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Solubility and solution thermodynamics of 2,5-thiophenedicarboxylic acid in (water + ethanol) binary solvent mixtures

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ABSTRACT

In this paper, we focused on solubility and solution thermodynamics of 2,5-thiophenedicarboxylic acid. By gravimetric method, the solubility of 2,5-thiophenedicarboxylic acid was measured in (water + ethanol) binary solvent mixtures from 278.15 K to 333.15 K under atmosphere pressure. The solubility data were fitted using modified Apelblat equation, a variant of the combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) model and Jouyban–Acree model. Computational results showed that the modified Apelblat equation has the lowest MD (mean deviation). In addition, the thermodynamic properties of the solution process, including the Gibbs energy, enthalpy, and entropy were calculated by the van't Hoff analysis.

1. Introduction

At present, the thiophene-containing compounds are attracting great interest due to their applications such as semi-conductors, liquid crystals, light emitting diodes, etc. [1]. 2,5-Thiophenedicarboxylic acid (Fig. 1, $C_6H_4O_4S$, CASRN:4282-31-9), an important organic intermediate, has been employed widely in the synthesis of a fluorescent brightening agent, an efficient agricultural fungicide and an anticancer drug [2]. The biggest use of 2,5-thiophenedicarboxylic acid is for producing the 2,5-bis-benzoxazoyl-thiophene (EBF), which is used in terylene, chinlon, plastic, and coating etc. [3]. More recently, 2,5-thiophenedicarboxylic acid is employed in the construction of metal–organic framework to produce a variety of properties including magnetic property, luminescent property, dielectric bistability and so on [4,5]).

In industrial mass production, 2,5-thiophenedicarboxylic acid is synthesized by chlorinating adipic acid and thionyl chloride (Fig. 2) [6]. As the purity is a significant part of a chemical substance, this work aims to provide some useful data to the recrystallization process of 2,5-thiophenedicarboxylic acid. To our knowledge, we find no report of the solubility of 2,5-thiophenedicarboxylic acid in (water + ethanol) binary solvent mixtures.

In this work, the solubility of 2,5-thiophenedicarboxylic acid in (water + ethanol) binary solvent mixtures was measured from 278.15 K to 333.15 K under atmosphere pressure. The modified Apelblat equation, a variant of the combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) model and Jouyban–Acree model were applied to correlate with the experimental data. The thermodynamic properties of the dissolution process, including enthalpy, entropy and Gibbs energy, were calculated by means of van't Hoff analysis and Gibbs equation.

2. Experimental

2.1. Materials and apparatus

2,5-Thiophenedicarboxylic acid, a white crystalline powder with a mass fraction purity of ≥0.980 was from Aladdin Reagent Co., Ltd. The double distilled water was produced by our laboratory with an ultrapure water system from Shandong Flom Co., Ltd. Ethanol (Shanghai Shenbo Chemical Co., Ltd.) was of analytical reagent grade with a purity higher than 0.997. More details about the solvents along with their CAS registry numbers are listed in Table 1. Analytical balance (model CPA225D) was provided by Satorius Scientific Instrument (Beijing) Co., Ltd., with an

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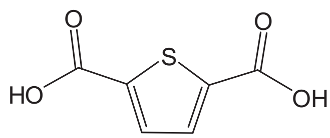

Fig. 1. Chemical structure of 2,5-thiophenedicarboxylic acid.

uncertainty of ±0.00001 g. Smart thermostatic bath (model: DC-2006) was provided by Ningbo Scientz Biotechnology Co., Ltd., with an uncertainty of ±0.1 K.

2.2. Methods

The method of measuring solubility is similar to our previous work [7–9]. 8 mL solvent mixtures and some excess 2,5-thiophenedicarboxylic acid were added into a 10 mL glass test tube with a stopper. The test tube was kept in a jacket glass vessel full of water, whose temperature was maintained at the desired value by circulating water through the outer jacket from a smart thermostatic water-circulator bath. Magnetically stirrers were used to mix the solid and binary solvent mixtures adequately. In order to ensure the solution reaching equilibrium, this stirring process would last at least 24 h. Then the magnetically stirrers were stopped and the solution was let to settle down, which took another 6 h. At last, 1 mL solution supernatant was transferred into a 5 mL beaker with a cover and weighted immediately. Of course, this beaker had been weighted before. All beakers were put into a dryer and weighted weekly until reaching constant weight. Each experiment was conducted three times, and the mean value was used to calculate the mole fraction solubility. The mole fraction solubility of 2,5-thiophenedicarboxylic acid (x) in (water + ethanol) binary solvent mixtures is calculated by Eq. (1). The mole fraction of ethanol (x_A) in the binary solvent mixtures is defined using Eq. (2).

$$x = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \quad (1)$$

$$x_A = \frac{m_2/M_2}{m_2/M_2 + m_3/M_3} \quad (2)$$

where m_1,m_2, m_3 represent the mass of 2,5-thiophenedicarboxylic acid, ethanol, water, and M_1, M_2, M_3 represent the molar mass of the 2,5-thiophenedicarboxylic acid, ethanol, water, respectively.

3. Results and discussions

3.1. Solubility data and correlation models

The solubility data of 2,5-thiophenedicarboxylic acid (x) in (water + ethanol) binary solvent mixtures with the temperature ranging from 278.15 K to 333.15 K are presented in Table 2. In order to compare the solubility under different condition vividly, these data are presented in Fig. 3.

3.2. Modified Apelblat equation

The changing trends of solubility against temperature in the solvent with same ratio are described by the modified Apelblat equation. This model is firstly used by Apelblat [10,11] which can give a relatively accurate correlation with three parameters:

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C\,\ln\left(\frac{T}{\mathrm{K}}\right) \quad (3)$$

where x represents the mole fraction solubility of 2,5-thiophenedicarboxylic acid, T is the experimental temperature in K, and A, B and C are the regression curve parameters in the equation which are listed in Table 3.

3.3. CNIBS/R–K model

The changing trends of solubility against different ratio of ethanol under isothermal condition are described by the combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) model [12–15], which is one of the theoretical models for calculating the solute solubility in binary solvents and represented in Eq. (4):

$$\ln\, x = x_A\,\ln X_A + x_B \ln X_B + x_A x_B \sum_{i=0}^{N} S_i (x_A - x_B)^i \quad (4)$$

where x represents the mole fraction solubility of 2,5-thiophenedicarboxylic acid. x_A and x_B represent the initial mole fraction composition of the binary solvent when the solute was not added. X_A and X_B respectively represent the saturated mole solubility of 2,5-thiophenedicarboxylic acid in pure ethanol and water. S_i is the model constant and N can be equal to 0, 1, 2 and 3. When $N = 2$ and substituting $(1 - x_A)$ for x_B, Eq. (4) can be rearranged as:

$$\ln x - (1 - x_A)\ln X_B - x_A \ln X_A = (1 - x_A)x_A[S_0 + S_1(2x_A - 1) + S_2(2x_A - 1)^2] \quad (5)$$

This is a variant of CNIBS/R–K model. The parameters S_i could be obtained by regressing

$\{\ln\ x - (1 - x_A)\ \ln X_B - x_A\ \ln\ X_A\}$ versus

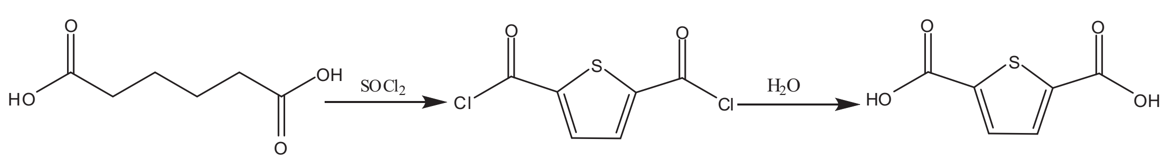

Fig. 2. Synthesis method of 2,5-thiophenedicarboxylic acid in industrial mass production.

Table 1
Mass fraction purities of 2,5-thiophenedicarboxylic acid and solvents with CAS registry number.

Compound	Source	Mass fraction purity	CAS No.
2,5-Thiophenedicarboxylic acid	Aladdin Reagent Co., Ltd.	≥0.980	4282-31-9
Ethanol	Shanghai Shenbo Chemical Co., Ltd	≥0.997	64-17-5
Water	Our Laboratory	Double distilled	7732-18-5