

## **Chalcones: A Solubility study at different temperatures**

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### **ABSTRACT**

Some new chalcones are synthesized by the condensation of aryl ketones with aromatic aldehydes and solubility of these synthesized chalcones is determined in chloroform and dichloromethane at temperatures ranging between 293.15 K and 313.15 K by gravimetric method. The experimental data was correlated well with modified Apelblat equation. Further, from the experimental solubility data, some thermodynamic parameters such as dissolution enthalpy, Gibb's energy and entropy etc. were evaluated using van't Hoff equation. The positive Gibb's energy and negative entropy suggests spontaneous dissolution and more ordered structure in solution.

**Keywords:** Chloroform, dichloromethane; thermodynamic parameters; dissolution enthalpy; Gibb's energy and entropy

### **1. INTRODUCTION**

The chalcones and their derivatives are an interesting class of compounds which are extensively investigated due to their biological and industrial applications. Many of these have been used as important intermediates in organic synthesis [1,2]. The compounds with the backbone of chalcones have been reported to possess various biological activities such as antimicrobial [3-5], antiinflammatory [6,7], antifungal [8,9], antioxidant [10,11], antileishmanial [12], antimalarial [13,14], antituberculosis [15,16], analgesic [17], anti HIV [18], antioxidant [19], antitumor [20,21] and neuro protective [22] activities.

As these compounds are biologically active, it will be interesting to study their solubilities in different solvents. The solubility data has been of fundamental importance in a large number of scientific disciplines and practice applications such as drug discovery, drug formulation, and crystallization based separation etc. Thus, due to biological importance of this class of compounds, in the present study, some new chalcones of vanillin derivatives have been synthesized.

Further, the solubility of these synthesized chalcones was determined in chloroform and dichloromethane at different temperatures (293.15 to 313.15 K). From the solubility data, some thermodynamic parameters such as enthalpy, Gibb's energy and entropy of solutions have also been evaluated.

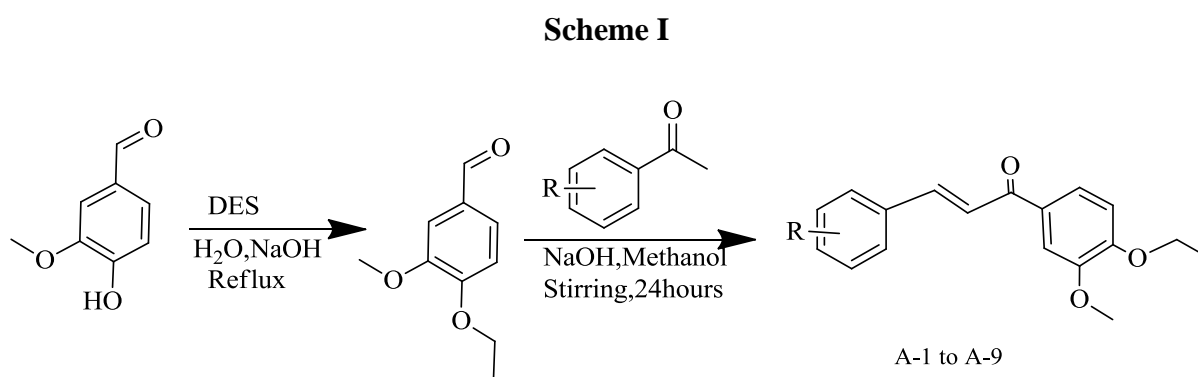
## 2. EXPERIMENTAL

### [A] Synthesis of 3-methoxy-4-ethoxybenzaldehyde:

An aqueous solution of vanillin (0.01 M) was refluxed at 95 °C to 97 °C for half an hour with stirring. To this solution, few drops of sodium hydroxide and diethyl sulphate (0.012 M) were added and reaction mixture was again refluxed for 5 to 7 hours with stirring. The organic layer was isolated and cooled at room temperature. The solid crude product was isolated and crystallized from absolute ethanol.

### [B] Synthesis of (2E)-1-(4-ethoxy-3-methoxyphenyl)-3-phenylprop-2-en-1-one:

A mixture of 3-methoxy-4-ethoxybenzaldehyde and substituted acetophenone in methanol was stirred for 24 hours in presence of few drops of aqueous sodium hydroxide solution. The product was filtered and dried. The recrystallization was done in ethanol. (Scheme I.)



All the synthesized compounds were crystallized and characterization of compounds was done by FTIR, <sup>1</sup>H-NMR and mass spectral data. The melting points of compounds were determined by Differential Scanning Colorimetry.

## 3. SOLUBILITY DETERMINATION

The solvents; chloroform and dichloromethane were of Allied chemical corporation and were purified by methods reported earlier

The solubility of synthesized compounds was determined in different selected solvents. The gravimetric method was chosen for the investigation. For each measurement, an excess mass of compound was added to a known mass of solvent. The equilibrium cell was heated to a constant temperature with continuous stirring for about 5h (the temperature of the water bath approached constant value, and then the actual value of the temperature was recorded). After 5 h, stirring was stopped, and the solution was kept for 2 h to approach equilibrium.

The equilibrium time of 2 h is optimized by checking the concentration of solution at different intervals of time. After 2 h, the change in concentration was less than 1%, so saturated solution was assumed to be equilibrium. Upper portion of this clear solution was filtered by a membrane (0.22 μm) and kept in a weighed vial. The vial with solution was quickly weighed to determine the mass of the sample and placed in vacuum oven at 323.15 K to fully evaporate solvents. When the mass of the residue reached at constant value, the final mass was recorded. All of the masses were taken using an electronic balance (Mettler Toledo AB204-S, Switzerland) with an uncertainty of ±0.0001 g. At each temperature, the measurement was conducted three times, and an average value was used to determine the mole fraction solubility. The saturated mole fraction solubility ( $x$ ) of compounds in each solvent can be calculated by using equation (1).

$$x = \frac{(m_2 - m_0) / M_1}{(m_2 - m_0) / M_1 + (m_1 - m_2) / M_2} \quad (1)$$

where  $M_1$  is the molar mass of chalcones and  $M_2$  is the molar mass of solvent. At each temperature, the measurement was conducted three times. By using the average value, mole fraction solubility  $x$  of chalcones in selected solvents were calculated.

#### 4. RESULTS AND DISCUSSION

Table I shows different substitution groups of chalcones [30-39]. The mole fraction solubilities  $x$  of chalcones in the chloroform and dichloromethane are listed in Table II at different temperatures (293.15 to 313.15 K) and more visually given in Figure I and Figure II for chloroform and dichloromethane respectively. In both the solvents, solubility is observed to increase almost linearly with temperature. Further, solubility is greater in dichloro methane than that in chloroform. The temperature dependence solubility has also been described by the modified Apelblat equation [23,24].

$$\ln x = A + \frac{B}{T} \quad (2)$$

where,  $x$  is the mole fraction solubility of chalcones,  $T$  is the absolute temperature.  $A$  and  $B$  are coefficients. The values of these coefficients are given in Table III. Using these values of  $A$  and  $B$ , the calculated solubilities ( $x_c$ ) were evaluated and are reported in Table II. Further, relative deviations ( $RD$ ) between the experimental and calculated values are also evaluated by eq. (3) and are listed in Table II.

$$RD = \frac{(x - x_c)}{x} \quad (3)$$

The, relative average deviations ( $ARD$ ) and root-mean-square deviations ( $RMSD$ ), calculated by equations (4) and (5) are listed in Tables III.

$$ARD = \frac{1}{N} \sum_i^N \frac{(x-x_c)}{x} \quad (4)$$

$$RMSD = \left[ \sum_{i=1}^N \frac{(x_c-x)^2}{N-1} \right]^{\frac{1}{2}} \quad (5)$$

where  $N$  is the number of experimental points.

## 5. THERMODYNAMIC FUNCTIONS OF SOLUTION

The dissolution of a substance in a solvent is associated with changes in thermodynamic functions such as enthalpies of solution ( $\Delta H_{sol}$ ), Gibbs energy change ( $\Delta G_{sol}$ ) and entropy of solutions ( $\Delta S_{sol}$ ). These functions have been evaluated from experimental solubility data. The changes that occur in the solute during dissolution process can be explained by these thermodynamic functions.

In recent thermodynamic treatments, the enthalpies of solution ( $\Delta H_{sol}$ ) was calculated by modified van't Hoff equation [25] i.e., from the slope of the plot of  $\ln x$  versus  $(1/T - 1/T_{hm})$ .

$$\frac{\partial \ln x}{\partial \left( \frac{1}{T} - \frac{1}{T_{hm}} \right)_P} = - \frac{\Delta H_{sol}}{R} \quad (6)$$

where  $T$  is the experimental temperature,  $\Delta H_{sol}$  is the heat of solution,  $R$  is universal gas constant (8.314 J/mol K).  $T_{hm}$  is mean harmonic temperature which is calculated by the following equation:

$$T_{hm} = \frac{n}{\sum_{1}^n \frac{1}{T}} \quad (7)$$

where  $n$  is the number of experimental temperatures studied. In the present case, the  $T_{hm}$  value obtained is 303.15 K. From the intercepts of these plots, Gibbs energy change ( $\Delta G_{sol}$ ) for the solubility process was evaluated by the following relation.

$$\Delta G_{sol} = -R \times T_{hm} \times \text{Intercept} \quad (8)$$

Using these evaluated  $\Delta H_{sol}$  and  $\Delta G_{sol}$  values, the entropies of solutions ( $\Delta S_{sol}$ ) were obtained by the equation .

$$\Delta S_{sol} = \frac{\Delta H_{sol} - \Delta G_{sol}}{T_{hm}} \quad (9)$$

## 6. NOMENCLATURE

$M_1$  = Molar mass of chalcone.

$x$  = Experimental mole fraction solubilities.

$A, B$  and  $C$  = Coefficients.

$ARD$  = Relative average deviations.

$N$  = Number of experimental points.

$T$  = Temperature /K.

$\Delta H_{sol}$  = Enthalpy change /kJ·mol<sup>-1</sup>.

$\Delta S_{sol}$  = Entropy change /J·mol<sup>-1</sup>.

$m.f.$  = molecular formula.

$M_2$  = Molar mass of solvent.

$x_c$  = Calculated mole fraction solubilities.

$RD$  = Relative deviations.

$RMSD$  = Root-mean-square deviations.

$n$  = Number of experimental temperatures studied.

$T_{hm}$  = Mean harmonic temperature.

$\Delta G_{sol}$  = Gibb's energy change /kJ·mol<sup>-1</sup>.

$R$  = Universal gas constant /J·mol<sup>-1</sup>·K<sup>-1</sup>.

$m.p.$  = melting point.

**Table I.** Different substitution groups of chalcones.

Compound Code	R
A-1	4-Cl
A-2	4-NO <sub>2</sub>
A-3	-H
A-4	4-CH <sub>3</sub>
A-5	4-OCH <sub>3</sub>
A-6	4-Br
A-7	4-OH
A-8	2,4-OCH <sub>3</sub>
A-9	3-Cl

**Table II.** The experimental solubility ( $x$ ), calculated solubility ( $x_c$ ) and relative deviation ( $RD$ ) of chalcones in chloroform and dichloromethane (DCM) at different temperatures.

$T / K$	Chloroform			DCM		
	$x \cdot 10^3$	$x_c \cdot 10^3$	$100RD$	$x \cdot 10^3$	$x_c \cdot 10^3$	$100RD$
	A-1			A-1		
293.15	5.6660	5.1774	8.6230	8.9330	10.0937	-12.9851
298.15	6.5141	5.8374	10.3886	14.6171	13.2873	9.1010
303.15	7.3912	6.5815	10.9554	19.5442	17.4921	10.5013

305.15	8.2940	7.4204	10.5327	23.8635	23.0272	3.5010
313.15	9.2345	8.3663	9.4014	27.6761	30.3153	-9.5339
	<b>A-2</b>			<b>A-2</b>		
293.15	0.8125	0.7866	3.1948	3.5648	3.4788	2.4138
298.15	0.8699	0.8394	3.5077	6.1866	4.8386	21.7894
303.15	0.9286	0.8958	3.5378	8.7791	6.7299	23.3417
305.15	0.9936	0.9559	3.7940	11.350	9.3605	17.5256
313.15	1.0552	1.0201	3.3239	13.8922	13.019	6.2788
	<b>A-3</b>			<b>A-3</b>		
293.15	3.7360	3.1901	14.6139	1.0250	1.2626	-23.1777
298.15	4.0605	3.4730	14.4687	2.3081	1.9398	15.9599
303.15	4.3825	3.7811	13.7226	3.5770	2.9802	16.6842
305.15	4.7020	4.1165	12.4571	4.8318	4.5787	5.2377
313.15	5.0191	4.4816	10.7085	6.0726	7.0345	-15.8408
	<b>A-4</b>			<b>A-4</b>		
293.15	0.3365	0.5229	-55.4173	20.7421	23.3183	-12.4199
298.15	1.6490	1.0066	38.9531	26.7072	27.3631	2.4564
303.15	2.9570	1.9377	34.4687	31.8882	32.1105	-0.6956
305.15	4.2650	3.7300	12.5439	38.8004	37.6811	2.8859
313.15	5.5685	7.1799	-28.9394	44.9301	44.2171	1.5863
	<b>A-5</b>			<b>A-5</b>		
293.15	6.2033	6.7354	-8.5778	0.7198	0.8754	-21.4893
298.15	6.6599	7.1340	-7.1192	1.4667	1.2860	12.283
303.15	7.1025	7.5415	-6.3874	2.1875	1.8924	13.4899
305.15	7.5415	8.0033	-6.1236	2.8768	2.8768	3.2358
313.15	7.9670	8.4769	-6.3993	3.5398	4.0948	-15.6789
	<b>A-6</b>			<b>A-6</b>		
293.15	6.0741	6.6551	-9.5651	3.3644	3.916	-16.4136

298.15	9.7428	9.1095	6.5002	5.9615	5.9615	7.7959
303.15	13.5748	13.5748	8.1441	8.5123	7.7145	9.3724
305.15	17.5713	17.0681	2.8640	11.012	10.827	1.6766
313.15	21.7481	23.3630	-7.4255	13.467	15.195	-12.8318
	<b>A-7</b>			<b>A-7</b>		
293.15	6.5624	5.1287	21.8470	2.0630	1.7280	16.2401
298.15	7.4556	5.6964	23.5957	2.9055	2.1856	24.7747
303.15	8.3636	6.3269	24.3510	3.7936	2.7645	27.1277
305.15	9.2687	7.0273	24.1828	4.1240	3.4967	15.2110
313.15	10.180	7.8051	23.3281	4.4228	4.4228	22.7194
	<b>A-8</b>			<b>A-8</b>		
293.15	9.9591	8.6000	13.6468	4.5115	3.6677	18.7033
298.15	10.0359	8.6431	13.8781	5.4687	4.3040	21.2977
303.15	10.1120	8.6864	14.0980	6.4837	5.0506	22.1028
305.15	10.1880	8.7299	14.3110	7.5618	5.9268	21.6221
313.15	10.2632	8.7737	14.5131	8.7093	6.9549	20.1434
	<b>A-9</b>			<b>A-9</b>		
293.15	16.321	15.020	15.020	9.2359	8.5974	6.9128
298.15	15.899	15.478	15.478	11.891	10.448	12.1311
303.15	16.417	15.949	15.949	14.639	12.697	13.2639
305.15	16.924	16.435	16.435	17.500	15.431	11.8256
313.15	18.458	16.2489	16.935	20.380	18.752	7.9841

**Table III.** Coefficients A and B of equation (1), Relative Average Deviation (*ARD*), Root Mean Square Deviation (*RMSD*) of Chalcones in Chloroform and Dichloromethane.

Compound code	A	B	$10^7$ RMDS	100ARD
Chloroform				
A-1	-12.300	0.024	1.4345	9.9798
A-2	-10.960	0.013	0.0026	3.4716

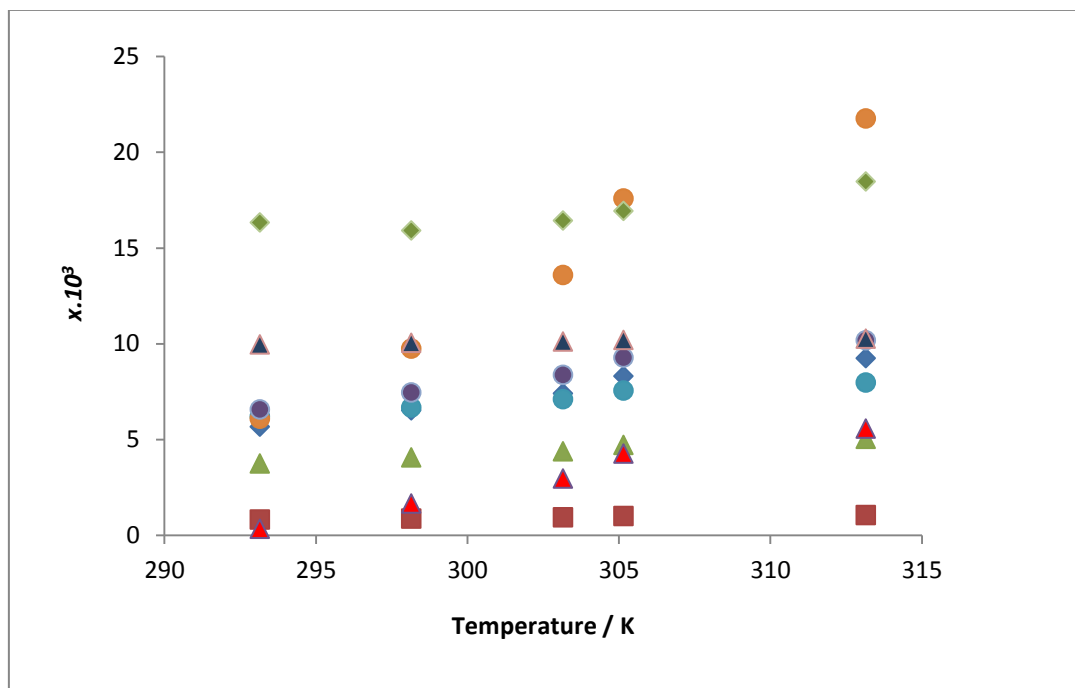
A-3	-10.732	0.017	0.8183	13.1933
A-4	-45.960	0.131	2.1847	0.3218
A-5	-8.373	0.012	0.5934	-6.9214
A-6	-23.423	0.063	2.4110	0.1034
A-7	11.430	0.021	9.9808	23.4609
A-8	-5.050	0.001	5.0819	14.0894
A-9	-5.958	0.006	2.3224	4.9211
Dichloromethane				
A-1	-20.72	0.055	7.4939	0.1168
A-2	-25.01	0.066	5.3705	14.2698
A-3	-31.85	0.085	0.7688	-0.2273
A-4	-13.14	0.032	4.4389	-2.2199
A-5	29.67	0.077	0.2300	-1.6318
A-6	-25.41	0.067	2.0889	-2.0800
A-7	-20.14	0.047	1.8868	21.2145
A-8	-14.99	0.032	4.9366	20.7738
A-9	-16.19	0.039	6.5944	10.4234

**Table IV.** The thermodynamic parameters of chalcones in chloroform and dichloromethane (DCM).

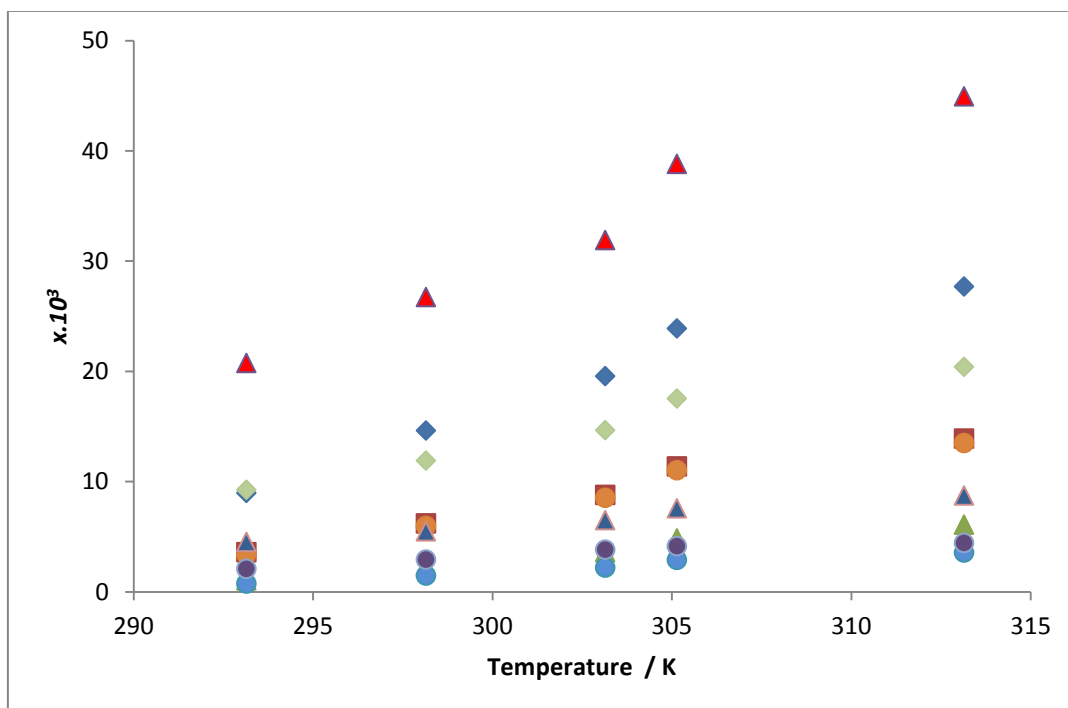
Compound Code	$\Delta H_{sol}$ /kJ·mol <sup>-1</sup>	$\Delta G_{sol}$ /kJ·mol <sup>-1</sup>	$\Delta S_{sol}$ /J·mol <sup>-1</sup>	$\Delta H_{sol}$ /kJ·mol <sup>-1</sup>	$\Delta G_{sol}$ /kJ·mol <sup>-1</sup>	$\Delta S_{sol}$ /J·mol <sup>-1</sup>
Chloroform			DCM			
A-1	0.0019	12.3839	-40.8846	0.0042	10.1776	-33.5771
A-2	19.1887	19.5098	-1.0597	50.9731	12.1971	127.9801
A-3	12.9948	14.0360	-3.4364	65.9051	14.6204	169.2648
A-4	100.8821	15.5675	281.5801	24.9370	8.7914	53.2886
A-5	9.5362	12.4742	-9.6969	59.1791	12.2903	154.7567
A-6	48.079	11.0333	122.2719	51.9043	12.2903	130.7458
A-7	16.7361	12.0787	15.3717	36.5400	14.2324	73.6260
A-8	1.1473	11.5724	-34.4078	25.0501	12.7336	40.6504
A-9	5.1522	10.2801	-16.9247	29.8888	10.7260	63.2469

$\Delta H_{sol}$  = Enthalpy change /kJ·mol<sup>-1</sup>,  $\Delta G_{sol}$  = Gibb's energy change /kJ·mol<sup>-1</sup>,  $\Delta S_{sol}$  = Entropy change /J·mol<sup>-1</sup>





**Figure I.** The mole fraction solubility ( $x$ ) against temperature for Chalcones in Chloroform.  
 ♦ A-1; ■ A-2; ▲ A-3; ▲ A-4; ● A-5; ● A-6; ● A-7; ▲ A-8; ◆ A-9.



**Figure II.** The mole fraction solubility ( $x$ ) against temperature for chalcones in dichloromethane.  
 ♦ A-1; ■ A-2; ▲ A-3; ▲ A-4; ● A-5; ● A-6; ● A-7; ▲ A-8; ◆ A-9.

## 7. ANALYTICAL AND SPECTRAL DATA

**A-1:** Yield: 73 %; m.p. 153 °C; m.f.  $C_{18}H_{17}ClO_3$ ; IR (KBr,  $cm^{-1}$ ): 1512.32 (C=C stretching), 1653.73 (C=O stretching), 1232.54 (C-O-C stretching), 2958 (C-H stretching), 844 (C-Cl stretching),  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.34 (3H, s, -OCH<sub>3</sub>), 4.01-4.08 (2H, q, -OCH<sub>2</sub>), 1.30-1.35 (3H, t, -CH<sub>3</sub>), 6.96-6.99 (1H, d, aromatic), 7.34-7.37 (1H, d, aromatic), 7.53 (1H, s, aromatic), 8.14-8.17 (2H, s, -CH-CH), 7.60-7.63 (2H, d, aromatic), 7.72-7.83 (2H, d, aromatic); MS: (m/z): 316 ( $M^+$  BP, 100 %), 288, 282, 254, 180, 155.

**A-2:** Yield: 59 %; m.p. 153 °C; m.f.  $C_{18}H_{17}NO_5$ ; IR (KBr,  $cm^{-1}$ ): 1495 (C=C stretching), 1678 (C=O stretching), 1248 (C-O-C stretching), 2953 (C-H stretching), 1318 (C-N stretching);  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.28 (3H, s, -OCH<sub>3</sub>), 3.98-4.05 (2H, q, -OCH<sub>2</sub>), 1.32-1.37 (3H, t, -CH<sub>3</sub>), 6.92-7.03 (1H, d, aromatic), 7.32 (1H, d, aromatic), 7.33 (1H, s, aromatic), 7.86-8.18 (2H, s, -CH-CH), 7.93 (2H, d, aromatic), 8.02 (2H, d, aromatic); MS: (m/z): 327 ( $M^+$  BP, 100 %), 298, 281, 176, 151.

**A-3:** Yield: 66 %; m.p. 132 °C; m.f.  $C_{18}H_{18}O_3$ ; IR (KBr,  $cm^{-1}$ ): 1488.64 (C=C stretching), 1682.32 (C=O stretching), 1257 (C-O-C stretching), 2955 (C-H asymmetrical stretching),  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.23 (3H, s, -OCH<sub>3</sub>), 4.05-4.10 (2H, q, -OCH<sub>2</sub>), 1.23-1.28 (3H, t, -CH<sub>3</sub>), 7.01-7.03 (1H, d, aromatic), 7.40-7.43 (1H, d, aromatic), 7.58 (1H, s, aromatic), 8.24-8.27 (2H, s, -CH-CH), 7.60-7.63 (2H, d, aromatic), 7.65-7.73 (2H, d, aromatic), 7.59 (1H, s, aromatic); MS: (m/z): 282 ( $M^+$  BP, 100 %), 282, 267, 253, 237, 151, 131.

**A-4:** Yield: 67 % m.p. 124 °C; m.f.  $C_{19}H_{20}O_4$ ; IR (KBr,  $cm^{-1}$ ): 1522.31 (C=C stretching), 1642.47 (C=O stretching), 1269.05 (C-O-C stretching), 2922 (C-H stretching), 2953 (C-C stretching),  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.29 (3H, s, -OCH<sub>3</sub>), 4.03-4.10 (2H, q, -OCH<sub>2</sub>), 1.21-1.32 (3H, t, CH<sub>3</sub>), 6.90-6.96 (1H, d, aromatic), 7.28-7.32 (1H, d, aromatic), 7.49 (1H, s, aromatic), 8.12-8.15 (2H, s, -CH-CH), 7.58-7.61 (2H, d, aromatic), 7.55-7.62 (2H, d, aromatic); 2.52 (3H, d, -CH<sub>3</sub>); MS: (m/z): 296 ( $M^+$  BP, 100 %), 281, 267, 251, 151.

**A-5:** Yield: 73 %; m.p. 151 °C; m.f.  $C_{18}H_{20}O_4$ ; IR (KBr,  $cm^{-1}$ ): 1512.32 (C=C stretching), 1665.14 (C=O stretching), 1273.05 (C-O-C stretching), 2977 (C-H stretching), 1276 (C-O-C stretching);  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.26 (3H, s, -OCH<sub>3</sub>), 3.96-4.03 (2H, q, -OCH<sub>2</sub>), 1.33-1.38 (3H, t, CH<sub>3</sub>), 6.90-6.93 (1H, d, aromatic), 7.30-7.34 (1H, d, aromatic), 7.58 (1H, s, aromatic), 8.13-8.16 (2H, s, -CH-CH), 7.63-7.66 (2H, d, aromatic), 7.90-7.93 (2H, d, aromatic), 3.93 (3H, s, -OCH<sub>3</sub>); MS: (m/z): 312 ( $M^+$  BP, 100 %), 283, 281, 197, 168, 151.

**A-6:** Yield: 57 %; m.p. 134 °C; m.f.  $C_{18}H_{17}BrO_3$ ; IR(KBr, $cm^{-1}$ ): 1524.85 (C=C stretching), 1654.84 (C=O stretching), 1248.21 (C-O-C stretching), 2967 (C-H stretching), 778 (C-Br stretching);  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.23 (3H, s, -OCH<sub>3</sub>), 4.05-4.10 (2H, q, OCH<sub>2</sub>), 1.23-1.28 (3H, t, CH<sub>3</sub>), 7.01-7.03 (1H, d ,aromatic), 7.40-7.43 (1H, d, aromatic), 7.58 (1H, s, aromatic), 8.24-8.27 (2H, s, -CH-CH), 7.60-7.63 (2H, d, aromatic), 7.65-7.73 (2H ,d, aromatic), 7.59 (1H, s, aromatic); MS: (m/z): 361 ( $M^+$  BP, 100 %), 345, 331, 329, 208, 151.

**A-7:** Yield: 59 %; m.p. 133 °C; m.f.  $C_{18}H_{18}O_4$ ; IR (KBr,  $cm^{-1}$ ): 1502.32 (C=C stretching), 1662.14 (C=O stretching), 1270.05 (C-O-C stretching), 2973 (C-H stretching), 3412 (O-H stretching);  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.44 (3H, s, -OCH<sub>3</sub>), 4.03-4.12 (2H, q, -OCH<sub>2</sub>), 1.38-1.42 (3H, t, CH<sub>3</sub>), 7.02-7.10 (1H, d, aromatic), 7.25-7.28 (1H, d, aromatic), 7.50 (1H, s, aromatic), 8.16-8.20 (2H, s, -CH-CH), 7.58-7.68 (2H, d, aromatic), 7.75-7.86 (2H, d, aromatic), 5.40 (1H, s, -OH); MS: (m/z): 281 (M<sup>+</sup> BP, 100 %), 269, 205, 151, 157.

**A-8:** Yield: 64 %; m.p. 129 °C; m.f.  $C_{20}H_{22}O_5$ ; IR (KBr,  $cm^{-1}$ ): 1518.12 (C=C stretching), 1677.65 (C=O stretching), 1272.42 (C-O-C stretching), 2912 (C-H stretching), 1231 (C-O-C stretching);  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.32 (3H, s, -OCH<sub>3</sub>), 4.15-4.21 (2H, q, -OCH<sub>2</sub>), 1.28-1.32 (3H, t, CH<sub>3</sub>), 7.03-7.12 (1H, d, aromatic), 7.34-7.37 (1H, d, aromatic), 7.53 (1H, s, aromatic), 8.20-8.24 (2H, s, -CH-CH), 7.58-7.62 (1H, d, aromatic), 7.72-7.83 (2H, d, aromatic), 7.70-7.75 (1H, s, aromatic), 3.88 (3H, s, -OCH<sub>3</sub>), 3.83 (3H, s, -OCH<sub>3</sub>); MS: (m/z): 327 (M<sup>+</sup> BP, 100 %), 297, 280, 311, 151.

**A-9:** Yield: 75 %; m.p. 170 °C; m.f.  $C_{18}H_{17}ClO_3$ ; IR (KBr,  $cm^{-1}$ ): 1498.64 (C=C stretching), 1679.12 (C=O stretching), 1243.65 (C-O-C stretching), 2970 (C-H stretching), 776 (C-Cl stretching);  $^1H$  NMR (BRUCKER Spectrometer 400 MHz DMSO- $d_6$ ,  $\delta$  ppm): 3.43 (3H, s, -OCH<sub>3</sub>), 4.13-4.19 (2H, q, -OCH<sub>2</sub>), 1.26-1.31 (3H, t, -CH<sub>3</sub>), 6.84-6.92 (1H, d, aromatic), 7.30-7.35 (1H, d, aromatic), 7.47 (1H, s, aromatic), 8.12-8.16 (2H, s, -CH-CH), 7.60-7.63 (1H, d, aromatic), 7.72-7.83 (2H, d, aromatic), 7.79-7.83 (1H, t, aromatic), 7.65 (1H, d, aromatic), 7.52 (1H, s, aromatic); MS: (m/z): 327 (M<sup>+</sup> BP, 100 %), 288, 282, 254, 180, 155.

## 8. CONCLUSIONS

It is evident from thermodynamic functions are reported in Table IV that for all the compounds,  $\Delta H_{sol}$  and  $\Delta G_{sol}$  values are positive where as  $\Delta S_{sol}$  values are both positive and negative for both the solvents. When stronger bonds are broken and weaker bonds are formed, energy is consumed and so  $\Delta H_{sol}$  becomes positive [26].

This indicates endothermic dissolutions of compounds. The positive values of  $\Delta G_{sol}$  indicate that the dissolution process is spontaneous. The negative entropy suggests more ordered structure in solution [29] whereas positive entropy is due to more randomness in solution.

As reported in Table I, all the compounds have same central moiety but different side chains, due to different in side chains behave differently in different solutions upon dissolution. Thus, different types of interactions affect entropy in solutions.

## ACKNOWLEDGMENT

Authors are thankful to Department of Chemistry for providing laboratory facilities. The authors are also thankful for the facilities and grants given under UGC-SAP for Department Research Support (DRS) and Department of Science and Technology (DST) New Delhi for Fund for Improvement of Science and Technology (FIST).

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( Received 12 March 2014; accepted 18 March 2014 )