



Determination and correlation of solubility and thermodynamic properties of pyraclostrobin in pure and binary solvents



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ABSTRACT

The solubility of pyraclostrobin in five pure solvents and two binary solvent mixtures was measured from 283.15 K to 308.15 K using a static analytical method. Solubility in five pure solvents was well correlated by the modified Apelblat equation and Wilson model. While the CNIBS/R–K model was applied to correlate the solubility in two binary solvent mixtures, the correlation showed good agreement with experimental results. The solubility of pyraclostrobin reaches its maximum value at a certain cyclohexane mole fraction in the two binary solvent mixtures. The solubility parameter of pyraclostrobin was calculated by the Fedors method and a new modified mixing rule with preferable applicability was proposed to determine the solubility parameter of solvents. Then the co-solvency in the binary solvent mixtures can be explained based on the obtained solubility parameters. In addition, the dissolution thermodynamic properties were calculated from the experimental values using the Wilson model.

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1. Introduction

Pyraclostrobin ($C_{19}H_{18}ClN_3O_4$, CAS No. 175013-18-0, Fig. 1), is a broad spectrum fungicide with protectant and curative properties developed by BASF [1]. It is an effective strobilurins fungicide for vegetables, peanuts, cereals and other field crops with good safety [2]. Because of the extensive and flexible applications, pyraclostrobin is classified as “reduced risk candidate” by the United States Environmental Protection Agency [1].

Many studies have focused on the functional mechanism of pyraclostrobin, but few attempt to seek a better method to manufacture pyraclostrobin with high quality. Solution crystallization is a significant procedure to separation and purification in industry, whose design and optimisation highly depend on solubility [3,4]. However, there was no solubility of pyraclostrobin reported in previous studies.

In this study, a static analytical method was adopted to measure the solubility of pyraclostrobin in ethanol, isopropanol, *n*-butanol, isobutanol, cyclohexane and (isopropanol + cyclohexane), (*n*-butanol + cyclohexane) mixtures at temperatures ranging from

283.15 K to 308.15 K under atmospheric pressure. The modified Apelblat equation and Wilson model were employed to correlate the experimental solubility in pure solvents, and the solubility in binary solvent mixtures was correlated by the CNIBS/R–K model. Using the Fedors method, the solubility parameter was calculated to explain the co-solvency in binary solvent mixtures. To calculate the solubility parameters of binary solvent mixtures accurately, a modified mixing rule was proposed. In addition, the dissolution thermodynamic properties (Gibbs energy, entropy and enthalpy) in pure solvents were calculated using the Wilson model and discussed for further understanding of the dissolution behaviour.

2. Experiment

2.1. Materials

Pyraclostrobin (≥ 0.990 mass fraction) was provided by Shandong Sino-Agri United Biotechnology Co., Ltd., China. The purity of pyraclostrobin was determined by HPLC (Agilent 1100, Agilent Technologies, USA). The organic solvents used in the experiment including ethanol, isopropanol, *n*-butanol, isobutanol and cyclohexane, are analytical grade (≥ 0.995 mass fraction) and were purchased from Tianjin Kewei Chemical Co., China. The above-mentioned materials were used without further purification and the details about these chemicals are listed in Table 1.

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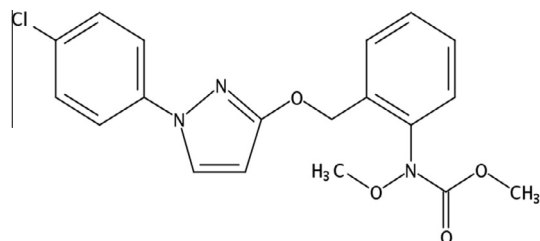


Fig. 1. Molecular structure of pyraclostrobin.

2.2. X-ray powder diffraction

To confirm the polymorph of pyraclostrobin used in this experiment, the X-ray powder diffraction (XRPD) was used. The experiment was carried out using the D/MAX-2500 (Rigaku, Japan) by Cu K α radiation (0.15405 nm) over a diffraction angle (2θ) range of 2–50° with a scanning rate of 1 step·s⁻¹. Raw pyraclostrobin and excess pyraclostrobin in solvents were analysed by XRPD and the patterns are shown in Fig. 2.

2.3. Differential scanning calorimetry

The melting temperature T_m and the enthalpy of fusion $\Delta_{fus}H$ of pyraclostrobin were determined by differential scanning calorimetry (DSC 1/500, Mettler-Toledo, Switzerland) under the protection of nitrogen gas flow. A pinch of pyraclostrobin (about 6 mg) was placed in a standard DSC aluminium pan and heated from 293.15 K to 358.15 K at the rate of 2 K·min⁻¹.

2.4. Solubility measurements

The solubility of pyraclostrobin was determined by the static analytical method [5–7]. Excessive amount of pyraclostrobin and about 25 mL solvent (pure solvent or prepared binary solvent mixtures) were added into a 50 mL Erlenmeyer flask. After that, the Erlenmeyer flask was maintained at the setting temperature controlled by a shaker (Tianjin Ounuo Instrument Co., China) with an inaccuracy of 0.05 K. Then the solution was constantly stirred for 24 h, which was confirmed that 24 h were sufficient to reach solid–liquid equilibrium. After that it was kept static for 2 h to allow the solid phase to precipitate. Then the supernatant was withdrawn by a syringe and injected into a pre-weighed 10 mL beaker through an organic filter membrane (0.45 μ m). The syringe and organic filter membrane were pre-heated/cooled. Finally, the beaker with the solution was weighed immediately and placed into an electric blast drying oven at $T = 308.15$ K until the weight remained constant. In the experiment, the solution and beaker were weighed by an electronic analytical balance (ML204, Mettler Toledo, Switzerland) with an accuracy of 0.0001 g. Each experiment was repeated three times and the mean value was adopted to calculate the solubility in different solvents.

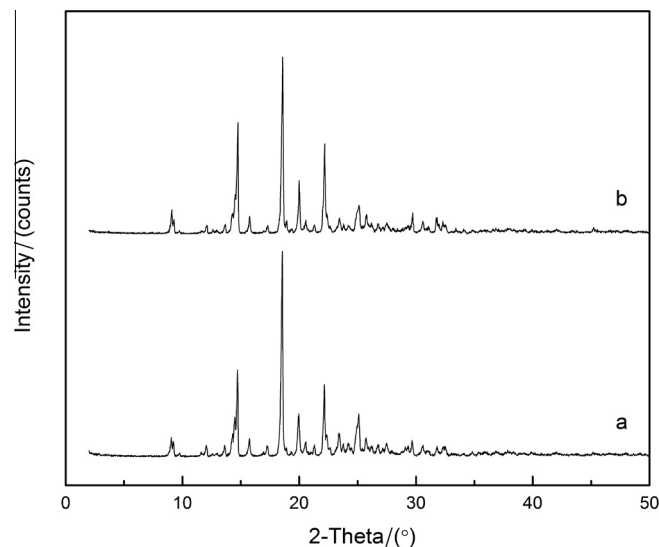


Fig. 2. X-ray power diffraction pattern of pyraclostrobin: (a) raw material; (b) excess solid in solvents.

In pure solvents:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

In binary solvent mixtures:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3} \quad (2)$$

Here x_1 is the mole fraction solubility of pyraclostrobin; m_1 refers to the mass of solute, m_2 and m_3 represent the mass of the solvents that constitute the solution. M_1 , M_2 and M_3 are the corresponding molecule mass of each solvent [7].

3. Thermodynamic models

3.1. Modified Apelblat equation

The modified Apelblat equation is a frequently used semi-empirical model, which is applied to correlate the mole fraction solubility and the absolute temperature in pure and mixed solvents. It is based on the solid–liquid equilibrium theory and can be expressed as follows [8,9]

$$\ln x_1 = A + B/T + C \ln T \quad (3)$$

where x_1 is the mole fraction solubility of pyraclostrobin; T represents the absolute temperature; A , B , and C are model constants.

Table 1
Sources and purity of the materials.

Chemical name	Source	Mass purity	Analysis method
Pyraclostrobin	Shandong Sino-Agri United Biotechnology Co. Ltd.	≥ 0.990	HPLC ^a
Ethanol	Tianjin Chemical Technology Co. Ltd	≥ 0.995	GC ^b
Isopropanol	Tianjin Chemical Technology Co. Ltd	≥ 0.995	GC ^b
<i>n</i> -butanol	Tianjin Chemical Technology Co. Ltd	≥ 0.995	GC ^b
Isobutanol	Tianjin Chemical Technology Co. Ltd	≥ 0.995	GC ^b
Cyclohexane	Tianjin Chemical Technology Co. Ltd	≥ 0.995	GC ^b

^a High performance liquid chromatography.

^b Gas chromatography.

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