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THERMODYNAMIC MODELING OF THE SOLID-LIQUID EQUILIBRIUM OF TWO PHENOLIC COMPOUNDS IN SEVERAL SOLVENTS AT TEMPERATURES RANGING FROM 283.15 K TO 323.15 K

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ABSTRACT. The solubility of two natural phenolic compounds (vanillic acid (*VA*) and vanillin (*V*)) in four individual solvents (ethanol, butan-2-ol, ethylene glycol, and ethyl acetate) was measured using the gravimetric method from 283.15 to 323.15 K at atmospheric pressure. The optimization of the complexes between *VA*–solvents and *V*–solvents using the B3LYP theoretic technique and the 6-31+G (d, p) basis set indicated that the absolute value of interaction energy was higher, suggesting that the interaction between solute and the solvent was stronger. In addition, two excellent activity coefficient models (NRTL and Wilson) were used to correlate and evaluate the equilibrium solubility results. The highest relative average deviation and root-mean-square deviation values for *VA* are 4.36% and 3.09×10^{-3}, respectively, and 3.35% and 5.52×10^{-3} for *V*. Furthermore, the excess enthalpy of the solution was determined on the basis of thermodynamic relations and the Wilson model. The findings indicate that the dissolution process was endothermic.

KEY WORDS: Solid–liquid equilibrium, Vanillin, Vanillic acid, NRTL and Wilson models, Thermodynamic parameters

INTRODUCTION

Vanillic acid (4-hydroxy-3-methoxybenzoic acid (*VA*), $C_8H_8O_4$) and vanillin (4-hydroxy-3-methoxybenzaldehyde (*V*), $C_8H_8O_3$) are phenolic compounds (Figure 1). These natural compounds can be found in plants (olive oil, white wine, etc.) [1, 2], a variety of fruits [3, 4], and are regularly added to human foods [5, 6]. It is additionally observed in many plants, spices and nuts [7]. The antioxidant, anti-inflammatory, anti-mutagenic, anti-tumor, and anti-cancer properties of phenolic compounds have been reported in the literature [7-12]. The solubility and thermodynamic properties of such compounds in monary solvents are of exceptional importance in their extraction, separation, purification, recrystallization, drug discovery, and device development [13-15].

In this paper, the study of solid-liquid equilibrium for two phenolic compounds in several solvents and their thermodynamic modelling at temperatures ranging from 283.15 to 323.15 K continues to discuss the impact of temperature on solubility.

In our previous papers [16], the solubility of VA was measured in different organic solvents from 293.15 to 318.15 K. Through semi-empirical equations such as the modified Apelblat, Buchowski, and Van't Hoff equations, the information obtained for the VA was correlated.

Furthermore, the solubility modeling of *V* has been documented in the literature in some organic solvents using semi-empirical equations [17]. However, to our knowledge, no theoretical research has been published in the literature concerning the solubility of selected phenolic compounds in pure solvents using activity coefficient models. This complementary research helps us to expand our database of solubility data on selected phenolic compounds [16, 18-21].

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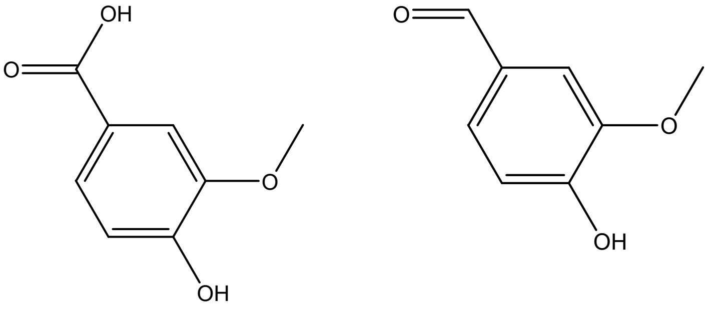

Vanillic acid (*VA*) Vanillin (*V*)

Figure 1. Structure of phenolic compounds.

In phase equilibrium calculations and material behavior prediction and/or correlation for *VA* and *V* at temperatures between 283.15 and 323.15 K, the activity coefficient models of Wilson and Nonrandom Two Liquid Theory (NRTL) are among the most widely used chemical thermodynamic models. In addition, using the Wilson model, the excess enthalpy (H^E), entropy (S^E), and Gibbs energy (G^E) of the studied phenolic compounds in organic solvents were measured.

EXPERIMENTAL

Materials

Vanillic acid and vanillin were obtained from Aladdin Biochemical Co., Ltd. (Shanghai, China). All the solvents of analytical grade (> 99.5%) were purchased from Tianjin Jiangtian Chemical Co., Ltd. The materials used in this study are summarized in Table 1.

Table 1. The origin and properties of phenolic compounds, as well as the solvents chosen.

Chemicals	CAS number	Fusion temperature / K	Enthalpy of fusion kJ·mol^{-1}	Mass fraction purity
Vanillicacid	121-34-6	482.95^a	29.460^a	$\geq$ 0.97
Vanillin	121-33-5	355.4^b	22.400^b	$\geq$ 0.99
Ethanol	64-17-5			$\geq$ 0.99
Butan-2-ol	78-92-2			$\geq$ 0.99
Ethylene glycol	107-21-1			$\geq$ 0.99
Ethyl acetate	141-78-6			$\geq$ 0.99

^{a}Taken from Ref. [16], ^{b}Taken from Ref. [17].

Experimental solubility determination

The solubility of *VA* and *V* in pure neat organic solvents was determined by gravimetric method at 283.15 K to 323.15 K, which was described and verified [20-23] in our previous works. For each solubility measurement, excess solid solute was mixed with the organic solvent in the jacketed reactor under vigorous stirring, which was limited by spreading water with a thermoelectric controller within 0.01 K. To achieve that solid-liquid equilibrium, the solutions were agitated for 12 hours. The solution then took two hours to settle. The solution was then sampled with a filter syringe (0.2 µm) and allowed to evaporate at 333.15 K in a vacuum drying oven. The mass of the dried samples was measured frequently using an analytical scale balance (A&D, GR-120, Japan, with a precision of 0.0001 g) until the weight remained unaltered. The mean value of the three measurements was used to calculate the mole fraction solubility of phenolic compounds. The mole fraction solubility ($x_1^{\mathrm{exp}tl}$) of phenolic compounds is calculated by equation (1).

$$x_1^{\mathrm{exp}tl} = \frac{m_1/M_1}{m_1/M_1+m_2/M_2} \tag{1}$$

where m_1 = mass of *solute*; m_2 = mass of neat solvent; M_1 and M_2 are the molecular weight of solute and solvent, respectively.

Simulation methods

The influence of the interaction between the solute and the solvent on solubility behaviour was investigated using density functional theory (DFT) computations [24, 25]. The DFT approach was used in this study to optimize molecules of phenolic compounds and solvents using the theoretical method B3LYP and the basis 6-31$^+$G (d, p) set without imposing symmetry constraints [24, 25].

The Gaussian 09W suite of programs was used to carry out the calculations [26]. The self-consistent-field computation met the 10^{-5} Hartree convergence criteria, and the geometry optimization tolerances for energy, maximal force, and maximal displacement were set to 10^{-4} au, 0.02 au, and 0.05 au, respectively. After all of the involved molecules' geometries were optimized at this level, the interaction energy (ΔE) was calculated as:

$$\Delta E = E(S - sol) - E(S) - E(sol) \tag{2}$$

The energies of the solute, solvent, and solute-solvent are *E(S)*, *E(Sol),* and *E(S-sol)*, respectively. The greater interaction between the phenolic compound and solvent molecules is demonstrated by the larger absolute values of $E(S - sol)$.

Table 2. The interaction energy $\Delta E(S - sol)$ and the hydrogen bond distance.

		ΔE/kJ mol^{-1}	Bond distance/Å
Vanillic acid	Ethanol	-13.5445	1.7215
	Butan-2-ol	-14.277	1.736
	Ethylene glychol	-59.378	1.729
	Ethyla cetate	-36.990	1.761
Vanillin	Ethanol	-22.627	1.921
	Butan-2-ol	-22.343	1.922
	Ethylene glychol	-65.225	1.859
	Ethyl acetate	-11.235	2.433

RESULTS AND DISCUSSION

Solubility data of VA and V

This research offers data on the effects of temperature on the solubility of *VA* and *V* in four neat solvents. The thermodynamic modeling and the thermodynamic properties of the transfer solution were calculated on the basis of these results. Data on the temperature effect on the solubility of *VA* in neat organic solvents within the temperature range (T = 298.15-318.15) K and pressure (p = 0.1 MPa) were published in a previous paper [16]. In the present work, the same study was continued using a gravimetric method for two phenolic compounds (*VA* and *V*) from 283.15 K to 323.15 K at p = 0.1 MPa. The obtained experimental solubility data is presented in Figure 2.

Literature data for vanillin in monary organic solvents was found only in the work of Shakeel *et al.* [17] but the disagreement with our data is relevant (Figure 3). It can be seen that the mean variation between the experimental values and literature values from 293.15 to 303.15 K is about 14% and relatively large from 303.15 to 318.15 K for ethanol and 25% for butan-2-ol (being larger at the higher temperatures). As mentioned earlier, to verify the uncertainty of measurement, a comparison of experimental solubility data for vanillic acid in ethanol and literature values was made in the previous work [18].

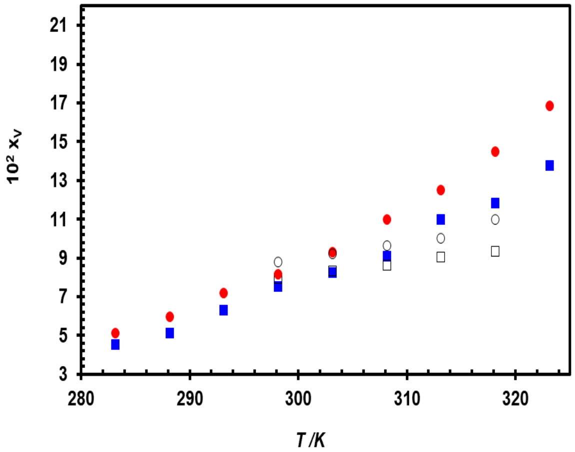

Figure 2. Solubility data comparison of vanillin in ethanol: ●, experimental values, ○; ref [17] and butan-2-ol: ■, experimental values, □; Ref .[17].

The determined mole fraction solubility of *VA* and *V* in the monary solvent is reported in Table 3 and graphically depicted in Figures 3 and 4 for the temperature range (283.15 to 323.15) K under an atmosphere pressure of 0.101 MPa. In the temperature range tested, the solubility mole fraction orders of studied compounds in selected mono-solvents as follows: ethanol > butan-2-ol > ethyl acetate > ethylene glycol for *VA* and ethyl acetate > butan-2-ol > ethanol > ethylene glycol for *V*.

The solubility in ethanol and ethylene glycol is far above that in selected solvents, which is not entirely consistent with the sequence of polarities of the four solvents (polarity: ethylene glycol (0.79) > ethanol = (0.654) > butan-2-ol = (0.506) > ethyl acetate (0.228). It means that the polarity of solvents isn't thought to have a significant effect on the solubility of *VA* and *V*. In this case, hydrogen bonding may potentially play a significant role in solute-solvent interactions.

The DFT calculations were performed to investigate the interactions between the selected phenolic compounds and the different organic solvent molecules in order to derive an explanation for the important difference in solubility. The hydrogen bonds estimated between VA and ethanol (a), butan-2-ol (b), ethylene glycol (c), and ethyl acetate (d) are shown in Figure 3.

The ΔE and hydrogen bond distances are shown in Table 2. It can be seen that the absolute value of ΔE for *VA* and *V* varies as: ethanol < butan-2-ol < ethyl acetate < ethylene glycol and ethyl acetate < butan-2-ol < ethanol < ethylene glycol, respectively, and the loss of ΔE leads to the extension of hydrogen bond distances. At the given temperature, the absolute value of ΔE order corresponded to the order of solubility.

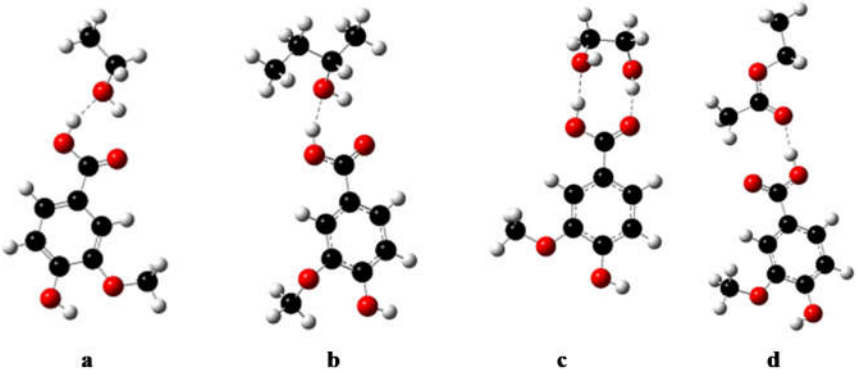

Figure 3. Interactions between vanillic acid and ethanol (a), butan-2-ol (b), ethylene glycol (c) and ethyl acetate (d), respectively. The dashed lines indicate hydrogen bonds.

Table 3. Experimental (x_{explt}) and calculated (x_{calcd}) mole fraction solubility of *VA* and *V* in four mono-solvents at various temperatures under 0.101 MPa^a.

T/K		NRTL	Wilson		NRTL	Wilson
	Vanillic acid			Vanillin		
	10^2x_{explt}	10^2x_{calcd}	10^2x_{calcd}	10^2x_{explt}	10^2x_{calcd}	10^2x_{calcd}
			Ethanol			
283.15	2.299	2.240	2.098	4.517	4.586	4.240
288.15	2.542	2.566	2.494	5.136	5.32	4.955
293.15	2.880	2.936	2.929	6.299	6.152	5.880
298.15	3.350	3.355	3.402	7.507	7.091	6.950
303.15	3.885	3.827	3.926	8.263	8.142	8.114
308.15	4.340	4.353	4.534	9.070	9.321	9.442
313.15	4.930	4.942	5.188	10.992	10.679	11.157
318.15	5.512	5.597	5.921	11.831	12.162	12.885
323.15	6.380	6.321	6.663	13.790	13.889	15.118
			Butan-2-ol			
283.15	2.251	2.313	2.353	5.118	5.146	4.895
288.15	2.648	2.788	2.837	5.971	6.018	5.748
293.15	3.235	3.333	3.385	7.195	7.017	6.826
298.15	3.929	3.956	4.009	8.170	8.148	8.038
303.15	4.603	4.669	4.722	9.298	9.434	9.440
308.15	5.456	5.470	5.519	10.994	10.919	11.120
313.15	6.507	6.361	6.404	12.505	12.596	13.011
318.15	7.915	7.334	7.363	14.501	14.538	15.258
323.15	9.081	8.434	8.449	16.868	16.793	17.911
			Ethylene glycol			
283.15	0.413	0.462	0.400	4.046	4.009	3.996
288.15	0.499	0.576	0.512	4.551	4.714	4.647
293.15	0.644	0.713	0.661	5.612	5.536	5.515
298.15	0.853	0.877	0.857	6.777	6.482	6.526
303.15	1.088	1.072	1.100	7.477	7.537	7.621
308.15	1.388	1.301	1.410	8.724	8.769	8.954
313.15	1.796	1.570	1.812	9.902	10.166	10.462
318.15	2.334	1.885	2.324	11.987	11.846	12.386

323.15	3.018	2.252	2.958	13.765	13.736	14.524
Ethyl acetate						
283.15	1.213	1.105	1.124	7.020	6.974	6.401
288.15	1.352	1.309	1.319	8.012	8.057	7.550
293.15	1.630	1.552	1.570	9.115	9.274	8.866
298.15	1.825	1.826	1.855	10.591	10.637	10.396
303.15	2.081	2.144	2.186	12.250	12.170	12.154
308.15	2.412	2.513	2.568	14.105	13.898	14.173
313.15	2.816	2.938	3.005	16.191	15.851	16.498
318.15	3.323	3.427	3.506	18.291	18.062	19.136
323.15	3.790	3.978	4.069	19.901	20.536	22.023

[a]Standard uncertainty u is u(T) = 0.1 K; the relative standard uncertainty u are $u_r(p) = 0.05$, $u_r(x) = 0.02$.

As a result, as the temperature rises, the solubility of *VA* and *V* rises as well. The most extreme solubility values of PhC are observed in ethanol. Besides, at the same temperature, *VA* and *V* are more soluble in ethanol than in ethyl acetate. This case may be due to the fact that the polarity of the solute molecule is weak.

Thermodynamic modeling

In recent years, with the rapid development of theoretical foundations, many solubility models have been used in the study of solid-liquid phase equilibrium, and good application results have been achieved. In order to extend the application of the measured solubility data, the experimental solubilities of *VA* and *V* in the selected pure solvents were correlated using two well established activity coefficient models, Wilson equation and NRTL equation.

Moreover, based on the solid–liquid phase equilibrium theory, the mole fraction solubility of VA and V can be simplified and given as follows:

$$ln(x\gamma_1) = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{3}$$

In Eq. 3, T_m *and* ΔH_{fus} signify, respectively, the melting temperature and enthalpy of fusion of solute; $\gamma_1$refers to the activity coefficient of the solute.

Wilson Model

The Wilson Model is an activity coefficient model that was first proposed by Wilson and can be used to correlate the experimental solubility data for the binary system. [27, 28]:

$$\ln(\gamma_1) = \ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1}\right] \tag{4}$$

$$\ln(\gamma_2) = -\ln(x_2 + \Lambda_{12}x_1) + x_1\left[\frac{\Lambda_{21}}{x_2+\Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2}\right] \tag{5}$$

In which, γ_1 and $\gamma_2$stand for the activity coefficients of the solute and solvent, respectively

$$\Lambda_{12} = \frac{V_{m,2}}{V_{m,1}}\exp\left(-\frac{\lambda_{12}-\lambda_{11}}{RT}\right) = \frac{V_{m,2}}{V_{m,1}}\exp\left(-\frac{\Delta\lambda_{12}}{RT}\right) \tag{6}$$

$$\Lambda_{21} = \frac{V_{m,1}}{V_{m,2}}\exp\left(-\frac{\lambda_{21}-\lambda_{22}}{RT}\right) = \frac{V_{m,1}}{V_{m,2}}\exp\left(-\frac{\Delta\lambda_{21}}{RT}\right) \tag{7}$$

In Eqs. 6 and 7, $\Delta\lambda_{21}$ and $\Delta\lambda_{21}$ are the Wilson parameters that can be regressed by experimental solubility data; the solute and organic solvent molar volumes are $V_{m,1}$ and $V_{m,2}$, respectively.

NRTL Model

The NRTL Model [29, 30] is expressed as follows to model the solubility of *VA* and *V* binary systems:

$$\ln(\gamma_1) = x_2^{\,2}\left[\frac{\tau_{21}{G_{21}}^2}{(x_1+G_{21}^2x_2)^2}+\frac{\tau_{12}{G_{12}}^2}{(x_2+G_{12}^2x_1)^2}\right] \quad (8)$$

$$\ln(\gamma_2) = x_1^2\left[\frac{\tau_{12}{G_{12}}^2}{(x_2+G_{12}^2x_1)^2}+\frac{\tau_{12}{G_{21}}^2}{(x_1+G_{21}^2x_2)^2}\right] \quad (9)$$

$$G_{12} = exp(-\alpha_{12}\,\tau_{12}) \quad (10)$$

$$G_{21} = exp(-\alpha_{12}\,\tau_{21}) \quad (11)$$

$$\tau_{12} = \frac{g_{12}-g_{22}}{RT} = \frac{\Delta g_{12}}{RT} \quad (12)$$

$$\tau_{21} = \frac{g_{21}-g_{11}}{RT} = \frac{\Delta g_{21}}{RT} \quad (13)$$

$$\alpha_{12} = \alpha_{21} \quad (14)$$

The mole fractions of the solute and the corresponding solvent are denoted by x_1 and x_2 respectively; Δg_{12} and Δg_{21} are the cross-interaction energy parameters that are independent of composition and temperature; α_{12} is an adjustable parameter and is considered to be 0.2.

In this study, the experimental solubility data were correlated using a nonlinear regression approach. The following is the definition of the objective function:

$$Min\ F = \sum_{i=1}^{n}\left(ln\gamma_1^{exptl} - ln\gamma_1^{calcd}\right)^2 \quad (15)$$

The logarithms of the experimental and calculated activity coefficients of a solute are represented by $ln\gamma_1^{exptl}$ and $ln\gamma_1^{calcd}$, respectively.

Through comparisons of fitting accuracy, as provided in Eqs. (16-18), the average relative deviation (ARD), relative deviation (RD), and root-mean-square deviation (RMSD) were used to evaluate the applicability and accuracy of the two activity coefficient models for VA and V in selected mono-solvents.

$$RAD = \frac{1}{n}\times\sum_{i=1}^{n}\left|\frac{x_{\mathrm{exp}tl}-x_{calcd}}{x_{\mathrm{exp}tl}}\right| \quad (16)$$

$$RD = \frac{x_{\mathrm{exp}tl}-x_{calcd}}{x_{\mathrm{exp}tl}} \quad (17)$$

$$RMSD = \left[\frac{1}{n}\times\sum_{i=1}^{n}\left(x_{calcd}-x_{\mathrm{exp}tl}\right)^2\right]^{1/2} \quad (18)$$

where $x_{\mathrm{exp}tl}$ and $x_{calcd}$are the mole fraction solubility of experimental and calculated values, respectively; *n* is the total number of experiment points.

Based on the experimental solubility values, the parameters ($\Delta\lambda_{21}$ and $\Delta\lambda_{12}$) in the Wilson model and ($\Delta g_{21}$and Δg_{12}) in the NRTL model are acquired by using the nonlinear least-squares method with Matlap software. The obtained values of model parameters together with the RAD and RMSD values are presented in Table 4. References [16, 17] provide the point of fusion of *PhC* necessary in the calculation method. In order to intuitively demonstrate the difference between the calculated and experimental data, the computed solubilities with the Wilson and NRTL equations are shown graphically in Figures 4 and 5, respectively.

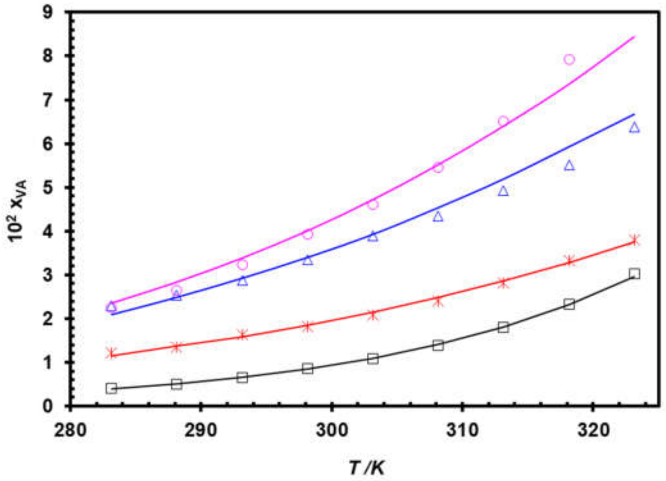

Figure 4. Mole fraction solubility of *VA* in pure solvents at various temperatures: ○; ethanol; Δ, ethylene glycol; *, butan-2-ol;□, ethyl acetate; line, calculated curves by the Wilson model.

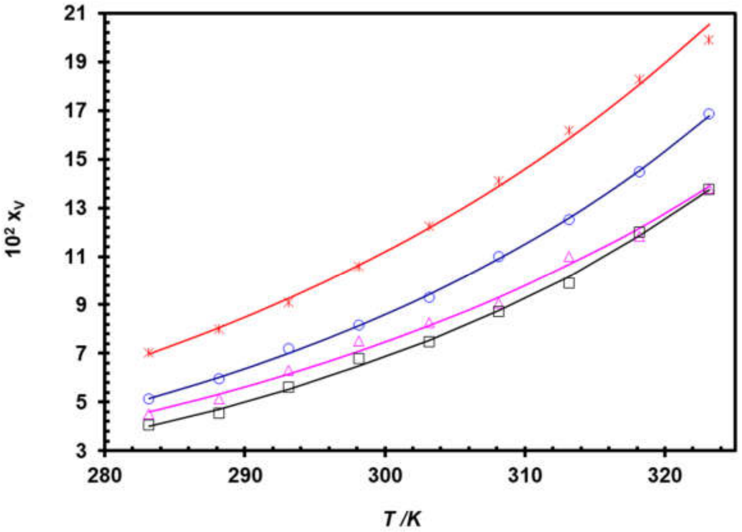

Figure 5. Mole fraction solubility of *V* in pure solvents at various temperatures: ○; ethanol; Δ, ethylene glycol; *, butan-2-ol; □, ethyl acetate (solid lines represents the value of calculated solubility by NRTL model).

As shown in Table 4, the average RAD values of the two adopted models were 3.07% (NRTL), 2.93% (Wilson) and 2.26% (NRTL), 2.68% (Wilson) for vanillic acid and vanillin, respectively. It can be clearly seen that they are both small. They give good agreement with the solubility data of vanillic acid and vanillin. The findings suggest that the two models used can provide a reasonable correlation solubility of *VA* and *V* in the industrial manufacturing process.

Table 4. Parameters of the equations for two phenolic compounds in monary solvent.

	Wilson				NRTL			
Solvent	$\Delta\lambda_{21}$	$\Delta\lambda_{12}$	10^3RMSD	10^2RAD	Δg_{21}	Δg_{12}	10^3RMSD	10^2RAD
Vanillic acid								
Ethanol	3008.0715	-1838.769	1.033	3.90	-4281.463	6931.099	0.489	1.125
Butan-2-ol	-4787.949	1512.124	1.234	4.360	1248.087	-4342.786	3.011	3.354
Ethylene glycol	6628	-1481.2	0.108	1.270	-190.980	674.435	3.094	3.761
Ethyl acetate	5271.6	-2823.9	0.144	2.185	-3683.799	6222.021	1.025	4.060
Vanillin								
Ethanol	-1400	278730	1.911	5.521	14741.406	-1518.7796	2.424	2.621
Butan-2-ol	-663	65412	0.818	3.66	1248.087	-4342.786	3.0107	3.353
Ethylene glycol	-1315	75643	0.108	1.270	11274.138	-1261.639	1.552	1.731
Ethyl acetate	-1218	67741	1.452	4.178	12323.150	2685.644	2.690	1.340

Table 5. Excess enthalpy H^E (kJ · mol^{-1}) of *VA* and *V* solutions studied at the temperature range from T = (283.15 To 323.15) K under 101.2 kPa.[a]

H^E (kJ · mol^{-1})				
T/K	Ethanol	Butan-2-ol	Ethylene glycol	Ethyl acetate
Vanillic acid				
283.15	-0.111	-0.085	0.000	-0.077
288.15	-0.119	-0.099	-0.001	-0.082
293.15	-0.131	-0.121	-0.002	-0.096
298.15	-0.148	-0.146	-0.003	-0.103
303.15	-0.166	-0.171	-0.006	-0.114
308.15	-0.179	-0.202	-0.009	-0.127
313.15	-0.197	-0.240	-0.015	-0.144
318.15	-0.213	-0.290	-0.025	-0.164
323.15	-0.236	-0.332	-0.038	-0.181
Vanillin				
283.15	-0.059	-0.032	-0.050	-0.060
288.15	-0.067	-0.037	-0.056	-0.070
293.15	-0.081	-0.044	-0.068	-0.083
298.15	-0.094	-0.049	-0.080	-0.093
303.15	-0.103	-0.055	-0.087	-0.105
308.15	-0.111	-0.063	-0.100	-0.122
313.15	-0.131	-0.071	-0.111	-0.136
318.15	-0.139	-0.080	-0.130	-0.154
323.15	-0.156	-0.090	-0.144	-0.175
[a]Standard uncertainties *u* are *u* (*T*) = 0.02 K, *u* (H^E) = 0.1 kJ×mol^{-1}.				

Excess enthalpy of solution

Utilizing the Wilson model [31, 32], we can represent the excess Gibbs free energy (G^E) and the excess enthalpy of solution in the neat solvent as follows:

$$G^E = RT\ln(x_1 ln\gamma_1 + x_2 ln\gamma_2) = -\mathrm{RT}[x_1 ln(x_1 + x_2\Lambda_{12}) + x_2 ln(x_2 + x_1\Lambda_{21})] \tag{19}$$

$$H^E = -T^2\left[\frac{\partial\left(G^E/_T\right)}{\partial T}\right] = x_1 x_2\left(\frac{\Delta\lambda_{12}\Lambda_{12}}{x_1+\Lambda_{12}x_2} + \frac{\Delta\lambda_{21}\Lambda_{21}}{x_2+\Lambda_{21}x_1}\right) \tag{20}$$

Here, H^E represents the excess enthalpy in real solutions. $\Delta\lambda_{12}$ and $\Delta\lambda_{21}$ are adjustable parameters in the Wilson model, and their values are shown in Table 4. The parameters of interaction (J×mol^{-1}) are also referred to in Λ_{12} and Λ_{21}, which are defined as equations (6) and (7).

The excess solution enthalpy (H^E) values were estimated using the Wilson model's regressed parameters (given in Table 4) and the experimental solubility (shown in Table 5). It turns out that the values of H^E is negative in all studied solvents, indicating that the dissolution process of *VA* and *V* in the above mono-solvents is exothermic, which is consistent with the fact that the solubility of *VA* and *V* increases with rising temperature.

CONCLUSION

In this work, the solubility of two phenolic compounds (*VA* and *V*) in four pure solvents (ethanol, butan-2-ol, ethylene glycol, and ethyl acetate) was measured via a gravimetric method at a temperature range of 283.15 K to 323.15 K under 0.1 MPa. Results indicated that the experimental solubility of *VA* and *V* increased with increasing temperature in the studied pure solvents. In addition, the ΔE between the solute and selected solvents was calculated by Gaussian 09W programs to explain the solubility behavior. The solubility of *VA* and *V* in selected solvents increases as the ΔE increases. The ΔE was not neglected in these binary solid liquid equilibrium systems, as evidenced by the good agreement between simulation results and experimental data. The Wilson and NRTL models were used to successfully correlate the solubility of *VA* and *V* in a selected pure solvent. In addition, the excess enthalpy of the solution was estimated on the basis of the Wilson equation, and all of the H^E values are negative and increase as the temperature increases, according to the findings. The solubility data, related equations and thermodynamic parameters can provide support for the extraction, purification and separation of *VA* and *V* in the pharmaceutical, cosmetic and food industries.

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