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Solid–liquid phase equilibrium and dissolution properties of ethyl vanillin in pure solvents

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ABSTRACT

The solubility of ethyl vanillin (EVA) in eight pure solvents were determined in different temperature ranges from (273.15 to 318.15) K by a static analytical method. In the temperature ranges investigated, it was found that the solubility of EVA in all the selected solvents increased with the rising of temperature. Furthermore, four thermodynamic models were used to correlate the experimental solubility data and the calculation results showed that selected models can be used to correlate the solubility data with satisfactory accuracy. Finally, the dissolution thermodynamic properties, including dissolution Gibbs energy, dissolution enthalpy and dissolution entropy of EVA in the eight selected solvents were calculated.

1. Introduction

As one of the important separation and purification methods, solution crystallization are widely used to make many kinds of products, such as pharmaceuticals, fine chemicals, spices and so on. The design and operation of crystallization processes will directly affect the quality of the final product, such as purity, yield, and crystal characteristics. The physiochemical properties, including solubility and dissolution thermodynamics, are the foundation of crystallization process. Compared with other process parameters, solubility of solute in different solvents will determine the selection of crystallization method and the optimization of crystallization process [1–3]. Therefore, it is crucial to know the accurate equilibrium solubility data of target product in different solvents.

Ethyl vanillin (EVA, CAS Registry NO. 121-32-4), 3-ethoxy-4-hydroxybenzaldehyde ($C_9H_{10}O_3$, as shown in Fig. 1), is one kind of white or pale yellow acicular crystal. It has been widely used as the flavor additives in the foods, perfumes and commodity industries, and also as the medical intermediates for the pharmaceutical industry [4]. As one of the most valuable synthetic perfumes, EVA has gradually become a substitute for vanillin [5]. It sends out a strong chocolate flavor and the aroma is approximately 3.5 times as rich as the same amount of vanillin, which can reduce the cost and enhance economic efficiency of industrial production [6–8]. In the production of EVA, crystallization process is one of the important unit operation which will directly determine the quality of the final product. The thermodynamic data of EVA, such as solubility and dissolution enthalpy, is important for the designing and optimizing of the crystallization process of EVA. However, little information on the thermodynamic data of EVA can be found from literature.

In this work, the solubility data of EVA in different pure solvents (including methanol, ethanol, n-propanol, i-propanol, acetonitrile, acetone, methyl acetate and ethyl acetate) were obtained from 273.15 K to 318.15 K by the synthetic method [9–10]. The Apelblat equation, the λh equation and two local composition models (Wilson and NRTL model) were chosen to correlate and analyze the experimental solubility data of EVA. In addition, to understand the dissolution behavior of EVA in the selected solvents, dissolution thermodynamic properties, such as the dissolution Gibbs energy, dissolution enthalpy and dissolution entropy, were calculated and discussed, basing on the experimental solubility data and the Wilson model.

2. Experimental section

2.1. Materials

Ethyl vanillin (EVA) with purity (mass fraction) of 0.990, supplied by Aladdin Industrial Corporation, Shanghai, China, was used

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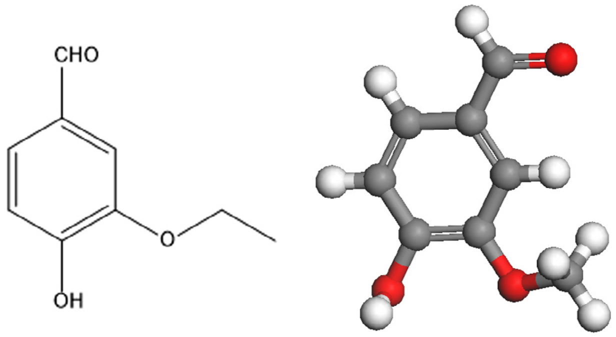

Fig. 1. Chemical (a) and sketch (b) of the molecule structure of EVA.

without further purification. All of the organic solvents used in this study, including methanol, ethanol, n-propanol, i-propanol, acetonitrile, acetone, methyl acetate and ethyl acetate, were purchased from Tianjin Jiangtian Chemical Co. of China with mass fraction purity higher than 0.995. The details, including source and purity of all the materials used in this work, are listed in Table 1.

2.2. X-ray powder diffraction

The crystal form of EVA used in this experimental was identified by the X-ray powder diffraction (XRPD) which was performed on a Rigaku D/max-2500 (Rigaku, Japan) using Cu Kα radiation (1.5405 Å) over a diffraction angle (2θ) range of 2°–50°, at a step size of 0.02° and a scanning rate of $0.067°\cdot s^{-1}$, with an electric current of 100 mA, and a voltage of 40 kV.

2.3. Differential scanning calorimetry

The differential scanning calorimetry (DSC 1/500, Mettler-Toledo, Swizerland) was used to obtain the melting temperature T_m and enthalpy of fusion $\Delta_{fus}H$ of EVA. The sample was scanned from 298.15 K to 373.15 K under a protection of nitrogen ($100\ mL\ min^{-1}$) at a heating rate of 10 K/min. Indium ($T_m = 429.8$ K; $\Delta_{fus}H = 0.25\ J\cdot mol^{-1}$) and n-dodecane ($T_m = 263.5$ K; $\Delta_{fus}H = 1.27\ J\cdot mol^{-1}$) were used to calibrate the instrument and an empty pan was used as reference.

2.4. Solubility measurement

The solubility of EVA in different pure solvents was determined by a gravimetric method that has been detailedly described in previous published literature [11–13]. The process can be briefly explained as follow. To begin with, excess amounts of solid state EVA was added into a jacketed glass vessel which contains a known amount of pure solvent. The temperature of solution was controlled by a thermostat (CF41, Julabo, Germany) with an uncertainty of ±0.05 K. The solution was agitated by a magnetic stirrer for 8 h to reach solid-liquid equilibrium. Afterwards, the agitation was stopped and the solution was kept static for 4 h to allow the undissolved particles to settle down. Then, about (1–3) mL upper clear saturated solution was taken out by a pre-heated (or pre-cooled) syringe with a 0.2 μm PTFE filter and moved into a pre-weighted beaker. The weight of solution and beaker was immediately measured using an electronic analytic balance (Mettler Toledo ML204, Swizerland) with an uncertainty of ±0.0001 g. Finally, the beaker was placed into a vacuum oven at 333.15 K for about 20 h until the total weight of solution and beaker did not change. The above process was repeated three times and the average value was used as the final result. The mole fraction solubility (x_1) of EVA in pure solvents can be calculated as the following equation [14].

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{1}$$

where m_1 and m_2 is the mass of the solute and solvent, respectively; M_1 and M_2 represent the molecular weight of EVA and the solvent.

3. Thermodynamic models

3.1. The modified Apelblat equation

The modified Apelblat equation is a widely used semi-empirical equation which was deduced from the Clausius-Clapeyron equation. It can be used to correlate the solid-liquid equilibrium and the equation is shown as following [15,16].

$$\ln x_1 = A + \frac{B}{T} + C \ln T \tag{2}$$

where x_1 is the mole fraction solubility of solute, T refers to the absolute temperature. A, B and C are empirical parameters. A and B refer to variation of activity coefficient in real solution, and C represents the effect of temperature on the fusion enthalpy.

3.2. The λh equation

The λh model, which was derived by Buchowski et al., is an empirical formula to describe the solid-liquid phase equilibrium system as following [17,18].

$$\ln\left[1 + \lambda\left(\frac{1 - x_1}{x_1}\right)\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right) \tag{3}$$

Table 1
The sources and mass fraction purity of the materials used in this paper.

Chemical name	Source	Mass purity	Purification method	Analysis method
EVA	Aladdin Industrial Co., Shanghai, China	0.990	None	HPLC [a]
Methanol	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]
Ethanol	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]
n-Propanol	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]
i-propanol	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]
Acetonitrile	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]
Acetone	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]
methyl acetate	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]
Ethyl acetate	Jiangtian Chemical Technology Co., Ltd., Tianjin, China	>0.995	None	GC [b]

[a] High-performance liquid chromatography, which was carried out by Aladdin Industrial Co., Shanghai, China.
[b] Gas chromatography, which was carried out by Jiangtian Chemical Technology Co., Ltd., Tianjin, China.