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Solubility and solution thermodynamics of Raspberry Ketone in pure organic solvents and binary solvent mixtures from T = (293.15 to 333.15) K

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ABSTRACT

The target of this work is to measure and correlate the solubility of Raspberry Ketone, and obtain the thermodynamic parameters simultaneously. In this study, the solubility of Raspberry Ketone in nine mono-solvents, including ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, acetic acid, methyl acetate, ethyl acetate, acetone, and binary mixtures of ethanol + acetone (the mass fraction of ethanol varied from 0.1 to 0.9, in intervals of 0.1) was measured at (293.15 to 333.15) K in atmospheric pressure by shake-flask method. The solubility of Raspberry Ketone both in mono- solvents and mixtures increased as the temperature increased. The deliquescent rules can be acquired by using modified Apelblat equation, van't Hoff equation, λh equation, Wilson model, Non-Random Two Liquid (NRTL) model, Universal Quasi–Chemical (UNIQUAC) Model and modified Jouyban-Acree model. The experimental data show highly conformance with the calculated data which obtain from all the selected models. Consequently, the solubility results of this study would be useful in purification, crystallization, recrystallization and a new synthetic route design of Raspberry Ketone.

1. Introduction

Raspberry Ketone, also known as 4-(4-hydroxyphenyl)-2-butanon, is found in natural raspberry juice which contain 0.15×10^{-6} mol·L^{-1}. As a natural flavor, Raspberry Ketone is widely used in food industry, cosmetic industry, agriculture, medicine manufacture etc. When used as an edible flavor, it can product strawberries, pineapples, peaches and plums spices. With certain whitening effect and anti-inflammatory effect, Raspberry Ketone is broadly applied in the synthesis of cosmetics, as well as fragrance materials production such as jasmine, tuberose perfume [1]. In medicine, the compound play an important role in the synthesis of the intermediate of polyamine and the treatment of nonalcoholic Steatohepatitis. It also has the function of anti-aging, anti-oxidation, hypoglycemic and so on [2].

Nonetheless, the source of nature Raspberry Ketone is too scarce to maintain the market's normal needs. A new and efficient synthetic route is urgent to be designed. Thus plenty of scholars pay great attention to the synthesis of Raspberry Ketone [3–5]. Study on the solubility and solution thermodynamics of Raspberry Ketone in different solvents, predicting the dissolution behavior and analyzing the dissolution phenomenon, is the valid way to obtain deliquescent rules. It is of great significance to improve the quality and yield of Raspberry Ketone, as well as to provide strong theoretical support for industrial production design.

The organics Raspberry Ketone is a white acicular crystalline or granular solids which gives off raspberry aromas and sweet flavor. For Raspberry Ketone, the formula is $C_{10}H_{12}O_2$, molar mass is 164.2 g·mol^{-1}, melting point is about 85 °C, CAS RN is 5471-51-2, the molecular structure is showed in Fig. 1. There are two production processes applied currently. One is condensed by hydrogenation of benzaldehyde and acetone [6], and the other is condensed from butanone acid with phenol [7]. No matter what route is used, production will eventually need to be refined to improve the quality and yield of the product. Crystallization and recrystallization are good ways to improve the purity of Raspberry Ketone. Using this method, we need to know the solubility data and thermodynamic parameters of Raspberry Ketone in various solvents so as to select the most suitable solvent for recrystallization operation according to the actual operating conditions. This is also the purpose of the subject.

In this study, the solubility of Raspberry Ketone in nine mono-solvents, including ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, acetic acid, methyl acetate, ethyl acetate, acetone, and binary mixtures of ethanol + acetone (the mass fraction of ethanol varied from 0.1 to 0.9, in intervals of 0.1) was measured at atmospheric pressure with experimental temperature rising from 293.15 K to 333.15 K. Modified

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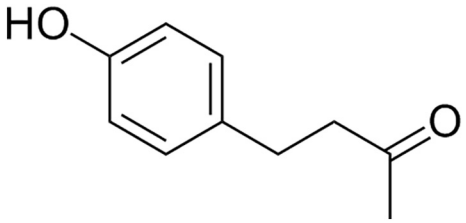

Fig. 1. Molecular structure of Raspberry Ketone.

Apelblat equation [8–12], van't Hoff equation [13], λh equation [14,15], Wilson model [16,17], Non-Random Two Liquid (NRTL) model [18,19], Universal Quasi–Chemical (UNIQUAC) Model [20,21] and modified Jouyban-Acree model [22–24] were used to establish solvation mathematical model. The model parameters could be gained synchronously. Furthermore, the thermodynamic functions (Gibbs free energy, the dissolution enthalpy, the dissolution entropy) were calculated. In order to select the most suitable solvation mathematical model, the experimental values were compared with the calculated ones. By calculating the relative deviations, the relative average deviations, we can choose the accurate model to predict the solubility of Raspberry Ketone at different temperatures.

2. Experimental

2.1. Materials

The chemical Raspberry Ketone was supplied by Beijing Bailingwei Technology Co., Ltd. Its mass fraction purity is higher than 0.99. The nine mono-solvents of ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, acetic acid, methyl acetate, ethyl acetate, acetone were purchased from Beijing Chemical Works of China with the mass fraction higher than 0.995. Both the compound and solvents used in this research without further purification, and the details of materials are listed in Table 1.

2.2. Differential scanning calorimetry

The thermodynamic parameters are indispensable data in the dissolution process. As the basic ones, the melting point T_m and the fusion enthalpy $\Delta_{fus}H$ of Raspberry Ketone were determined by differential scanning calorimetric (DSC). The differential perusing calorimetric instrument (TGA/DSC1/1600LF, Mettler Toledo Co., Switzerland) was calibrated by using high purity indium and tin sample in a nitrogen atmosphere. About 5 mg Raspberry Ketone without any pretreatment sample was added to an airtight DSC pan, with a heating rate of 10 $K \cdot min^{-1}$. The standard uncertainty of experiments were calculated to be 0.2 K for T_m and 0.02 $kJ \cdot mol^{-1}$ for the $\Delta_{fus}H$ [25,26].

Table 1
Sources and Purity of materials in the experiments.

Chemical	Mass fraction purity	Source	Analysis method
Raspberry Ketone	≥0.990	Beijing Bailingwei Technology Co., Ltd.	HPLC[a]
ethanol	≥0.995	Beijing Chemical Works, China	GC[b]
1-Propanol	≥0.995	Beijing Chemical Works, China	GC[b]
2-Propanol	≥0.995	Beijing Chemical Works, China	GC[b]
1-Butanol	≥0.995	Beijing Chemical Works, China	GC[b]
2-Butanol	≥0.995	Beijing Chemical Works, China	GC[b]
Acetic acid	≥0.995	Beijing Chemical Works, China	GC[b]
Methyl acetate	≥0.995	Beijing Chemical Works, China	GC[b]
Ethyl acetate	≥0.995	Beijing Chemical Works, China	GC[b]
Acetone	≥0.995	Beijing Chemical Works, China	GC[b]

[a] High-performance liquid chromatography.
[b] Gas chromatography.

The melting point of Raspberry Ketone is 84.43 °C. The fusion enthalpy $\Delta_{fus}H$ is $-138.57\ J \cdot g^{-1}$, which is translated to $-22.75\ kJ \cdot mol^{-1}$ by multiplying by molar mass. The DSC curve is shown in Fig. 2.

2.3. Solubility measurement

Multifarious experimental methods have been reported to measure chemicals solubility [27–31]. In our work, shake-flask method [13] was used to determine the solubility of Raspberry Ketone. Briefly, the excess solutes are placed in the conical flasks (the capacity is 100 mL) with solvent respectively. The bottles were maintained at a specified temperature from 293.15 K to 333.15 K by shaker-incubator (Shanghai Yiheng Scientific Instrument Co., LTD) and allowed to equilibrate. In the condition that flasks reach the solid-liquid equilibrium state, the actual temperature was measured by mercury thermometer (the standard uncertainty of temperature u(T) = 0.1 K) which was placed in a conical flask with deionized water. The oscillation time and the static duration are determined by preliminary experiments and literature reference. Thus the 72 h for shaking, 48 h for static settlement are the suitable schedule. Subsequently, the supernatant was taken by syringe (the volume is 5 mL), then poured into an evaporating dish which had been weighed by analytical balance (Sartorius CP124S, Germany) with an accuracy of ±0.0001 g immediately. The evaporating dish marked with numbers were placed in vacuum drying oven (Tianjin Taisite Instrument Co., Ltd.) at temperature of 313.15 K which were dried until two adjacent weights could not exceed ±0.0005 g. Repeat the procedures in triplicates, and take average value as the final experimental data. The mole fraction solubility of Raspberry Ketone (x_1) in mono-solvents was calculated by Eq. (1)

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

where m_1 and m_2 represent the mass of Raspberry Ketone and the solvent; M_1 and M_2 represent the respective molar mass.

The ethanol and acetone mixed solvents were prepared by mass quantities of 40.000 g with the electronic analytical balance. The mass fraction of ethanol (w_2) in mixed solvents varied from 0.1 to 0.9 in intervals of 0.1 which equation quoted as Eq. (2)

$$w_2 = \frac{m_2}{m_2 + m_3} \tag{2}$$

where m_2 and m_3 are the mass of the ethanol and acetone, respectively.

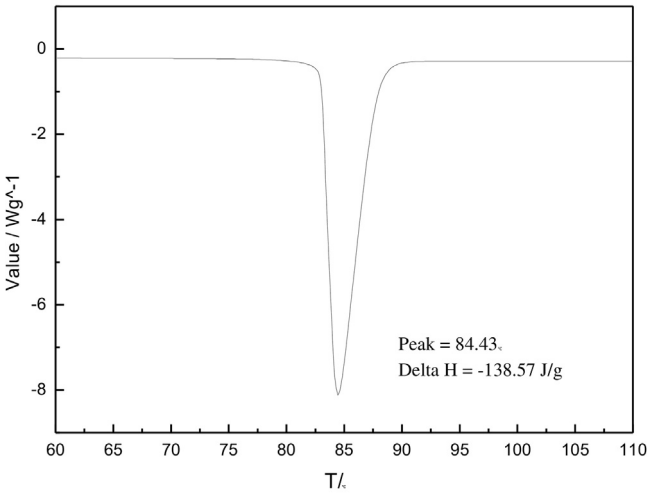

Fig. 2. DSC curve of Raspberry Ketone.