

## Solid–liquid phase equilibrium of glyphosate in selected solvents

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### ABSTRACT

Solid–liquid equilibrium (SLE) data for the glyphosate in methanol, ethanol, *n*-propanol, 2-propanol, acetone, benzene and ethyl acetate, and aqueous sodium chloride solutions were measured with a temperature range from (283 to 352) K. The hypothetical enthalpy of fusion and melting temperature of glyphosate were estimated. The Wilson model, the nonrandom two-liquid (NRTL) model, the universal quasi-chemical (UNIQUAC) model, and the Scatchard–Hildebrand (SH) model were applied to correlate the solid–liquid equilibrium. It is shown that the Wilson model can give better results than NRTL and UNIQUAC model. The solubility parameter of glyphosate was obtained based on the SH model. In aqueous sodium chloride solutions, the solubility of glyphosate increases with the molality of sodium chloride increasing. The system of glyphosate + sodium chloride + water is found to exhibit a synergistic effect.

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### 1. Introduction

Excessive release of toxic organic wastewater into the environment due to industrialization has created great global concern in recent years. Glyphosate (N-(phosphonomethyl) glycine, CAS registry no. 1071-83-6) is a highly effective post-emergence, broad-spectrum and non-selective herbicide that has been widely applied in agriculture [1,2]. Glyphosate contains a phosphonate, a carboxylate and an amine group, all capable of taking part in stable five-membered chelate rings (Fig. 1). Glyphosate was prepared by the reaction of chloromethylphosphonic acid with glycine in the sodium hydroxide solution, then acidified using hydrochloric acid, and finally purified from crystallization. The wastewater from the crystallization process usually contains 1–2% glyphosate, 10–20% NaCl and a high concentration of organic by-products [2]. Currently, several strategies are being pursued to prevent the pesticide plant from offering 10% glyphosate aqueous solution. How to deal with this wastewater and effectively reclaim glyphosate has already been an important research topic. Because of the toxicological effects of glyphosate and by-products, its subsequent removal from aqueous solution has been mandatory.

A number of methods have been proposed and reported for the removal of glyphosate including advanced oxidation technologies [3–6], biodegradation [7,8], ion exchange and adsorption [9–13].

Recently, interest has increased in further development of adsorption technology. It is noteworthy that the adsorption capacity of the adsorbent is strongly dependent on its property and the solubility of the glyphosate. In order to effectively separate the glyphosate from a reactive mixture by physical or chemical method and assess environmental partitioning of different compounds, it is necessary to determine the solubility of glyphosate in different solvents. The solubility of glyphosate in water, ethanol + water, 1-propanol + water, and 2-propanol + water has been reported by Fu et al. [14]. However, the solubilities of glyphosate in organic solvents and in aqueous sodium chloride solutions have not been found in the literature. In this study, for the purpose of further investigations on the solubility of glyphosate as well as the investigation on the synergistic effect, the measurements were carried out in methanol, ethanol, *n*-propanol, 2-propanol, acetone, benzene, ethyl acetate, and aqueous sodium chloride solutions. The sodium chloride molality, *h* (moles of sodium chloride in kg of water, mol kg<sup>-1</sup>) was range from 0.0 to 4.5 over a temperature range from (283 to 352) K. The Wilson model, the nonrandom two-liquid (NRTL) model, and the universal quasi-chemical (UNIQUAC) model were applied to describe the experimental solid–liquid equilibrium (SLE) data. Finally, the possible reason for the relatively smaller discrepancy appearing in the Wilson model was discussed.

### 2. Experimental

#### 2.1. Materials

A white crystalline powder of glyphosate (C<sub>3</sub>H<sub>8</sub>NO<sub>5</sub>P, with a molar mass 169.07 g mol<sup>-1</sup>) was purified by twice recrystallizing

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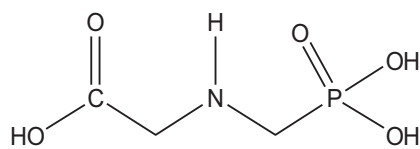


Fig. 1. Glyphosate.

from water. Its mass fraction purity, determined by high-performance liquid chromatography (HPLC) [13]. Other reagents are analytical research grade reagents. All of the solvents used in the experiments have a minimum purity of 99.5% (Table 1).

## 2.2. Glyphosate characterization

The melting points and enthalpy of fusion of glyphosate were studied using a Q100 (TA Instruments) differential scanning calorimeter (DSC) in flowing nitrogen at a heating rate of  $10\text{ K min}^{-1}$ . The uncertainty of DSC measurement is the same as that described in the literature [15]. Thermogravimetric analysis (TGA) was carried out with an SDT Q600 (TA Instruments) thermogravimetric analyzer at a heating rate of  $10\text{ K min}^{-1}$  under nitrogen from (298.15 to 1073.15) K.  $^{31}\text{P}$  NMR spectra was recorded on a BRUKER AV 500 spectrometer operating at 202.42 MHz using the standard pulse sequence at the room temperature. The  $^{31}\text{P}$  NMR of the obtained glyphosate powders and a characteristic peak at 9.15 ppm is observed, which agrees with the data in previous reports [16,17].

## 2.3. Apparatus and procedures

The solubility of glyphosate was determined by the balance method. The setup for the solubility measurement was the same as that described in the literature [18,19]. Fig. 2 shows the schematic diagram of the experimental apparatus. A jacketed equilibrium cell was used for the solubility measurement with a working volume of  $120\text{ cm}^3$  and a magnetic stirrer, and a circulating water bath was used with a thermostat (type  $50\text{ dm}^3$ ), made from Shanghai Laboratory Instrument Works Co., Ltd., China, which is capable of maintaining the temperature within  $0.05\text{ K}$ . Glyphosate solute and solvents mixtures were heated slowly (less than  $0.2\text{ K h}^{-1}$  close to the SLE temperature) inside a vessel with continuous stirring. An analytical balance (AU120 Shimadzu Corp., Japan) with a precision of  $\pm 0.1\text{ mg}$  was used during the mass measurements. In the experiment, the molality of aqueous sodium chloride solutions  $h$  ( $\text{mol kg}^{-1}$ ) was determined by the following equation:

$$h = \frac{m_S/M_S}{m_W/1000} \quad (1)$$

where  $m_W$  and  $m_S$  represent the masses of the water and sodium chloride, respectively, and  $M_S$  is the molecular weight of the sodium chloride.

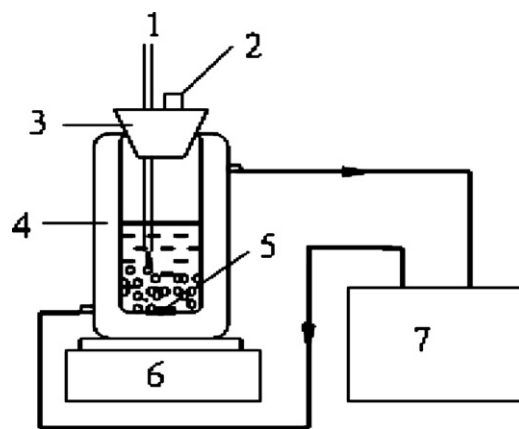


Fig. 2. Schematic diagram of the experimental apparatus: (1) thermocouple; (2) sample gauge; (3) rubber plug; (4) jacket; (5) equilibrium cell; (6) magnetic stirrer; and (7) water cycling bath.

## 2.4. Solubility measurement

The amount of the glyphosate in the saturated solution was determined by a gravimetric method. For each measurement, an excess mass of glyphosate was added to a known mass of solvent. Then the equilibrium cell was heated to a constant temperature with continuous stirring. After at least 5 h (the temperature of the water bath approached a constant value, then the actual value of the temperature was recorded), the stirring was stopped, and the solution was kept until it was clear. A preheated on-off injector with a cotton filter withdrew  $2\text{ cm}^3$  of the clear upper portion of the solution to another previously weighed measuring vial ( $m_0$ ). The vial was quickly and tightly closed and weighed ( $m_1$ ) to determine the mass of the sample ( $m_1 - m_0$ ). Then the vial was put in an oven to allow the solvent to evaporate. When the mass of the residue reaches constant, the final mass ( $m_2$ ) was recorded. Then the solubility of glyphosate in mole fraction,  $x$ , could be determined from a mass balance [20].

$$\begin{aligned} m_W &= m_1 - m_2 \\ m_S &= \frac{hM_S(m_1 - m_2)}{1000} \\ m_G &= (m_2 - m_0) - m_S \\ x &= \frac{m_g/M_g}{m_g/M_g + m_w/M_w + m_s/M_s} \end{aligned} \quad (2)$$

where  $m_W$ ,  $m_S$  and  $m_G$  represent the masses of the water, the sodium chloride and the glyphosate in a specific sample saturated solution, respectively, and  $M_W$ ,  $M_S$  and  $M_G$  are the molecular weight of the water, the sodium chloride and the glyphosate, respectively.

During our experiments, three parallel measurements were performed at the same composition of solvent for each temperature,

Table 1  
Sample description.

Chemical name	Source	Mass purity	Purification method
Glyphosate	Shandong Qiaochang Chemical Industry Co., Ltd.	0.991	Recrystallized
Sodium chloride	Beijing Chemical Works	>0.998	None
Methanol	Beijing Chemical Works	>0.995	None
Ethanol	Beijing Chemical Works	>0.995	None
<i>n</i> -Propanol	Beijing Chemical Works	>0.995	None
2-Propanol	Beijing Chemical Works	>0.995	None
Acetone	Beijing Chemical Works	>0.995	None
Benzene	Beijing Chemical Works	>0.995	None
Ethyl acetate	Beijing Chemical Works	>0.995	None

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