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Solubility and dissolution mechanism of 4-chlorotoluene in subcritical water investigated in a fused silica capillary reactor by in situ Raman spectroscopy

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ABSTRACT

The solubility of 4-chlorotoluene in subcritical water was measured using an optically transparent fused silica capillary reactor (FSCR). The total dissolution temperature of 4-chlorotoluene in subcritical water was visually determined. The dissolution uniformity of 4-chlorotoluene in subcritical water was confirmed by Raman spectroscopy. The solubility of 4-chlorotoluene linearly increased with increasing temperature in the range 262.3–293.8 °C. The dissolution mechanism of 4-chlorotoluene in subcritical water is proposed based on the Raman spectra of 4-chlorotoluene and water during the dissolution process in the FSCR.

1. Introduction

Sub- and supercritical water are regarded as promising and interesting solvents for industrial applications such as biomass liquefaction [1–3], synthesis [4,5], extraction [6], hydrolysis [7], polymer depolymerization [8,9], and treatment of toxicants or recalcitrant organic waste [10–14]. With the growing interest in sub- and supercritical fluid technology, a number of novel methods to measure the solubility of organic compounds in sub- and supercritical water have been proposed. These methods can be basically divided into static [15–24] and dynamic [25–34] methods.

In the static method, an excess amount of solute and a specific volume of solvent are both loaded into an equilibration cell, and aliquots of the sample solution are periodically withdrawn from the cell for analysis until equilibrium is established. Kayan et al. [18] used the static method to measure the solubility of benzoic and salicylic acid in subcritical water at temperatures ranging from 25 to 200 °C. Huang et al. [23] used the static method to investigate the solubility of fatty acids in subcritical water from 80 to 200 °C. Kapalavavi et al. [24] used the static method to investigate the solubility of parabens in subcritical water. However, withdrawing the sample solution from the equilibration cell causes a considerable pressure drop and disturbs the phase equilibrium process.

In the dynamic method, the solvent continuously flows through a solubility equilibrium vessel containing an excess amount of the solute under experimental temperature and pressure conditions. After equilibration at a particular temperature and pressure conditions, aliquots of the sample solution are withdrawn through a valve or restrictor for analysis. Miller et al. [25,26] used the dynamic method to measure the solubility of hydrophobic organics in subcritical water. Zhang et al. [31] used the dynamic method to investigate the solubility of carbohydrates in subcritical water. Takebayashi et al. [34] used the dynamic method to investigate the solubility of terephthalic acid in subcritical water from 75 to 275 °C. The experimental procedure of the dynamic method is easy and quick, but solute is lost in the valve or restrictor.

Furthermore, for both static and dynamic methods, most studies are performed in large-scale stainless-steel reactors, and they all require subsequent analyses. In addition, these methods are

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difficult for in situ investigation of the dissolution mechanism of organic compounds in sub- and supercritical fluid during the dissolution process.

Microreactor systems have been increasingly adapted for many chemical applications because of their low reagent consumption, efficient heat and mass transfer, and fine degree of process control. Also, Raman spectroscopy has been widely applied as an important nondestructive testing technique [35]. It is significant to understand the changes, if any, in composition and/or molecular structure of the materials under investigation during experiments, and in situ Raman analysis can efficiently provide this information.

As an important raw material and intermediate, 4-chlorobenzene has been used for many chemical products such as pesticides, drugs, and dyestuff. However, data on its solubility in subcritical water are rare. In this study, a high-temperature and -pressure optically transparent fused silica capillary reactor (FSCR) combined with Raman spectroscopy has been developed to investigate phase changes, determine the solubility, and investigate the dissolution mechanism of 4-chlorotoluene in subcritical water. The feasibility of the solubility apparatus has previously been confirmed [36]. The solubility of 4-chlorotoluene was determined and the dissolution uniformity of 4-chlorotoluene in subcritical water was confirmed by Raman spectroscopy. In addition, the dissolution mechanism of 4-chlorotoluene in subcritical water is proposed based on the Raman spectra of 4-chlorotoluene and water during the dissolution process in the FSCR. These results constitute useful information for the chemical production and supercritical water oxidation treatment of 4-chlorotoluene.

2. Experimental

2.1. Materials

4-Chlorotoluene (C_7H_7Cl, 99.9% purity) was supplied by Aladdin Chemistry Co., Ltd. (Shanghai, China). Deionized water was purified with secondary reverse osmosis system (UPT-II-20, Ulupure, China) in the laboratory. The fused silica capillary tubing (665 μm outer diameter (OD), 300 μm inner diameter (ID)) and the fused quartz tube (4 mm OD, 2 mm ID) used in this study were purchased from Polymicro Technologies LLC (Phoenix, AZ, USA) and Beijing Zhong Cheng Quartz Glass Co., Ltd. (Beijing, China), respectively. Table 1 shows the detailed information of these materials.

2.2. Experimental apparatus and methods

The experimental apparatus included a FSCR, heating/cooling stage, microscope, digital camera, and confocal Raman spectrometer. To prepare the sample, a section of silica capillary (665 μm OD, 300 μm ID, and about 1.5 cm long) was cut. The polyimide protective layer was burnt off and then one of the open ends was sealed with an oxyhydrogen flame. A moderate volume (about 0.02–0.06 μl) of 4-chlorotoluene was then injected into the capillary tube by a modified microsyringe. The volume of 4-chlorotoluene was measured with a micrometer (OLYSIM, accuracy ±l μm), and then converted to mass. Water was then immediately injected into the FSCR, and centrifuged to the closed end. To reduce the free space above the liquid phase, the vapor phase was partially filled with a silica rod. The closed end of the capillary was immersed in liquid nitrogen and the open end of the tube was quickly sealed with an oxyhydrogen flame to form a FSCR (Fig. 1(a)). The volume of injected water was measured with a micrometer at ambient temperature and then converted to mass.

The FSCR was loaded in the heating/cooling stage (INS0908051, Instec, USA), and the temperature was adjusted by a digital temperature controller (STC200, Instec, USA). The temperature of the FSCR was intermittently increased or kept constant (from room temperature to 220 °C at a rate of 5 °C/min, above 220 °C at a rate of 0.1 °C/min) until 4-chlorotoluene completely dissolved in the subcritical water.

The sample changes during heating were observed under a microscope (DM2500P, Leica, Germany) and recorded using a digital camera (TK-C9501, JVC, Japan). The homogeneity of the solution in the FSCR during 4-chlorotoluene dissolution was checked using an in situ Raman system. Raman spectra were acquired using a Raman spectrometer (HR 800 Lab RAM, Horiba Jobin Yvon, France) equipped with a 531.95 nm laser (frequency-doubled Nd:YAG, 20 mW) and a charge-coupled device (CCD) detector (multichannel, air cooled). Approximately 8 mW laser light was focused on the central level of the horizontal FSCR to acquire Raman signals in the liquid phase (characteristic peaks: 4-chlorotoluene 374, 792, 1088, 2927, and 3060 cm^{-1}; water 2800–3800 cm^{-1}). The experimental apparatus and other details have been described elsewhere [36,37].

3. Results and discussion

3.1. Solubility of 4-chlorotoluene in subcritical water

Before the study in the FSCR, an amplification experiment was

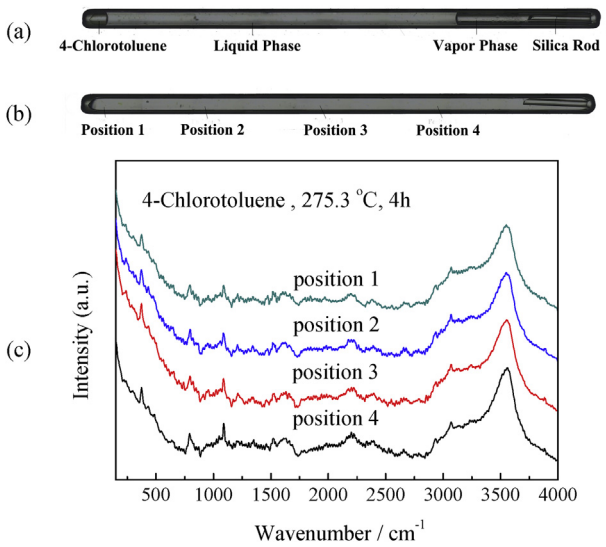

Fig. 1. (a) Image of the FSCR showing 4-chlorotoluene, liquid phase, vapor phase, and silica rod at room temperature. (b) Image of 4-chlorotoluene completely dissolved in the FSCR. Positions 1–4 indicate the spots for Raman spectroscopic analysis. (c) Raman spectra of liquid phase in the FSCR at the four positions at 275.3 °C after being kept at this temperature for 4 h.

Table 1
Detailed information of the materials used.

Materials	Chemical formula	Molecular weight	Sources	Purity (mass %)
4-Chlorotoluene	C_7H_7Cl	126.59	Aladdin Chemistry	98.0
Water	H_2O	18.015	Purified in lab	