



Temperature dependent solubility of vanillic acid in aqueous methanol mixtures: Measurements and thermodynamic modeling



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ABSTRACT

The solid-liquid equilibrium data of vanillic acid (VA) in pure ethanol and in various (methanol + water) mixed solvents were measured over the temperature range from (293.15 to 318.15) K at atmosphere pressure using a thermostatted reactor and UV/vis spectrophotometer analysis. The effects of the composition of binary systems and temperature on the solubility were discussed. The obtained solubility data were correlated with the Van't Hoff model, the modified Apelblat equation and the λh equation. In general, the regressed results with the three models were all within the acceptable limit for the solubility of vanillic acid in the (methanol + water) mixed solvents. Furthermore, thermodynamic properties of dissolution of the vanillic acid in the selected systems were estimated. Consequently, the experimental data and model parameters would be useful for optimizing the process of purification of vanillic acid in industry.

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1. Introduction

Vanillic acid (4-hydroxy-3-methoxybenzoic acid) (VA), a flavoring agent used in pharmaceuticals, foods, and perfumery [1,2], obtained naturally from many plants [3,4]. Vanillic acid is an intermediate in the production of vanillin from ferulic acid [5,6]. It is also a metabolic by-product of caffeic acid. This compound is antioxidant, anti-inflammatory [7–9], antibacterial [10], and has antimicrobial effects [11]. The molecular structure of vanillic acid is illustrated in Fig. 1.

The solubility of solid compounds in pure and mixed solvents played a crucial role for the determination of proper solvents of crystallization processes. Moreover, solubility is an important physicochemical parameter in the process of drug discovery development [12–14].

In previous works, the solubility of vanillic acid in pure water has been determined as function of temperature [15]. Unfortunately, no experimental solubility data of vanillic acid in pure methanol and aqueous methanol mixtures are currently available in the literature. The main goal of the present work was to (1) measure the solubility of vanillic acid in the pure methanol and the binary solvent mixtures of (methanol + water) over the temperature range from (293.15 to 318.15) K, (2) correlate the solubility data with the Van't Hoff equation, the modified Apelblat equation and the λh equation, and (3) evaluate the thermodynamic properties of the solutions.

2. Experimental

2.1. Materials

Vanillic acid ($M_w = 168.14$, mass fraction purity > 97%) was purchased from Sigma-Aldrich (Germany). Vanillic acid was used without prior treatment, but stored in a desiccator with P_2O_5 once the bottle has been opened. The absolute methanol (mass fraction purity > 99.8%) was supplied by Sigma-Aldrich. Freshly prepared deionized doubly distilled water (Maxima Ultra Pure Water, Elga-Prima Corp, UK) was used throughout this study. The detailed information of these materials was presented in Table 1.

2.2. Differential scanning calorimetry

The melting temperature T_m of vanillic was determined previously [16–19], however the difference between them is a large ($T_m = 485.15$ K, determined by Miller [16]; and $T_m = (480.5)$ K, by Manic [19]). In the present work, the melting point T_m of vanillic acid required for modeling the solid-liquid equilibrium were obtained by means of a differential scanning calorimetric instrument (DSC 131 evo-Setaram) under a nitrogen atmosphere. Before experiment, the DSC instrument was pre-calibrated with an empty crucible as reference. About 5 mg of vanillic acid was placed in a DSC pan, and then sample was heated under a nitrogen stream over a temperature range of 350 to 550 K using a $3 \text{ K} \cdot \text{min}^{-1}$ heating rate. The standard uncertainty for T_m is 0.5 K.

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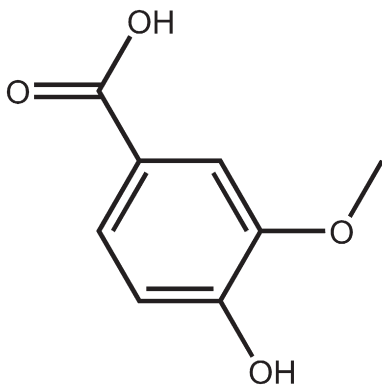


Fig. 1. Chemical structure of vanillic acid.

2.3. Solubility measurement

The apparatus and detailed procedure for solubility measurement have already been described in our previous work [20–22]. A magnetically stirred, double jacketed reactor thermostatted at $T \pm 0.01$ K (Polystat Huber CC2) was used to measure the solubility. For each measurement, excess amounts of solid solute were added to 25 g of organic solvent introduced into a reactor and the mixture was continuously stirred. A 0.2 μm pore syringe filter was used to take a sample of the liquid phase. Then, the concentration was measured by UV/visible spectrophotometry (JASCO UV–Visible/NIR spectrophotometer model V–700 Series) at 260 nm in the order to check equilibrium. The wavelength of 260 nm was determined to be most adequate for vanillic acid quantification because of its maximum absorbance at this wavelength. After 6 h, the concentration of vanillic acid in the liquid phase remained constant. The time period of 6 h was enough to reach equilibrium as reported previously [23–26]. The maximum deviation from the average value was found to be $\pm 5\%$. In addition, to confirm the reliability and accuracy of experimental apparatus and method, solubility data of gallic acid in methanol and methanol were compared with literature values [27] made in the previous work [24,25]. The uncertainty in the experimental solubility values is about 2%. It was proved that this experimental technique was reliable.

Consequently, experimental mole fraction solubility of vanillic acid (x_{VA}^{exptl}) in the aqueous ethanol mixtures was calculated using the following equation Eq. (1):

$$x_{VA}^{\text{exptl}} = \frac{m_{VA}}{\left(m_{VA} + \frac{1000}{(x_W \times M_W + x_M \times M_M)} \right)} \quad (1)$$

Table 1
The sources and purity of experimental materials.

Materials	Mass fraction purity	Melting temperature/K	Sources
Vanillic acid	>97.0%	482.95 ^a	Sigma-Aldrich
		485.15 ^b	
		484.9 ^c	
		483.0 ^d	
		480.5 ^e	
Methanol	~99.8%		Sigma-Aldrich
Water	Made from Maxima Ultra Pure Water (Elga-Prima Corp, UK) machine		

the relative standard uncertainty u are $u_r(p) = 0.05$.

^a This work was determined under 101.3 kPa. The standard uncertainty u are $u(T) = 0.5$ K, the relative standard uncertainty u are $u_r(p) = 0.05$.

^b Taken from reference [16].

^c Taken from reference [17].

^d Taken from reference [18].

^e Taken from reference [19].

In which, m_{VA} , x_W and x_M are the molality of vanillic acid, the mole fraction of water and methanol, respectively. M_{VA} , M_M and M_W are the molecular weights of vanillic acid, methanol and water, respectively. Experimental (x_{VA}^{exptl}) solubility of vanillic acid are presented in Table 2.

3. Results and discussion

3.1. Solubility data

The solubilities of vanillic acid in (water + methanol) mixed solvents with methanol mole fraction of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0, on a solute-free basis were determined at $T = (293.15, 298.15, 303.15, 308.15, 313.15$ and $318.15)$ K. Literature data for vanillic acid in mixed solvents was found only in the work of Zhang et al. [17]. In this work, the solubility of vanillic acid in ethanol at the temperature range of (293.15 to 318.15) K was also measured using the method used. The graphical correlation between experimental and literature solubilities of vanillic acid in ethanol is presented in Fig. 2. The results showed good correlation between experimental and literature values of vanillic acid in ethanol [17].

Vanillic acid solubilities in a binary (water + methanol) mixture are listed in Table 2 and shown in Fig. 3.

Based on obtained results shown in the Table 2 and Fig. 3, some conclusions can be drawn. (1) For each solvent composition studied, the equilibrium solubility mole fraction of vanillic acid increases with increasing temperature. (2) The solubility of vanillic acid in the mixed solvents decreases with the increasing of mole fraction of water. Similar results were reported by Cheng et al. [28] in their study of the solubility of triclin in (ethanol + water) at different temperatures.

3.2. Solubility modeling

In the present work, the obtained solubility data of vanillic acid in water, pure methanol and in binary solvents mixtures are correlated by three thermodynamic models, which are Van't Hoff equation Eq. (2), modified Apelblat equation Eq. (6), and λh equation Eq. (7). This additional study helps us to extend our solubility data basis of vanillic acid [15,20,21].

3.2.1. Van't Hoff equation

The solubility data of (VA) was fitted by a Van't Hoff equation [29, 30]. It is expressed as:

$$\ln x_{VA} = \frac{a}{T/K} + b \quad (2)$$

where x_{VA} is the mole fraction, T is the absolute temperature of the solution (K), a and b are the models constants. Table 3 presents the regressed values of a and b together with the root-mean-square deviations (RMSD) which is defined as.

$$RMSD = \left[\frac{1}{n} \sum_{i=1}^n \left(x_{VA}^{\text{calcd}} - x_{VA}^{\text{exptl}} \right)^2 \right]^{1/2} \quad (3)$$

where n is the number of experimental points, x_{VA}^{calcd} and x_{VA}^{exptl} are the calculated and the experimental solubility of vanillic acid in (methanol + water) mixed solvents, respectively. Calculated and experimental solubilities of vanillic acid, shown in Fig. 4 demonstrate a very good agreement. The relative deviations (RD) between the evaluated and the experimental values are also listed in Table 3. The RD is defined as:

$$RD = \frac{x_{VA}^{\text{exptl}} - x_{VA}^{\text{calcd}}}{x_{VA}^{\text{exptl}}} \quad (4)$$

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