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## Measurement and Modeling of the Solubility of Vanillin Constituent of Olive Mill Wastewater in Binary Water + Ethanol Solvents Mixtures between 278.15 K and 308.15 K

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### ABSTRACT

The aim of this study was to investigate the solubilities of vanillin (*Van*) in water + ethanol solvents mixtures from (278.15 to 308.15) K at atmospheric pressure using a thermostatted reactor and UV/vis spectrophotometer analysis. The effects of binary solvents composition and temperature on the solubility were discussed. The solubility data were correlated with the modified Apelblat equation and semi-empirical Buchowski-Ksiazczak  $\lambda h$  equation. The calculated solubilities show good agreement with the experimental data in the temperature range studied. Using the experimentally measured solubilities, the thermodynamic properties of dissolution of the vanillin such as Gibbs energy ( $\Delta_{sol}G^o$ ), molar enthalpy of dissolution ( $\Delta_{sol}H^o$ ), and molar entropy of dissolution ( $\Delta_{sol}S^o$ ) were calculated. Therefore, the experimental solubility and correlation equation in this work can be used as essential data and models in the purification process of vanillin.

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## INTRODUCTION

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is one of a major naturally phenolic compounds present in Olive Mill WasteWater (OMWW) (Cabrera *et al.*, 1996; Chung *et al.*, 1998), in a variety of fruits, and vegetables. Vanillin is used as sweetener in foods, in cosmetics, in the manufacture of agrochemical products and pharmaceuticals. This phenolic compound is antioxidant and anti-inflammatory (Maknia *et al.*, 2011; Wu *et al.*, 2009; Suryavanshi *et al.*, 2013). The chemical structure of vanillin is shown in Fig.1.

The solubility of solid compounds in pure and mixed solvents plays an important role in their industrial, pharmaceutical, separation and environmental applications (Hamdi, 1993; Ran *et al.*, 2002; Grant and Higuchi, 1990). Moreover, solubility data in pure and mixed solvents can help in the extraction and purification processes of organic compounds from different matrices.

In some recent works (Lu and Lu, 2007; Daneshfar *et al.*, 2008; Noubigh *et al.*, 2007 a,b; Noubigh *et al.*, 2008 a,b), solubilities of vanillin in several pure solvents have been measured as a function of temperature. However, to our knowledge no experimental or theoretical study concerning the solubility of vanillin in (ethanol+ water) binary solvents has been reported in the literature.

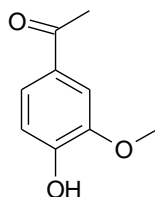
In continuation of our earlier work concerning the phenolic compound solubility in binary mixed solvent (Noubigh *et al.*, 2012; Noubigh *et al.*, 2013), we report here on the effects of (ethanol + water) binary solvents composition and temperature on the solubility of vanillin. The solubility data were correlated with the modified Apelblat equation and the Buchowski-Ksiazczak  $\lambda h$  equation. Obtained data were used to calculate appropriate dissolution thermodynamic properties.

## MATERIALS AND METHODS

Vanillin (C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>, MW = 152.12, >98% pure) and absolute ethanol were purchased from Sigma-Aldrich

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(Germany). Vanillin was used without prior treatment, but stored in a dessicator with  $P_2O_5$  once the bottle has been opened. Absolute ethanol was of analytical grade (purity, 99.9 %). Distilled water (conductivity around  $1.5 \mu S \cdot cm^{-1}$ ) has been used.



**Fig. 1:** Molecular structure of vanillin.

The solubility apparatus and method use are the same as in our former work (Noubigh *et al.*, 2008,b ; Noubigh *et al.*, 2012; Noubigh *et al.*, 2013). Also, the solubility of a solid in different binary solvents was measured by a thermostatted reactor and UV/vis spectrophotometer analysis (Beckman Coulter UV/vis spectrophotometer model DU-520). The wavelength of 312 nm was determined to be the most adequate for vanillin quantification because of the maximum absorbance at this wavelength. When the concentration of vanillin in the liquid phase remained constant, it was assumed that the system was at equilibrium. Several equilibrium times have been tested (from 1 to 6 h), and it appears that 3 h is always sufficient to reach equilibrium. Two independent experiments were realised to determine the vanillin solubility. The reproducibility of the data was within 0.5%.

Experimental solubilities were used to calculate the mole fraction solubility  $x_{Van}^{expl}$  in different (water + ethanol) mixtures based on the following equation:

$$x_{Van}^{expl} = \frac{m_V}{\left(m_V + \frac{1000}{(x_W \times M_W + x_E \times M_E)}\right)} \quad (1)$$

where  $m_{Van}$ ,  $x_W$  and  $x_E$  represent the malality of the vanillin, the mole fraction of water and ethanol, respectively, and  $M_{Van}$ ,  $M_E$  and  $M_W$  are the molecular weights of the vanillin, ethanol and water, respectively. Experimental ( $x_{Van}^{expl}$ ) solubility of vanillin are given in Table 1.

## RESULTS AND DISCUSSION

The vanillin solubility in pure water, ethanol and (water + ethanol) mixtures were determined at different temperatures ranging from (278.15 to 308.15) K using the previously described method. This complementary study permits us to extend our solubility data basis of phenolic compounds (Noubigh *et al.*, 2007a,b; Noubigh *et al.*, 2008a,b; Noubigh *et al.*, 2012; Noubigh *et al.*, 2013).

The relationship between mole fraction of the solubility and temperature is correlated by the modified Apelblat equation (Eq.2) and the  $\lambda h$  equation (Eq.3).

The solubility temperature dependence of vanillin in the binary system of ethanol and water can be described by the modified empirical E.q. (2) (Apelblat and Manzurola, 1997; Apelblat and Manzurola, 1999; Apelblat and Manzurola, 2002):

$$\ln x_{Van} = A + \frac{B}{T/K} + C \ln(T/K) \quad (2)$$

where  $x_{Van}$  is the mole fraction solubility of vanillin in ethanol + water mixed solvents,  $T$  is the absolute temperature (K);  $A$ ,  $B$ , and  $C$  are empirical parameters determined by the experimental solubility data which are listed in Table 2.

The  $\lambda h$  model equation, a semi-empirical equation, is shown as follows (Ksiazczak and Kosinski, 1988; Ksiazczak *et al.*, 1994):

$$\ln\left(1 + \frac{\lambda(1 - x_{Van})}{x_{Van}}\right) = \lambda h \left[ \frac{1}{(T/K)} - \frac{1}{(T_m/K)} \right] \quad (3)$$

where  $x_{Van}$  is the mole fraction of the solubility of vanillin;  $T$  and  $T_m$  are the experimental temperature and normal melting temperature, respectively;  $\lambda$  and  $h$  are the model parameters obtained from the experimental solubility data in the systems which are listed in Table 2, respectively. As for Buchowski-Ksiazaczak  $\lambda h$  equation, recasting Eq.(3) into an exponential form yields.

$$\frac{1}{x_{Van}} = \frac{1}{\lambda} \left[ e^{h\lambda\left(\frac{1}{T} - \frac{1}{T_m}\right)} - 1 \right] + 1 \quad (4)$$

The root-mean-square deviations (rmsd's) for modified Apelblat and the  $\lambda h$  equation are also listed in Tables 2 and 3. The rmsd is calculated according to the formula:

$$rmsd = \left[ \frac{1}{n} \sum_{i=1}^n (x_{Van}^{cal} - x_{Van}^{exp})^2 \right]^{1/2} \quad (5)$$

where  $n$  is the number of experimental points and  $x_{Van}^{cal}$  and  $x_{Van}^{exp}$  represent the solubility of vanillin calculated from Eq.(1) and the experimental solubility value, respectively. The relative deviations (RD) between the calculated and the experimental values are also listed in Table 1. The RD is defined as:

$$RD = \frac{x_{Van}^{exp} - x_{Van}^{cal}}{x_{Van}^{exp}} \quad (6)$$

The relative average deviations (RAD) and the RMSD are also listed in Tables 2. The RAD is calculated according to:

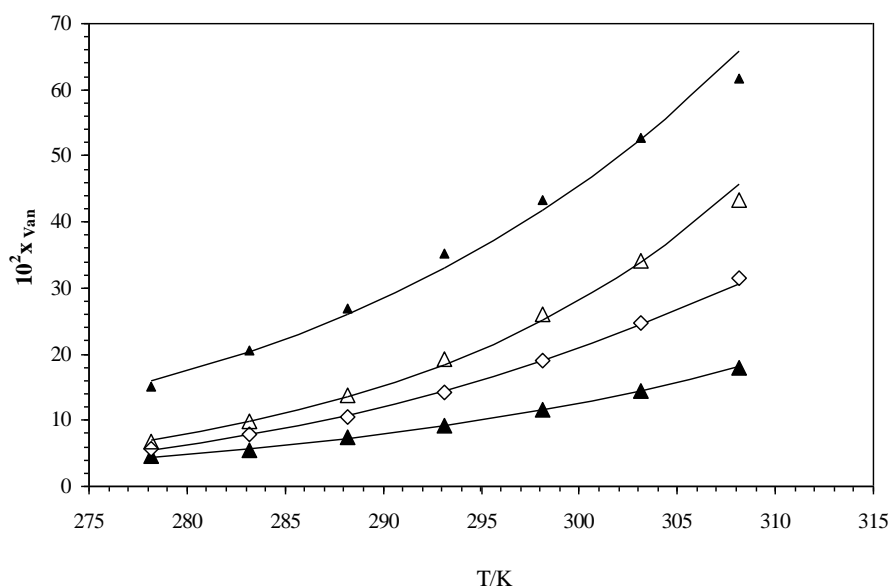
$$RAD = \frac{1}{n} \sum_{i=1}^n \left| \frac{x_{Van}^{exp} - x_{Van}^{cal}}{x_{Van}^{exp}} \right| \quad (7)$$

**Table 1:** Experimental ( $x_{Van}^{exp}$ ) and calculated ( $x_{Van}^{cal}$ ) solubility of vanillin in different (ethanol + water) mixed solvents at various temperatures and atmospheric pressure.

T/K	$x_{Van}^{exp} \times 10^2$	Apelblat equation		$\lambda h$ equation	
		$x_{Van}^{cal} \times 10^2$	RD	$x_{Van}^{cal} \times 10^2$	RD
$x_E = 0.016$					
278.15	4.5866	4.4612	0.0273	4.3593	0.0495
283.15	5.4010	5.6930	-0.0540	5.6926	-0.0539
288.15	7.3572	7.2340	0.0167	7.3355	-0.0029
293.15	9.2620	9.1544	0.0116	9.3267	-0.0069
298.15	11.6628	11.5385	0.0106	11.6986	-0.0030
303.15	14.5466	14.4876	0.0040	14.4732	0.0050
308.15	17.9056	18.1227	-0.0121	17.6575	0.0138
$x_E = 0.033$					
278.15	3.0350	2.8999	0.0445	2.7872	0.0816
283.15	3.6813	3.8504	-0.0459	3.8270	-0.0395
288.15	5.0743	5.0872	-0.0025	5.1774	-0.0203
293.15	6.9681	6.6891	0.0400	6.9003	0.0097
298.15	8.0901	8.7547	-0.0821	9.0566	-0.1194
303.15	12.1666	11.4071	0.0624	11.7001	0.0383
308.15	16.2842	14.7987	0.0912	14.870	0.0816
$x_E = 0.052$					

278.15	5.6540	5.5272	-0.0100	5.5272	0.0224
283.15	7.7658	7.7905	0.0014	7.7905	-0.0031
288.15	10.5780	10.7511	0.0099	10.7511	-0.0163
293.15	14.1603	14.5071	0.0062	14.5071	-0.0244
298.15	18.9296	19.1133	0.00618	19.1133	-0.0097
303.15	24.7016	24.5556	-0.0132	24.5556	0.0059
308.15	31.5486	30.7329	-0.0506	30.7329	0.0258
$x_E = 0.072$					
278.15	6.8180	7.0931	-0.0403	6.6664	0.0222
283.15	9.7800	9.8053	-0.0025	9.8175	-0.0038
288.15	13.8001	13.4780	0.02335	14.0534	-0.0183
293.15	19.1470	18.4250	0.03771	19.4987	-0.0183
298.15	25.9420	25.0547	0.03419	26.1502	-0.0080
303.15	34.1304	33.8964	0.0068	33.8283	0.0088
308.15	43.389	45.6321	-0.0517	42.1737	0.0280
$x_E = 0.116$					
278.15	15.0060	15.9571	-0.0633	14.8534	0.0101
283.15	20.5355	20.4152	0.0058	20.5544	-0.0009
288.15	26.9507	26.0063	0.0350	27.4576	-0.0188
293.15	35.1897	32.9910	0.0424	35.3420	-0.0043
298.15	43.2864	41.6833	0.0370	43.8100	-0.0120
303.15	52.7067	52.4614	0.00465	52.3626	0.0065
308.15	61.7009	65.7782	-0.0660	60.5127	0.01925

The solubilities of vanillin in (water + ethanol) mixed solvents with ethanol mole fraction of 0.0, 0.016, 0.033, 0.052, 0.071, 0.116 and 1, on a solute-free basis were determined at  $T = (278.15, 283.15, 288.15, 293.15, 298.15, 303.15 \text{ and } 308.15) \text{ K}$ . Based on obtained results shown in the Tables 2 and 3, we can reach the following conclusions. For each solvent composition studied, the equilibrium solubility mole fraction of vanillin increases with increasing temperature. The solubility of vanillin in (ethanol + water) mixed solvents increases with increasing ethanol concentration at constant temperature, which may be explained by the «like dissolves like» principle. As shown in Fig. 2, we can see that the solute possesses lower polarity. In addition, the solvent's polarity is in the following order: water > ethanol.



**Fig. 2:** Mole fraction solubility of vanillin ( $x_{Van}$ ) in ethanol + water systems as a function of temperatures, where  $x_E$  is the mole fraction of ethanol:  $\blacktriangle$ ,  $x_E = 0.016$ ;  $\diamond$ ,  $x_E = 0.052$ ;  $\triangle$ ,  $x_E = 0.072$ ;  $\blacksquare$ ,  $x_E = 0.116$ ; line calculated by equation (2).

From Table 1 and Fig. 2, it can be noticed that Eqs. (2) and (3) can be used to correlate the experimental results of the solubility of vanillin in ethanol and binary (water + ethanol) mixtures at different temperatures. Calculated solubilities of vanillin in (water + ethanol) mixed solvents show good agreement with experimental values. The RD calculated by modified Apelblat equation among all the values do not exceed 4.59 % and the RAD are 1.901, 0.352, 1.396, 2.810, 3.922 and 2.339 %. The RD calculated by the  $\lambda h$  equation were less than

5.39%, and the RAD are 1.935, 5.654, 1.542, 1.538, 1.030 and 3.343%. The precision of solubilities calculated by the models can meet the demands of engineering application. From Tables 2 and 3, the RMSD of the modified Apelblat model were lower than those of the Buchowski-Ksiazaczak  $\lambda h$  model. As stated previously, we can draw the conclusion that the modified Apelblat equation is more accurate than the Buchowski-Ksiazaczak  $\lambda h$  equation in the mixed solvents. Afterwards, these experimental solubility values and the correlation equation can be used as essential data and models in practical purification process of vanillin.

**Table 2:** Apelblat equation and  $\lambda h$  equation fitting parameters of vanillin in different (ethanol+water) mixed solvents.

$x_E$	Apelblat equation				
	A	B/K	C	$10^4$ RMSD	$10^2$ RAD
0.016	-80.082	-2.238	13.677	6.233	1.901
0.033	-93.048	-2.239	15.904	27.244	0.352
0.0515	-99.439	-2.239	17.160	0.651	1.396
0.072	-104.880	-2.239	18.166	10.702	2.810
0.116	-79.612	-2.238	13.820	21.347	3.922
1.000	-104.369	-11.436	17.866	2.941	2.339
$x_E$	$\lambda h$ equation				
	$\lambda$	h	$10^4$ RMSD	RAD $\times 10^2$	
0.016	0.532	8314.527	8.078	1.935	
0.033	0.596	8660.757	45.732	5.654	
0.0515	1.983	2918.694	3.631	1.542	
0.072	4.703	1411.252	3.015	1.538	
0.116	8.210	756.123	1.481	1.030	
1.000	0.552	9849.267	2.479	3.343	

From an energetic aspect, the dissolution of a vanillin into a liquid is related to some thermodynamic changes, specifically the Gibbs energy ( $\Delta_{sol}G^o$ ), molar enthalpy ( $\Delta_{sol}H^o$ ) and molar entropy ( $\Delta_{sol}S^o$ ) of dissolution. These thermodynamic's parameters can be calculated using the experimental solubility data fitted to Eq. (2). These parameters reflect the modification of the solution properties due to the presence of the solute at its infinite dilution state at a given temperature (Sridhar *et al.*, 1978; Zhang and Gobas, 1995; Zielenkiewicz *et al.*, 1999). We assume that the activity coefficient of water in aqueous phase is equal to 1. Therefore, with the help of the Gibbs-Helmholtz equation, the following equation can be obtained (Adkins, 1968):

$$\Delta_{sol}H^o = RT^2 \left( \frac{d \ln x}{dT} \right)_P \quad (8)$$

where the molar enthalpy of dissolution  $\Delta_{sol}H^o$  is the difference between the partial molar enthalpy of vanillin in solution,  $H_{van}^{*,liquid}$  and the molar enthalpy of vanillin in the solid state,  $H_{van}^{o,solid}$ , at temperature T:

$$\Delta_{sol}H^o = H_{Van}^{o,solid} - H_{Van}^{*,liquid} \quad (9)$$

The remaining parameters,  $\Delta_{sol}G^o$  and  $\Delta_{sol}S^o$ , can be calculated as follows (Zhang and Gobas, 1995; Dohanyosova *et al.*, 2003; Freire *et al.*, 2008):

$$\Delta_{sol}G^o = -RT \ln(x)_P \quad (10)$$

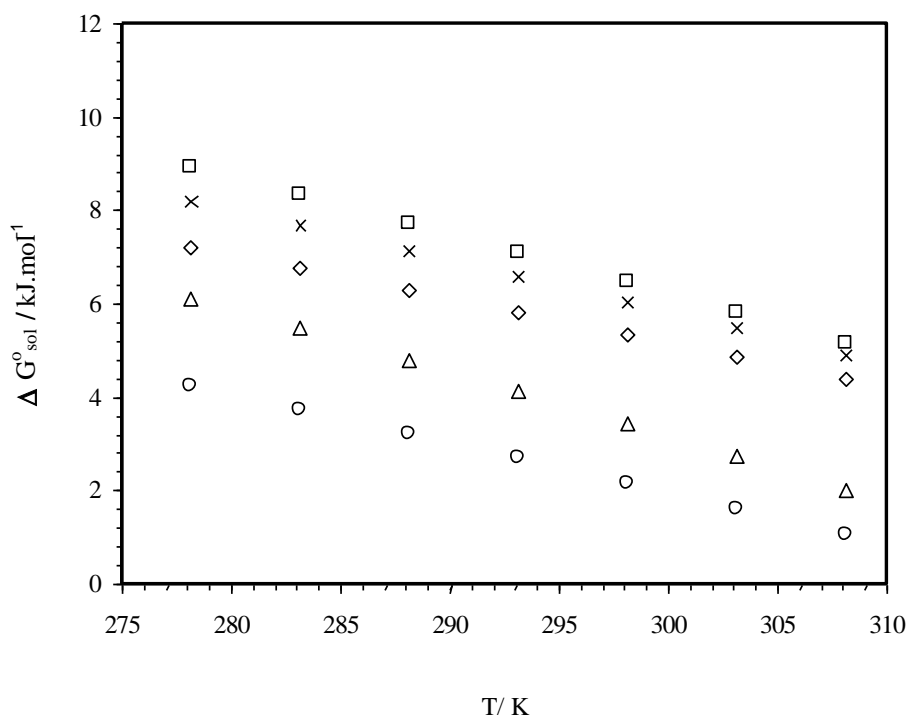
$$\Delta_{sol}S^o = R \left( \frac{d(\ln x)}{d(\ln T)} \right)_P \quad (11)$$

The values of the thermodynamic functions,  $\Delta_{sol}H^o$ ,  $\Delta_{sol}G^o$ , and  $\Delta_{sol}S^o$ , of the vanillin dissolution in different concentrations of ethanol-water solutions were calculated using Eqs. 8, 10, and 9, respectively, and are reported in Table 3.

The molar Gibbs energy of dissolution versus temperature, derived from experimental solubility data for each solution, is depicted in Fig. 3. Estimated enthalpies of dissolution from solubility measurements of vanillin in each mixed solvent at different temperatures are comparable, with the major deviation corresponding to the less concentrated ethanol solution. For all the studied solutions, it was found that the enthalpy of dissolution is a linear function of temperature, thus giving a constant heat capacity of solution. When the solubility is at a maximum, the enthalpy of dissolution spent for the formation of solvent structure cavities is a minimum.

**Table 3:** Thermodynamic properties of the dissolution of vanillin in different (ethanol + water) mixed solvents at various temperatures:  $\Delta_{sol}G^{\circ}$  (kJ.mol<sup>-1</sup>),  $\Delta_{sol}H^{\circ}$  (kJ.mol<sup>-1</sup>), and  $\Delta_{sol}S^{\circ}$  (J.mol<sup>-1</sup>K<sup>-1</sup>).

T/K	$x_M = 0.016$			$x_M = 0.033$		
	$\Delta_{sol}H^{\circ}$	$\Delta_{sol}G^{\circ}$	$\Delta_{sol}S^{\circ}$	$\Delta_{sol}H^{\circ}$	$\Delta_{sol}G^{\circ}$	$\Delta_{sol}S^{\circ}$
278.15	31.671	7.196	87.993	36.825	8.193	102.939
283.15	32.240	6.751	90.021	37.487	7.672	105.297
288.15	32.809	6.296	92.013	38.149	7.140	107.613
293.15	33.378	5.831	93.970	38.810	6.596	109.890
298.15	33.947	5.356	95.895	39.472	6.041	112.128
303.15	34.516	4.872	97.787	40.134	5.475	114.328
308.15	35.085	4.378	99.649	40.795	4.898	116.493
T/K	$x_M = 0.052$			$x_M = 0.072$		
	$\Delta_{sol}H^{\circ}$	$\Delta_{sol}G^{\circ}$	$\Delta_{sol}S^{\circ}$	$\Delta_{sol}H^{\circ}$	$\Delta_{sol}G^{\circ}$	$\Delta_{sol}S^{\circ}$
278.15	39.732	6.625	119.027	42.059	6.123	129.195
283.15	40.446	6.023	121.571	42.814	5.470	131.888
288.15	41.160	5.409	124.070	43.570	4.804	134.534
293.15	41.874	4.782	126.527	44.326	4.125	137.134
298.15	42.588	4.144	128.941	45.082	3.433	139.690
303.15	43.301	3.493	131.316	45.837	2.728	142.204
308.15	44.015	2.831	133.652	46.593	2.011	144.676
T/K	$x_M = 0.116$			$x_M = 1.000$		
	$\Delta_{sol}H^{\circ}$	$\Delta_{sol}G^{\circ}$	$\Delta_{sol}S^{\circ}$	$\Delta_{sol}H^{\circ}$	$\Delta_{sol}G^{\circ}$	$\Delta_{sol}S^{\circ}$
278.15	32.002	4.247	99.786	41.442	8.917	116.934
283.15	32.577	3.743	101.834	42.185	8.325	119.583
288.15	33.152	3.228	103.847	42.929	7.721	122.185
293.15	33.727	2.704	105.825	43.672	7.104	124.742
298.15	34.302	2.170	107.770	44.415	6.474	127.256
303.15	34.877	1.627	109.682	45.158	5.831	129.728
308.15	35.452	1.073	111.563	45.902	5.176	132.160

**Fig. 3:** The standard molar Gibbs energy of dissolution of vanillin in the (ethanol + water) at different temperatures:  $\Delta$ ,  $x_E = 0.016$ ;  $\times$ ,  $x_E = 0.052$ ;  $\diamond$ ,  $x_E = 0.072$ ;  $\circ$ ,  $x_E = 0.116$ ;  $\square$ ,  $x_E = 1.00$ . The  $x_E$  is the mole fraction of ethanol.

From Table 3, it is found that the course information of vanillin dissolving in the binary system of methanol and water in the experimental temperature range was endothermic,  $\Delta_{sol}H^{\circ}$  and  $\Delta_{sol}S^{\circ}$  for vanillin dissolving in the binary system methanol and water was relatively large. Thermodynamic's parameters values prove that

the whole process is endergonic ( $\Delta_{sol}G^o > 0$ ), therefore non-spontaneous. Even though  $\Delta_{sol}S^o$  is positive, the  $\Delta_{sol}H^o$  is sufficiently positive to provide positive  $\Delta_{sol}G^o$  values. At a certain temperature, the increase of entropy increases solubility with the increasing mol fraction of ethanol in the binary system of ethanol water.

### Conclusions:

Using a thermostatted reactor and UV/vis spectrophotometer analysis, new experimental results for the solubility of vanillin in (water + ethanol) mixed solvents as function of temperature not previously reported in the literature have been obtained and presented in this work. The solubility of vanillin in binary ethanol + water solvent mixtures increases with increase of the temperature, while it decreases with increase the water content in the solvent mixture. The solubilities calculated by the modified Apelblat equation and the Buchwiski-Ksiazczak  $\lambda h$  equation show good agreement with the experimental data. The Apelblat equation can regress the solubility data much better than  $\lambda h$  equation. Data presented in this study can be used for the vanillin purification or its optical resolution by the preferential crystallization procedure.

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