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Review

Thermodynamic equilibrium of 4-hydroxy-2,5-dimethyl-3(2H)-furanone in different solvent systems

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ABSTRACT

Crystalline state 4-hydroxy-2,5-dimethyl-3(2H)-furanone with high purity was prepared by recrystallization. Powder X-ray diffraction pattern (PXRD) and differential scanning calorimetry (DSC) were used to identify and characterize the samples. The solubility of 4-hydroxy-2,5-dimethyl-3(2H)-furanone samples in six pure solvents and one kind of binary solvent system from (283.15 to 318.15) K was determined by using a gravimetric method under atmospheric pressure. To extend the application range of the experimental solubility data, the modified Apelblat equation, the van't Hoff equation and the λh equation were used to correlate the experimental solubility in the pure solvents. For the correlation of binary solvent systems, the CNIBS/R-K model and Jouyban–Acree model were used instead. According to the Akaike Information Criterion (AIC), the λh equation was found to be better for pure solvent systems and the Jouyban–Acree model was confirmed to be better for binary solvent systems. In addition, the dissolution thermodynamic properties of 4-hydroxy-2,5-dimethyl-3(2H)-furanone were also calculated by the van't Hoff equation.

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1. Introduction

4-Hydroxy-2,5-dimethyl-3(2H)-furanone (HDMF, Furaneol, CAS Registry No: 3658-77-3, figure 1), as a natural flavour component which has a strong caramel-like odor, is extensively used as food flavouring due to its low odour threshold at 160 $\mu g \cdot L^{-1}$ and flavour enhancing properties [1,2]. HDMF widely exists in fruits such as pineapples, strawberries, citrus etc. It can be isolated from a variety of food fermentations like beer, sauce, miso and cheese [3,4]. It is also an important reaction intermediate for producing muscarine in pharmaceutical industry.

It is well-known that crystallization is a key step during manufacturing processes of HDMF, which will directly affect the quality of final products, including particle size, purity, yield and so on. In order to design an optimized crystallization process, it is essential to know the physicochemical and thermodynamic properties of HDMF. Solubility is one of the most important properties that has a major impact on the design and optimization of the crystallization process. No quantitative solubility data of HDMF have been reported through the bibliographic retrieval to our knowledge.

In this work, crystalline state HDMF with high purity was prepared by recrystallization. PXRD and DSC were used to identify and characterize the obtained samples. The solubility data of HDMF samples in six pure solvents (methanol, ethanol, ethyl acetate, butyl acetate, isopropyl acetate and water) and mixed solvents (ethanol + water) were experimentally determined over the temperature range from (283.15 to 318.15) K by using a gravimetric method. The modified Apelblat equation, the λh equation and the van't Hoff equation were used for correlating the experimental solubility data of HDMF in pure solvents and the CNIBS/R-K model and Jouyban–Acree model were applied for the binary solvent mixtures. In addition, the Akaike Information Criterion (AIC) was introduced to evaluate the models used in this work. Furthermore, the molar dissolution enthalpy, entropy and Gibbs energy change during the dissolution process were also deduced by using the van't Hoff equation.

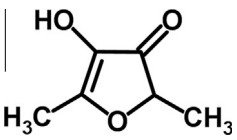

FIGURE 1. Chemical structure of HDMF.

2. Experimental

2.1. Materials

The details of all the materials used in this work are listed in table 1. HDMF was supplied by Bestally Spice Co., Ltd. of China. HDMF samples used in this study were purified by recrystallization from ethanol solution. Its mass fraction purity was higher than 0.999, which was determined by high-performance liquid chromatography (HPLC, Agilent 1100, Agilent Technologies, USA). The crystal forms of HDMF used in this work were also identified and characterized by PXRD and DSC. Methanol, ethanol, ethyl acetate, butyl acetate and isopropyl acetate, which were purchased from Tianjin Jiangtian Chemical Co., Ltd., China, were analytical grade reagents (mass fraction purity $\geqslant 0.995$). The distilled-deionised water was provided by Nankai University, China.

2.2. Apparatus and methods

The solubility was determined by using a gravimetric method as described in references [5,6]. Excess amount of HDMF was added into a 50 mL double-jacketed glass vessel containing solvents. A thermostat (type 501A, Shanghai Laboratory Instrument Works Co., Ltd., China) was utilized to control the temperature of the solution, of which the accuracy is ±0.05 K. First of all, the (solid + liquid) mixtures were kept under agitation for 10 h, which was experimentally verified to be long enough to reach equilibrium. After that, the agitation was stopped and the solution was kept still for 3 h at constant temperature. Then the saturated supernatant was withdrawn into a Petrie dish through a membrane filter (0.2 μm). The dishes were dried in a vacuum oven at $T = 303.15$ K under 0.05 MPa until the mass of samples did not change any more. The mass of samples was measured with an analytical balance (type AB 204, Mettler Toledo, Switzerland) with an accuracy of ±0.0001 g. The same experiment was repeated three times and the average data were used to calculate the solubility data.

The mole fraction solubility of HDMF was calculated by the following equation [7]:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + \sum(m_i/M_i)} \quad (1)$$

where x_1 represents the mole fraction solubility of HDMF; m_1 and m_i represent the mass of HDMF and the solvents respectively; M_1, M_i represent the molecular mass of HDMF and solvents, respectively.

TABLE 1
Details of HDMF and solvents.

Material	Mass fraction purity	Source	Purification method	Analysis method
HDMF	⩾0.999	Bestally Spice Co., Ltd., China	Recrystallization	HPLC[a]
Methanol	⩾0.995	Tianjin Jiangtian Chemical Co., Ltd., China	None	GC[b]
Ethanol	⩾0.995	Tianjin Jiangtian Chemical Co., Ltd., China	None	GC[b]
Ethyl acetate	⩾0.995	Tianjin Jiangtian Chemical Co., Ltd., China	None	GC[b]
Butyl acetate	⩾0.995	Tianjin Jiangtian Chemical Co., Ltd., China	None	GC[b]
Isopropyl acetate	⩾0.995	Tianjin Jiangtian Chemical Co., Ltd., China	None	GC[b]

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