



# Measurement and correlation of solubility of pronamide in five organic solvents at (278.15–323.15) K



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## ABSTRACT

The solubility of pronamide in five organic solvents (ethanol, methanol, isopropanol, toluene and cyclohexane) at the temperature range from (278.15 to 323.15) K was measured by a dynamic equilibrium method. The results showed that the solubility of pronamide increased with the increasing temperature in all the solvents involved. The experimental values were correlated by the Apelblat equation, and a good fitting result was confirmed by the low level of root-mean-square deviations ( $<4.0 \times 10^{-4}$ ). Moreover, the apparent dissolving enthalpies and entropies, were derived from simplified van't Hoff equation. The positive values of enthalpies and entropies revealed that the dissolution of pronamide in the selected solvents was an endothermic and entropy-driven process.

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## 1. Introduction

Pronamide (3,5-Dichloro-N-(1,1-dimethyl-2-propynyl) benzamide, CAS Registry No. 23950-58-5, presented in Fig. 1) is a selective herbicide, whose action mode is to interfere with mitosis in the root systems of a select group of weeds [1,2]. It is the active ingredient in many herbicide formulations [3]. Pronamide has been successfully used as a pre- and post-emergent herbicide for various plants all over the world in the past thirty years [4–8], and demonstrated to have a distinctive efficiency on the control of broad-leaved weeds.

Pronamide was first developed and synthesized in early 20th century by Rohm & Haas Co., the purity of which was a little higher than 95% [9]. Then the synthetic method was improved a lot as much effort was focused on it, and the purity was increased to 98% by Dow AgroSciences LLC recently. As the technical products may display different toxicities if the impurities possess toxicologic properties [10], research work is still needed to enhance the purity further. It has been reported in the literature that pronamide can be purified by recrystallization from methanol [11]. Therefore thermodynamic data are needed for the design of the recrystallization process. However, up to now, most research work was focusing on the synthesis, metabolism and toxicology of pronamide [12–15], but no solution dynamics were reported.

In this work, the solubility of pronamide in five pure organic solvents (ethanol, methanol, isopropanol, toluene and cyclohex-

ane) was determined at the temperature range from 278.15 K to 323.15 K, and the solubility values were correlated by the Apelblat equation. Solution thermodynamic parameters, such as enthalpy, entropy and Gibbs energy, were calculated from the modified van't Hoff equation. The relative contribution rates of enthalpies and entropies to Gibbs energy were discussed, simultaneously.

## 2. Experimental

### 2.1. Materials

Pronamide was purchased from Chengdu Yuancheng Group Chemistry Co., Ltd. China, and was recrystallized from methanol before used, whose final mass fraction purity was 0.990 determined by high-performance liquid chromatography. The crystal structure of pronamide was determined by X-ray single-crystal and powder diffraction, and the relevant information is given in Fig. 2 and Table 1. The solvents (ethanol, methanol, isopropanol, toluene and cyclohexane) of analytical grade were obtained from Kemiou Chemical Reagent Co., Ltd. China. They were directly used without any purification.

The detailed information is presented in Table 2.

### 2.2. Solubility measurements

The solubility of pronamide at the temperature range from 278.15 K to 323.15 K was measured by a dynamic method using the laser-monitoring technique as presented in our previous work [16,17]. The solvent was weighed by an electronic balance with

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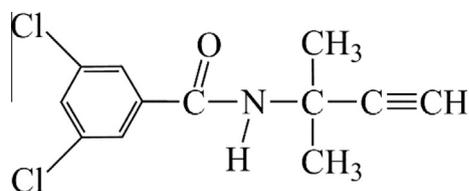


Fig. 1. Molecular structure of pronamide.

uncertainty of  $\pm 0.0002$  g (Toledo AB204-S, Switzerland), before it was transferred to a jacketed glass crystallizer (YPD, China, 500 mL) which connected with a temperature-controlled water bath (SHP DC-2015, China). The solvent inside the crystallizer was stirred by a magnetic stirrer (Bante Instrument MS200, China), and a condenser was installed to prevent the volatilization of the solvent. The required temperature was maintained by the liquid-circulating from water bath to crystallizer and was accurately measured by a mercury thermometer (TD 200, China), whose uncertainty was designed to be  $\pm 0.05$  K. When the system reached a steady state, an amount of pronamide was delivered to the solvent. Simultaneously the laser intensity penetrating the crystallizer decreased as the solid particles blocked the laser propagation. The laser intensity returned back approximately to its maximum again when the solute was completely dissolved. The addition of pronamide was continued until the last addition (2–5 mg, less than 1% of the dissolved) could not be dissolved. A saturated solution was obtained and the mole fraction solubility ( $x_0$ ) of pronamide was calculated according to Eq. (1). Each data point was confirmed by triplicate experiments.

$$x_0 = \frac{m_0/M_0}{m_0/M_0 + m_1/M_1} \quad (1)$$

where  $m_i$  (g) and  $M_i$  ( $\text{g} \cdot \text{mol}^{-1}$ ) represent the mass and molar mass values of solute ( $i = 0$ ) and solvent ( $i = 1$ ), respectively.

### 3. Results and discussion

#### 3.1. Solubility of pronamide

The experimental solubility of pronamide in the selected solvents (ethanol, methanol, isopropanol, toluene and cyclohexane) at temperature range from (278.15 to 323.15) K is listed in Table 3 and plotted in Fig. 3. The results show that, in each solvent, the solubility of pronamide increases with the increasing temperature. Over the temperature range in this work, the solvency of pronamide ranked as ethanol > methanol > isopropanol > toluene > cyclohexane. Specifically, in the cyclohexane, the solubility values illustrated a slightly soluble behaviour of pronamide (only

Table 1  
Lattice parameters of pronamide.

Crystal system	Monoclinic phase	
Space group	P2 <sub>1</sub> /c	
Lattice Parameters	<i>a</i>	1.2211 nm
	<i>b</i>	1.0887 nm
	<i>c</i>	1.0167 nm
	$\alpha$	90°
	$\beta$	111.07°
		90°
Cell volume	1.2613 nm <sup>3</sup>	
Cell density	1.349 mg · m <sup>-3</sup>	

Table 2  
Description of materials used in this paper.

Chemical name	Source	Purification methods	Final mass fraction purity	Analysis method
Pronamide	a	Double refined in methanol	>0.990	HPLC
Ethanol	b	None	0.995	GC
Methanol	b	None	0.997	GC
Isopropanol	b	None	0.995	GC
Cyclohexane	b	None	0.997	GC
Toluene	b	None	0.980	GC

a, Chengdu Yuancheng Group Chemistry Co., Ltd. China.

b, Tianjin Kemiou Chemical Reagent Co., Ltd. China.

$0.1240 \times 10^{-3}$  at 323.15 K), and almost did not change with the temperature. While the compound was freely soluble in ethanol and methanol ( $2.948 \times 10^{-2}$  and  $2.829 \times 10^{-2}$  at 323.15 K respectively), and it also should be noted that the solubilities in the two solvents increased faster with temperature than those in other solvents. Therefore, ethanol and methanol could be used as good solvents while the cyclohexane was the poor solvent (antisolvent).

The solubility diversity of pronamide in different solvents were attributed to molecular structures of solvents, which could be explained by the interaction between solute and solvent molecules. Pronamide molecules contained some single electronegative atoms or electron rich groups such as “O” and “N” (see Fig. 1). Obviously, these negative charge groups would attract the “H” with positive charge from the solvent molecules. These types of strong interaction, known as the hydrogen bonds, were evaluated by the solvents’ charge density. As hydroxyl groups in ethanol and methanol provided the “H” with high density of positive charge, pronamide formed strong hydrogen bonds with ethanol and methanol molecules, which enhanced the solubility of pronamide [18,19].

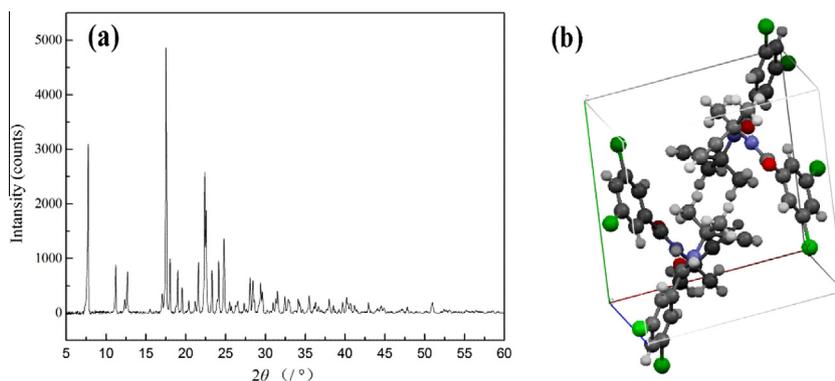


Fig. 2. (a) X-ray diffraction pattern and (b) Lattice structure of pronamide sample.

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