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Measurement of solid solubilities of diuron in supercritical carbon dioxide and analysis of recrystallization by using the rapid expansion of supercritical solutions process

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ABSTRACT

A semi-flow type apparatus was used to measure the solid solubilities of diuron, an herbicide, in supercritical carbon dioxide (CO_2) from 10 to 20 MPa at 308.2, 318.2, and 328.2 K. The mole fraction of solid diuron dissolved in supercritical CO_2 was between 8.72×10^{-7} and 1.63×10^{-5}. The measured solubility data were correlated using three thermodynamic models: the Chrastil equation, Mendez-Santiago and Teja equation, and regular solution model coupled with the Flory–Huggins equation. These models yielded satisfactory results with the average relative deviations being less than 6%. Furthermore, an analysis using the rapid expansion of supercritical solutions (RESS) process was conducted to determine the effects of three operating temperatures on recrystallization of diuron. Three extraction temperatures (T_{ext}) (308, 318, and 328 K), three pre-expansion temperatures (T_{pre}) (433, 453, and 473 K), and three post-expansion temperatures (T_{post}) (273, 293, and 313 K) were used to determine the effect of operating temperatures. A lower post-expansion temperature of 273 K and higher pre-expansion temperature of 473 K were associated with the production of smaller diuron particles with a narrower size distribution. The effect of extraction temperature remained insignificant. The mean particle size of diuron could be successfully reduced to approximately 6 μm by using the RESS process.

1. Introduction

Supercritical carbon dioxide (CO_2), a green solvent, is widely used in various applications for its nontoxic, nonflammable, environmental friendly, and mild supercritical properties. Several review studies have investigated the applications of supercritical CO_2 in the analytical chemistry, dyeing industry, extraction, biodiesel production, and nanoencapsulation [1–6]. In recent years, supercritical CO_2 is used in processing specialty chemicals for particle formation and solid-state property modification. These supercritical particle formation techniques have advantages such as a trace residual amount of the solvent, availability for processing of thermal-labile compounds, and easy manipulation of particle characteristics. Classification and selection of supercritical particle formation techniques have been reviewed [7–10]. Among these techniques, the rapid expansion of supercritical solutions (RESS) process is frequently used for being a solvent-free procedure.

The RESS process includes two major steps for solid solute extraction at a high pressure and rapid expansion at a low pressure. The solid solute is extracted using supercritical CO_2 in an extraction vessel and subsequently depressurized through a nozzle to attain an atmospheric pressure for producing fine particles. Several studies have reported the production of specialty chemicals through the RESS process. Yim et al. recrystallized adefovir dipivoxil by using the RESS process and measured its solid solubility in supercritical CO_2 [11]. Huang et al. investigated the formation of fine particles of progesterone by using the RESS process and compared the solid-state properties of processed progesterone with those of original progesterone [12]. Hiendrawan et al. micronized fenofibrate by using the RESS process and examined the effects of operating parameters with Taguchi's orthogonal array [13]. Baseri and Lotfollahi micronized gemfibrozil by using the RESS process and studied the effects of extraction temperature, extraction pressure, and nozzle diameter [14]. Montes et al. used both the RESS and supercritical antisolvent (SAS) processes to recrystallize naproxen and presented the results of recrystallization [15].

Fundamental thermodynamic studies, such as solubility measurement and data correlation, are crucial to design and select a proper supercritical particle formation technique. In the last few decades, binary solubility data of solid solutes, especially pharmaceutical and biological compounds, in supercritical CO_2 have been

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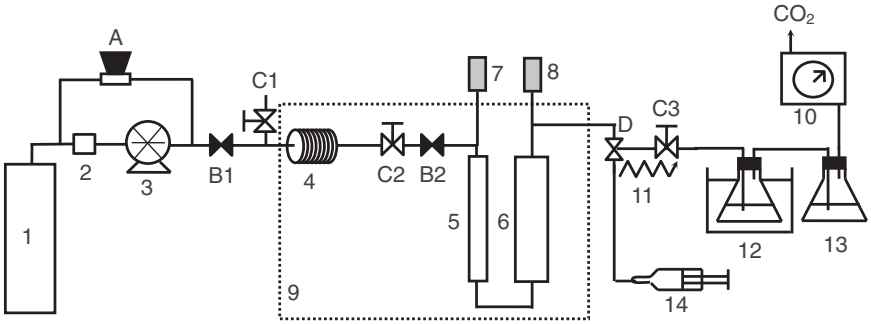

Fig. 1. Experimental apparatus for measuring the solid solubility ((1) CO_2 cylinder; (2) cooler; (3) CO_2 pump; (4) preheater; (5) pre-equilibrium cell; (6) equilibrium cell; (7) pressure transducer; (8) thermocouple; (9) water bath; (10) wet test meter; (11) heating tape; (12) solvent cold trap; (13) saturator; (14) syringe; (A) back pressure regulator; (B) check valve; (C) two-way needle valve; and (D) three-way needle valve).

widely studied and published [16–18]. To further extend the solubility database of biological compounds, new solid solubility data of diuron in supercritical CO_2 at three temperatures were analyzed in the present study. The measured solubility-related data were also correlated using various thermodynamic models. Diuron, a substituted urea, acts as an inhibitor of photosynthesis and is used as an herbicide. It is widely applied in agriculture owing to its superior properties of water solubility, feasibility of controlled release, and bioavailability to the target subject. However, because of its accumulation and toxicity, its use as a pesticide has caused various environmental threats. Therefore, developing a novel delivery system with a low dose, low toxicity to nontarget species, and low pesticide residue is particularly important to reduce its harmful effects. Design and development of the controlled release system by using the novel particle design technology seems to offer these advantages more prominently compared with the conventional formulations. Taki et al. and Boutin et al. have used the SAS process to recrystallize diuron and designed a controlled release system by coprecipitating diuron with polymeric materials [19,20]. However, Taki et al. showed that the recrystallization of diuron by using the SAS process is unsatisfactory. Needle-like diuron particles larger than 200 μm were produced when methylene chloride was used as a solvent. Therefore, in addition to solubility measurement, in the present study, the RESS process was adopted for recrystallizing diuron and examining the effects of operating parameters.

2. Materials and methods

2.1. Chemicals

Carbon dioxide with a minimum purity of 99.9% was purchased from Cheng-Feng Gas Co., Taiwan. Diuron ($C_9H_{10}Cl_2N_2O$) with a minimum purity of 98% was purchased from Sigma-Aldrich Co. Both chemicals were used without further purification.

2.2. Experimental apparatus and procedure for solubility measurement

The experimental apparatus used in the present study for solid solubility measurements is shown in Fig. 1. The solubility measurement system was divided into three parts, each for supercritical CO_2 feeding, solute extraction, and solubility analysis, respectively. Pure CO_2 from the CO_2 cylinder (1) was liquefied to 278.2 K by using a cooler (2). The liquefied CO_2 was subsequently pressurized using a HPLC pump (3) to reach a desired pressure. The system pressure was regulated and controlled using a back pressure regulator (A). CO_2 with the desired high pressure was passed through a preheating coil (4) to reach a supercritical state. This preheating coil was immersed in a water bath (9). Supercritical CO_2 from the preheating coil was charged into the pre-equilibrium and equilibrium cells (5 and 6). The volume of the equilibrium cell was 75 cm^3. Approximately 10 g of the solid solute with glass beads was packed inside. To avoid physical entrainment, two stainless filters were plugged at each end of the equilibrium cell. The system temperature and pressure were measured using a thermocouple (8) and a pressure transducer (7) having resolutions at 0.1 K and 0.01 MPa, respectively.

Following solute extraction with supercritical CO_2, the solute-saturated supercritical solution was expanded to the atmospheric pressure through a needle valve (C3). This needle valve was wrapped with heating tape (11) to avoid blockage of the sampling line. After expansion was achieved, the total volume of CO_2 was measured using a wet test meter (10), and the solid was separated from the gaseous phase and was dissolved in ethyl acetate, an organic solvent, in a flask (12). To recover the residual solute in the sampling line, approximately 30–50 mL of ethyl acetate was injected using a syringe (14). The concentration of the organic solution in the flask was finally analyzed using a UV/vis spectrometer (Thermo Scientific Evolution 60S). The published data on saturated solubility of the solute at a given temperature and pressure was averaged from three independent measurements. The repeated measurements were taken at various flow rates of effluent CO_2 between 3 L/h and 10 L/h to ensure that data on saturated solubility were obtained. To confirm the solid–fluid equilibrium and avoid melting of the solid solute while measuring the solubility owing to the melting-point depression, residual diuron powder was collected and checked after solubility measurement. The appearance of diuron after solubility measurement was consistent with the original sample, and no agglomeration occurred, indicating no melting of diuron during the solubility measurement.

2.3. Correlation of solid solubility data

In addition to solubility measurement, the correlation of solubility data has been studied using three thermodynamic models, namely the Chrastil equation, Mendez-Santiago and Teja (MST) equation, and the regular solution model coupled with the Flory–Huggins equation [21–24]. The Chrastil equation and MST equation were converted into their dimensionless forms. The Chrastil equation in its dimensionless form is expressed as [23]

$$\ln\ S_2^* = k^* \ln\ \rho_{r,1} + \frac{a^*}{T_r} + b^* \tag{1}$$

$$S_2^* = \frac{S_2}{\rho_{c,1}} \tag{2}$$

where S_2 is the concentration (kg/m^3) of diuron in the supercritical solution. $\rho_{r,1}$ is the reduced density of pure CO_2. T_r is the reduced temperature. $\rho_{c,1}$ is the critical density of pure CO_2. k^*, a^*, and b^*