods, the modified semi-empirical Apelblat model[9] including three parameters (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.

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

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, methanol 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 listed in Table 3.

ii) 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

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

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.

3.3 Thermodynamic parameters of dissolution: The thermodynamic dissolution process of pimelic acid in pure and binary solvent mixture 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 (Table 5) are calculated according to van’t Hoff equation[13, 14].

$$\Delta H^0_{sol} = -R\left(\frac{\partial \ln x_b}{\partial(1/T)}\right) = -R\left[\frac{\partial \ln x_b}{\partial\left(\frac{1}{T}-\frac{1}{T_{mean}}\right)}\right] \quad (5)$$

$$\Delta G^0_{soln} = -R.T \times \text{intercept} \quad (6)$$

$$\Delta S^0_{soln} = \frac{\Delta H^0_{soln} - \Delta G^0_{soln}}{T_{mean}} \quad (7)$$

In Eq. 5, T_{mean} is the mean harmonic temperature i.e. T_{mean} = 303.03 K. In addition, the relative contribution of enthalpy (%ζH) and entropy (%ζTS) were calculated by using following Eq. 8. The values of %ζH and %ζTS could be used to evaluate the effect of enthalpy and entropy to Gibbs energy in solution process

$$\%\zeta H = \frac{\Delta H^0_{soln}}{|\Delta H^0_{soln}|+|T\Delta G^0_{soln}|} \times 100 \quad \text{and} \quad \%\zeta TS = \frac{|T\Delta G^0_{soln}|}{|\Delta H^0_{soln}|+|T\Delta G^0_{soln}|} \times 100 \quad (8)$$

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 5.

The ΔH^0_{soln}values for dissolution of PA in all mixtures are all positive indicating that dissolution process of PA in all mixtures is endothermic. The ΔH^0_{soln}value in pure water is 39.0425 $KJK^{-1}mol^{-1}$and in methanol is 16.1674 $KJK^{-1}mol^{-1}$. This indicates that more energy is required for the dissolution of PA in water as compared to dissolution of PA in methanol. The value of ΔG^0_{soln} and ΔS^0_{soln} are positive, which means the dissolution process occurs with an increase of entropy and process is non-spontaneous. Table 5 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 PA. Overall the dissolution of PA in all binary solvent mixtures is enthalpy driven endothermic process.

DFT study: The optimized structures and theoretical IR of PA + water and PA + methanol are shown in Figure 5 and 6-8 respectivly. 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 PA with water and methanol are determined. These properties are listed in Table 6.

Table 6 shows that the bond distance of carboxylic –OH group of PA increases when the molecule combines with water and methanol. The trend for carboxylic (-OH) bond distance of PA in pure solvents is: PAM (0.9908 Å) > PAW (0.9863 Å) which correlates the solubility order of PA in pure solvents. Fig. 5 shows that intermolecular interactions and H-bonding between PA and solvent molcules. H-bonding is formed in all cases with different intermolecular distances. For PAW and PAM complexs, carboxylic acid group in PA 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 PA and one O atom from solvent (-H---O-) is PAM (1.7601 Å) < PAW (1.8058 Å). The order for second intermolecular H-bond distance (Å) between one O atom of carboxylic group of PA and one H atom from solvent (-O---H-) is PAM (1.9917 Å) < PAW (2.0414 Å).

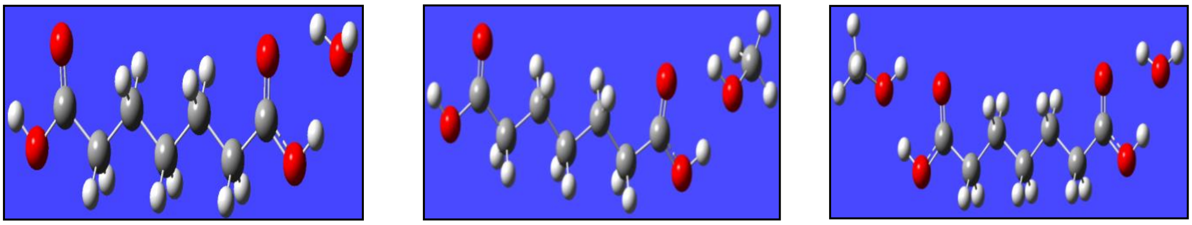

(a) (b) (c)

Fig 5. Optimized structure of a) PA + Water b) PA + methanol and c) MA + water + methanol

Similarly solubility trend of PA in pure solvents can be explained by using theoretically computed stretching fequency of –OH in carboxylic group of PA as presented in Table 6 and graphically shown in Figure 6. From these data, it is seen that υ-OH of PA is 3758.60 cm^{-1} which is very large as compared to υ-OH of PA with its solvent combinations. Higher value υ-OH means –OH group is free or less associated. The υ-OH of PA in PAW combination is 3419.28 cm^{-1} which slighlty higher than υ-OH of PA in PAM (3330.44 cm^{-1}) combination. This confirms the effect of H-bonding on the υ-OH of PA which explains that solubility of PA in water is low as compared to that of in methanol.

CONCLUSION

Solubility of PA in pure solvents found to increase with the increase in experimental temperature. Solubility is found to be higher in methanol than water. Solubilities of PA in all studied binary system increases with the initial mole fraction of methanol (X_C^0) and temperature. The measured solubilities of PA are well correlated with temperature by Apelblat and van't Hoff model. Thermodynamic study from measured solubilities of PA indicates that dissolution of PA 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 PA. In addition, DFT study provides important data which indicates that solubility of PA is also depends on H-bonding between solute and solvent. The theoretical IR study is useful to explain the solubility of PA in pure and binary solvent mixtures.

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Table 1: - Experimental X_b value of mole fraction solubility of PA in pure water and methanol at T = (293.15 - 313.15 K).

T/K	X_b	
	Water	Methanol
293.15	0.0044	0.1338
296.15	0.0053	0.1335
298.15	0.0058	0.1439
300.15	0.0066	0.1543
303.15	0.0077	0.1608
305.15	0.0093	0.1673
308.15	0.0095	0.1795
310.15	0.0109	0.1873
313.15	0.0120	0.1990

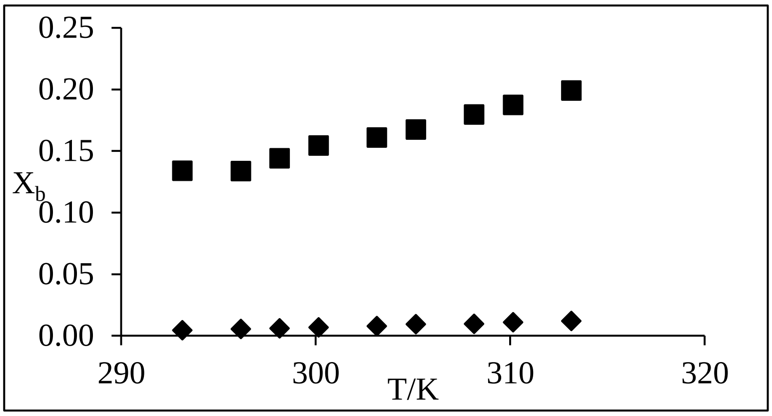


Fig.2. Mole fraction solubility (X_b) variation with temperatures for water (◆), methanol (■)

Table 2 Experimental (X_b) and calculated mole fraction solubility of PA in various initial mole fraction X_C^0 of methanol at T= 293.15 to 313.15 K

PA+ Water + Methanol								
T/K	X_C^0	X_b^{Expt}	X_b^{Apel}	$X_b^{van't}$	T/K	X_b^{Expt}	X_b^{Apel}	$X_b^{van't}$
293.15	0.0000	0.0044	0.0043	0.0045	296.15	0.0053	0.0053	0.0053
	0.0588	0.0063	0.0062	0.0062		0.0074	0.0075	0.0075
	0.1232	0.0099	0.0095	0.0099		0.0110	0.0125	0.0125
	0.1942	0.0156	0.0156	0.0155		0.0194	0.0192	0.0192
	0.2726	0.0331	0.0328	0.0335		0.0376	0.0380	0.0381
	0.3599	0.0460	0.0447	0.0446		0.0480	0.0497	0.0497
	0.4575	0.0695	0.0682	0.0666		0.0734	0.0774	0.0771
	0.5675	0.0944	0.0934	0.0949		0.1042	0.1049	0.1051
	0.6922	0.1045	0.1060	0.1067		0.1158	0.1166	0.1167
	0.8350	0.1132	0.1133	0.1161		0.1264	0.1261	0.1265
	1.0000	0.1338	0.1310	0.1298		0.1335	0.1390	0.1388
298.15	0.0000	0.0058	0.0059	0.0059	300.15	0.0066	0.0067	0.0065
	0.0588	0.0083	0.0085	0.0085		0.0096	0.0097	0.0096
	0.1232	0.0159	0.0148	0.0147		0.0187	0.0174	0.0171
	0.1942	0.0221	0.0220	0.0220		0.0247	0.0251	0.0252
	0.2726	0.0409	0.0418	0.0415		0.0463	0.0457	0.0452
	0.3599	0.0526	0.0533	0.0533		0.0560	0.0571	0.0571
	0.4575	0.0886	0.0844	0.0849		0.0926	0.0922	0.0934
	0.5675	0.1127	0.1129	0.1125		0.1189	0.1212	0.1202
	0.6922	0.1275	0.1240	0.1238		0.1361	0.1316	0.1312
	0.8350	0.1346	0.1347	0.1338		0.1421	0.1433	0.1414
	1.0000	0.1439	0.1447	0.1451		0.1543	0.1508	0.1515
303.15	0.0000	0.0077	0.0078	0.0076	305.15	0.0093	0.0086	0.0084
	0.0588	0.0123	0.0116	0.0115		0.0126	0.0130	0.0129
	0.1232	0.0205	0.0220	0.0216		0.0267	0.0255	0.0251
	0.1942	0.0281	0.0307	0.0309		0.0389	0.0351	0.0352
	0.2726	0.0520	0.0519	0.0512		0.0570	0.0562	0.0555
	0.3599	0.0648	0.0632	0.0633		0.0716	0.0676	0.0677
	0.4575	0.1015	0.1057	0.1075		0.1137	0.1161	0.1178
	0.5675	0.1343	0.1339	0.1325		0.1449	0.1427	0.1413
	0.6922	0.1390	0.1435	0.1429		0.1494	0.1517	0.1512
	0.8350	0.1570	0.1560	0.1535		0.1666	0.1643	0.1620
	1.0000	0.1608	0.1605	0.1615		0.1673	0.1676	0.1685
	0.0000	0.0095	0.0099	0.0098		0.0109	0.0108	0.0108
	0.0588	0.0156	0.0154	0.0154		0.0175	0.0172	0.0173

308.15	0.1232	0.0302	0.0315	0.0313	310.15	0.0366	0.0360	0.0362
	0.1942	0.0433	0.0427	0.0428		0.0476	0.0487	0.0486
	0.2726	0.0627	0.0629	0.0626		0.0669	0.0675	0.0678
	0.3599	0.0718	0.0747	0.0747		0.0790	0.0798	0.0798
	0.4575	0.1388	0.1342	0.1349		0.1550	0.1481	0.1475
	0.5675	0.1578	0.1560	0.1554		0.1637	0.1649	0.1654
	0.6922	0.1645	0.1645	0.1642		0.1725	0.1733	0.1734
	0.8350	0.1722	0.1764	0.1754		0.1861	0.1840	0.1848
	1.0000	0.1795	0.1789	0.1792		0.1873	0.1870	0.1867
313.15	0.0000	0.0120	0.0121	0.0125				
	0.0588	0.0199	0.0202	0.0204				
	0.1232	0.0437	0.0435	0.0449				
	0.1942	0.0589	0.0591	0.0587				
	0.2726	0.0748	0.0746	0.0762				
	0.3599	0.0885	0.0880	0.0878				
	0.4575	0.1660	0.1723	0.1682				
	0.5675	0.1776	0.1785	0.1813				
	0.6922	0.1889	0.1868	0.1879				
	0.8350	0.1948	0.1948	0.1995				
	1.0000	0.1990	0.2000	0.1982				

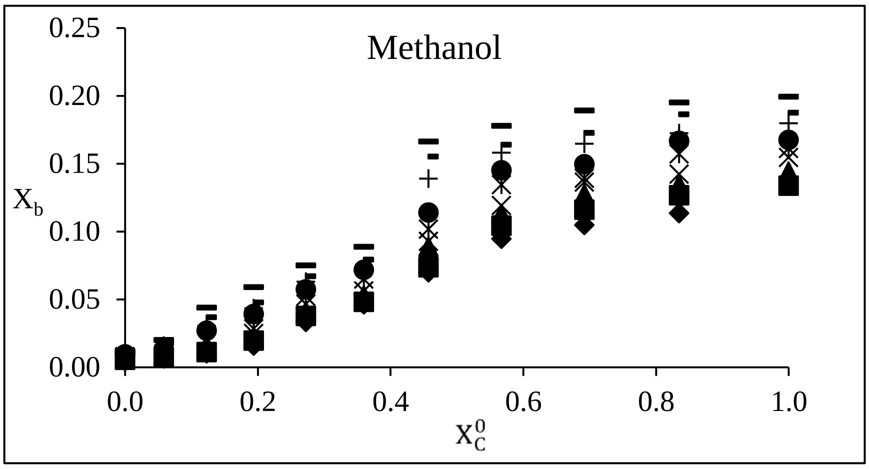


Fig. 3 Mole fraction solubility (X_b) variation with Initial mole fraction (X_C^0) of methanol, at various temperatures (◆T=293.15 K, ■T=296.15 K; ▲T=298.15 K; ×T=300.15 K; ×T=303.15K; ●T=305.15 K; +T=308.15 K; -T=310.15 K and ▬T=313.15 K).

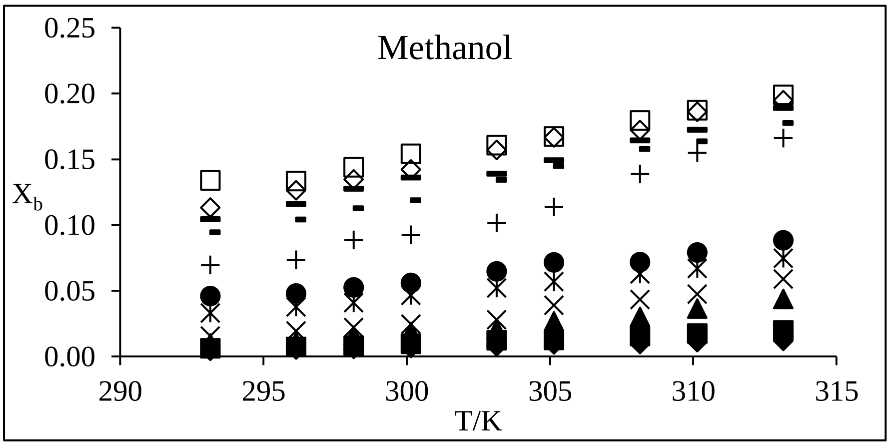


Fig. 4 Mole fraction solubility (X_b) variation with temperature at initial mole fraction (X_C^0) of methanol (◆= wt. fraction 0.0; ■ = 0.1; ▲= 0.2; × = 0.3; × = 0.4; ● = 0.5; + = 0.6; - = 0.7; ▬ = 0.8 and ◇= 0.9; □ =1)

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

Solvent	X_C^0	Parameters			R^2	100*RAD	100*RMSD
		A	B	C			
Methanol	0.0000	780.3133	-39429.21	-114.644	0.9915	2.3042	0.0262
	0.0588	242.2464	-15764.79	-34.0729	0.9943	2.4339	0.0336
	0.1232	673.283	-36480.99	-97.4338	0.9825	5.4497	0.1107
	0.1942	-118.452	-11.7953	20.12667	0.9874	3.0582	0.1623
	0.2726	447.7282	-23550.60	-65.2757	0.9981	0.9827	0.0536
	0.3599	-38.3446	-1036.82	6.825637	0.9803	2.5833	0.1952
	0.4575	-485.202	18173.81	74.02665	0.9845	3.3643	0.4307
	0.5675	329.844	-17504.98	-47.9699	0.9973	0.9032	0.1396
	0.6922	132.8233	-8294.20	-18.796	0.9873	1.6178	0.2710
	0.8350	504.1279	-24950.26	-74.1451	0.9962	0.7471	0.1816
	1.0000	-184.094	6569.93	28.10398	0.9838	1.1561	0.2412

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

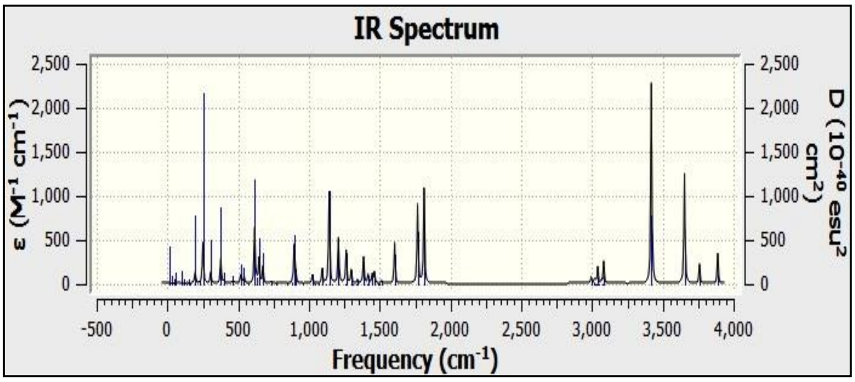
Solvent	X_C^0	Parameters		R^2	100*RAD	100*RMSD
		A	B			
Methanol	0.0000	10.6150	-4696.06	0.9867	2.6137	0.0348
	0.0588	13.4865	-5441.85	0.9939	2.3614	0.0371
	0.1232	19.1283	-6961.82	0.9810	5.4698	0.1202
	0.1942	16.6752	-6109.50	0.9874	3.1343	0.1609
	0.2726	9.4776	-3774.25	0.9957	1.5407	0.0922
	0.3599	7.4817	-3104.76	0.9803	2.6207	0.1947
	0.4575	11.8013	-4253.79	0.9821	3.6366	0.4277
	0.5675	7.7820	-2971.72	0.9952	1.2339	0.2129
	0.6922	6.6299	-2599.64	0.9874	1.6222	0.2663
	0.8350	6.3293	-2486.78	0.9891	1.5125	0.2916
	1.0000	4.5916	-1944.63	0.9821	1.2928	0.2501

Table 5 Thermodynamic parameters relative to solution process of PA at T_{hm}= 303.15K

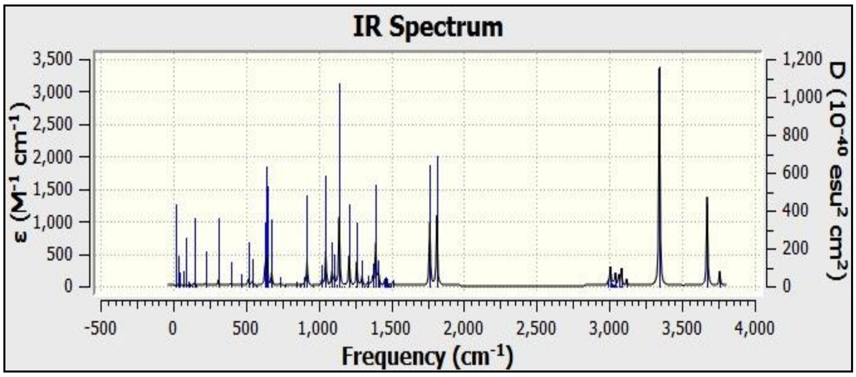
X_C^0	ΔH^0_{sol} KJK^{-1} mol^{-1}	ΔG^0_{sol} KJK^{-1} mol^{-1}	ΔS^0_{sol} KJK^{-1} mol-1	ΔS^0_{sol} JK^{-1} mol^{-1}	$T\Delta S^0_{sol}$ KJK^{-1} mol^{-1}	ζH%	ζTS%
PA + Water+ Methanol							
0.0000	39.0425	12.2990	0.0883	88.2511	26.7435	59.3477	40.6523
0.0588	45.2365	11.2645	0.1121	112.104	33.9719	57.1107	42.8893
0.1232	57.8738	9.6873	0.1590	159.011	48.1864	54.5669	45.4331
0.1942	50.7902	8.7803	0.1386	138.629	42.0099	54.7308	45.2692
0.2726	31.3770	7.5007	0.0788	78.7896	23.8763	56.7876	43.2124
0.3599	25.8125	6.9630	0.0622	62.2013	18.8494	57.7953	42.2047
0.4575	35.3653	5.6330	0.0981	98.1136	29.7322	54.3266	45.6734
0.5675	24.7067	5.1004	0.0647	64.6990	19.6063	55.7550	44.2450
0.6922	21.6131	4.9097	0.0551	55.1196	16.7034	56.4068	43.5932
0.8350	20.6744	4.7285	0.0526	52.6199	15.9459	56.4562	43.5438
1.0000	16.1674	4.5993	0.0382	38.1737	11.5681	58.2913	41.7087

Table 6. 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

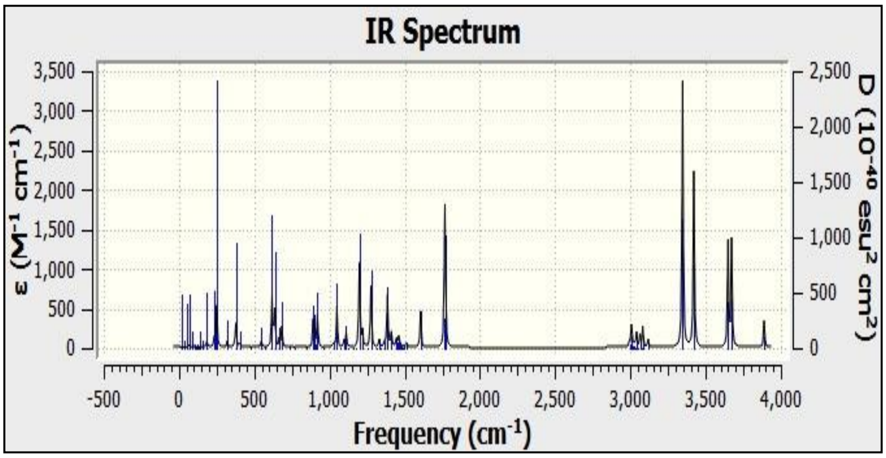
System (Gas)	Carboxylic υ-OH cm^{-1}	Carboxylic (-OH) Bond Dist. (Å)	Intermolecular H-Bond Dist. (Å) O-H	Intermolecular H-Bond Dist. (Å) C=O-H	Zero point vibration energy Kcal/mol	Nuclear Repulsion Energy Hartrees
PA	3758.60	0.9691	-	-	119.558	582.982
PAW	3419.28	0.9863	1.8058	2.0414	135.306	679.349
PAM	3330.44	0.9908	1.7601	1.9917	153.245	763.453
PAWM	3421.42 3346.96	0.9862 0.9899	1.8085 1.7659	1.9862 2.0147	168.985	866.803



Theoretical IR of PAW



Theoretical IR of PAM



Theoretical IR of PAWM

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