AIChE Letter: Thermodynamics and Molecular-Scale Phenomena

Solubility of 2,4-Dichlorotoluene in Water Determined in Fused Silica Capillary Reactor by *In Situ* Raman Spectroscopy

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Significance

The solubilities of hydrophobic organic compounds (HOCs) in hot compressed water (HCW) were measured using an optically transparent fused silica capillary reactor (FSCR). The total dissolution temperatures of HOCs in HCW were determined visually; the solution homogeneity in the FSCR during HOCs dissolution was checked using Raman spectroscopy. The solubility of 2,4-dichlorotoluene increased linearly with increasing temperature in the range of 266.3–302.4°C. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 2721–2725, 2013

Keywords: hot compressed water, solubility, Raman spectroscopy, capillary reactor

Introduction

Hot compressed water (HCW, water above 200°C and at sufficiently pressure[1]) is regarded as one of the most interesting solvents for industrial applications such as extraction,[2,3] hydrothermal conversion of biomass,[4,5] polymer depolymerization,[6,7] cleaning for dyeing,[8] and precipitation.[9] The advantages of HCW are that it is nontoxic, environmentally friendly, and low cost. In addition, HCW has unique properties and has been used as an organic solvent to dissolve a variety of hydrophobic organic compounds (HOCs).[10,11] HCW is able to act as an organic solvent because of the reduction in its dielectric constant at high temperatures.[12] It has been reported that the dielectric constant of water can be reduced from 80 (at 25°C) to 35 (at 200°C), which is almost equivalent to that of ethanol under ambient conditions.[13] Therefore, HOCs that are water-insoluble at ambient temperature become soluble in HCW.

As a starting point for further research or industrial application design, large amounts of solubility data of organic chemicals in HCW have been reported. Srinivas et al.[14–16] used a continuous flow type apparatus to measure the solubility of quercetin, quercetin dehydrate, gallic acid hydrate, protocatechuic acid, (+)-catechin hydrate, and carbohydrates in subcritical water. Karásek et al.[17] studied the solubility of selected organic electronic materials in pressurized hot water at elevated temperature (up to 260°C) by dynamic flow method. The solubility of terephthalic acid in water was studied as a function of temperature from 76 to 274°C at 10.0 MPa using a semibatch flow method.[18] Pereda[19] investigated the solubilities of n-hexane, cyclo-hexane and iso-octane in pure water by using a static-analytic technique, and his experimental data agreed well with previously reported values.

In previous studies, methods for measuring the solubilities of HOCs in HCW can be divided into two types: static and dynamic methods.[20] In the static solubility measurement technique, excess amount of solute and certain volume of solvent were both loaded into an equilibration cell, and aliquots of sample solution were withdrawn from the cell for analyses from time to time until equilibrium was established. The main advantage of static methods is that they can be used for systems with more than two compositions without significant complications.[21] However, withdrawing the sample solution from the equilibration cell cause a considerable pressure drop and disturb the phase equilibrium process. The dynamic solubility measurement technique allows a continuous flow of solvent through a solubility equilibrium vessel containing excess amount of solute under the experimental temperature and pressure conditions. After equilibration at a particular temperature, aliquots of the sample fluid were withdrawn through a valve or restrictor for analyses. The

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Additional Supporting Information may be found in the online version of this article.

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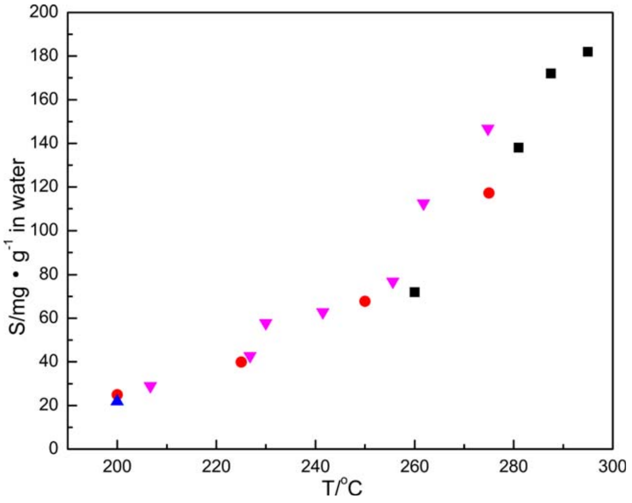

Figure 1. Solubilities of benzene from different sources. ■, Connoly[32] ▲, Miller[33] •, Chandler et al[34] ▼, of this study.

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main advantage of dynamic solubility is that no sampling is necessary, and the experimental procedure is often easy and quick. The major limitation is the loss of solute in the valve or restrictor.[22] Furthermore, whether using static methods or dynamic methods, most studies are performed in large-scale stainless-steel reactors, and they all require subsequent analyses such as gravimetric,[23] GC,[24] generator column,[25] or X-ray analyses.[26]

Raman spectroscopy is one of the most specialized methods for qualitative or quantitative determination of molecular compositions and structures in liquids, solids, and gases. Raman spectroscopy has attracted increasing attention as a versatile and rapid tool because it is nondestructive and, requires little preparation of samples.[27] Samples can be analyzed directly *in situ* even under elevated temperature and pressure conditions. In this study, we determined the homogeneity of HOCs in a fused silica capillary reactor (FSCR), based on quantitative analysis using Raman spectroscopy.

Our group has developed a new high-temperature and -pressure optically transparent FSCR system, which was used successfully in the determination of chlorobenzene solubilities in subcritical water (SBCW),[28] hydrolysis of polycarbonate in SBCW,[29] supercritical water oxidation of chlorobenzene,[30] and hydrolysis of carbon tetrachloride in HCW.[31] In this study, we determined the solubilities of benzene and 2,4-dichlorotoluene using the FSCR combined with a microscope recorder system, and investigated the homogeneities of benzene and 2,4-dichlorotoluene in water in the FSCR using *in situ* Raman spectroscopy. This experimental method does not require sampling and subsequent analysis, has low energy and materials consumptions, and is safe and environmental friendly.

The experimental apparatus included an FSCR, heating/cooling stage, microscope, digital camera, and confocal Raman spectrometer. The reliability of the heating/cooling stage was calibrated before starting the experiments. A section of silica capillary (665 μm O.D., 300 μm I.D., and 1.5 cm long) was prepared; it contained water, 2,4-dichlorotoluene, and a silica rod. To construct the FSCR, one end of the tube was sealed in an oxyhydrogen flame and 2,4-dichlorotoluene was injected into the capillary tube using a microsyringe. The mass was measured as follows: the

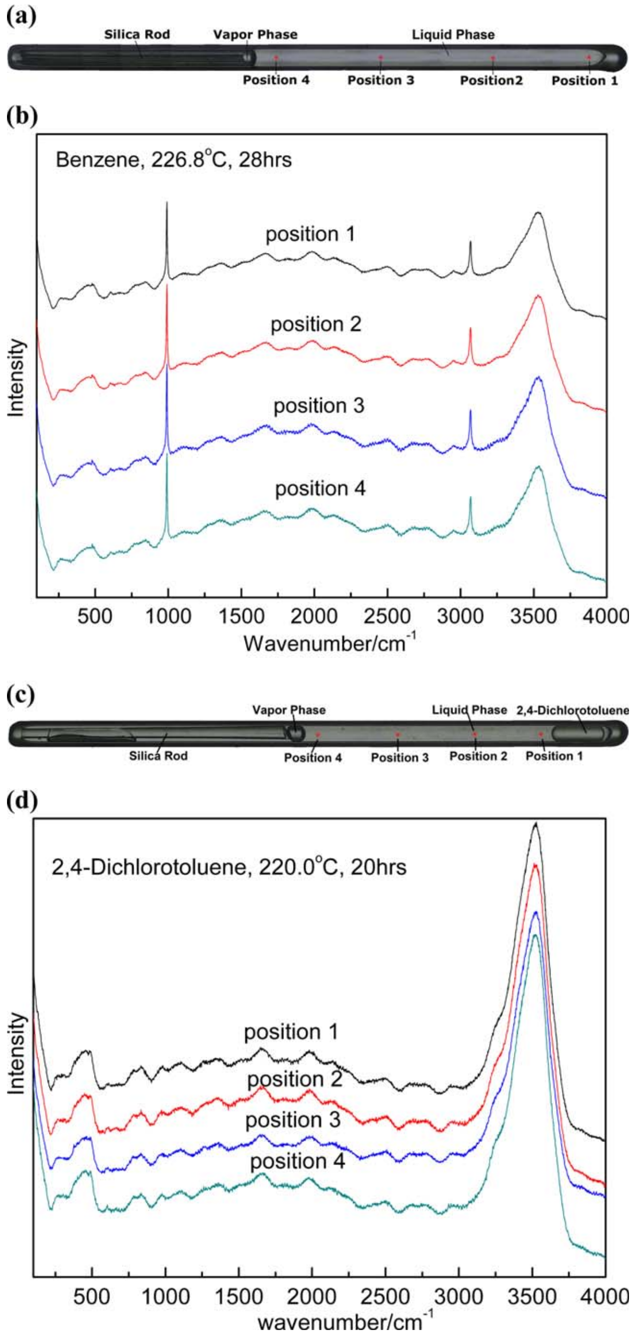

Figure 2. (a) Image of benzene in FSCR, showing liquid phase, vapor phase, and silica rod after benzene dissolved totally.

Positions 1 to 4 indicate the spots for Raman spectroscopy analyses, (b) Raman spectra of liquid phase in the FSCR at four spots, at 226.8°C, 28 h, (c) image of 2,4-dichlorotoluene in FSCR showing 2,4-dichlorotoluene, liquid phase, vapor phase, and silica rod at 220.0°C, and four spots for Raman analyses, and (d) Raman spectra of liquid phase in the FSCR at four spots, at 220.0°C, 20 h.

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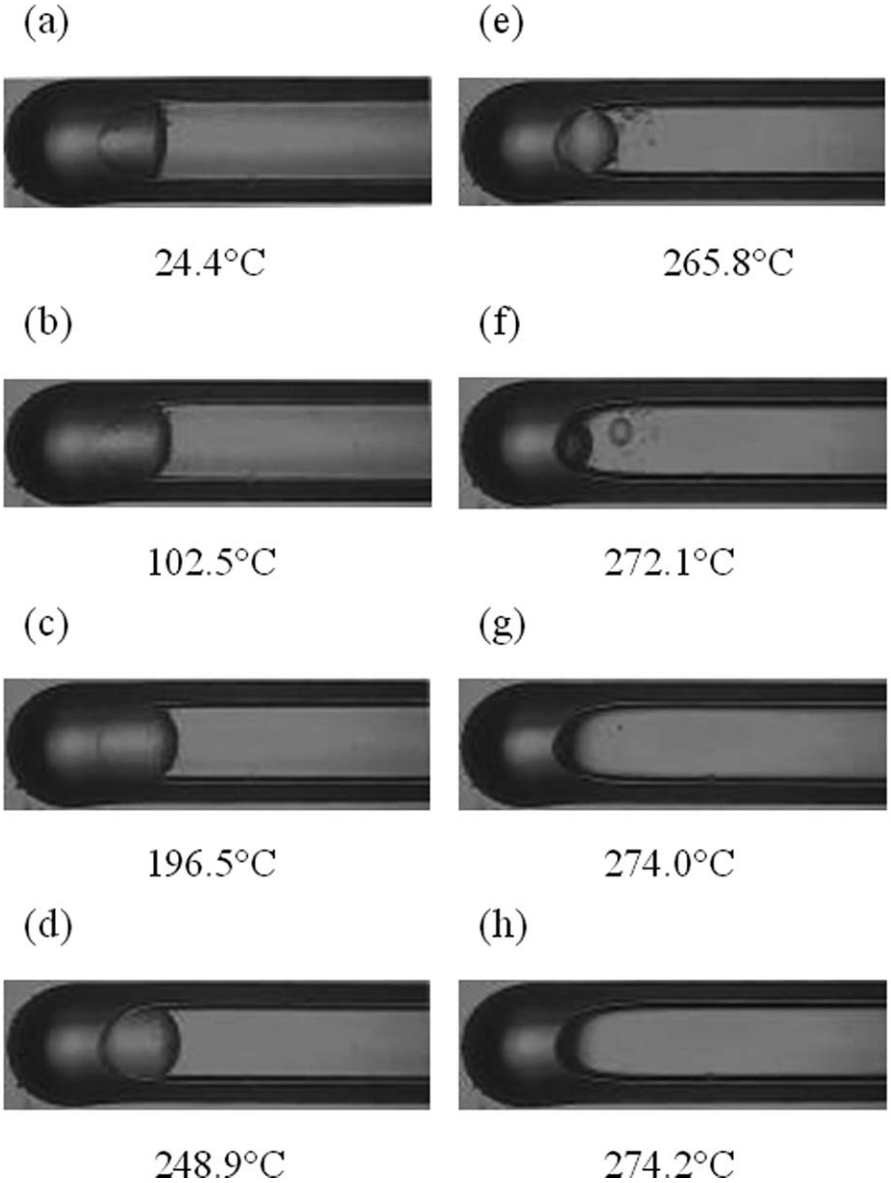

Figure 3. Dissolution of 2,4-dichlorotoluene in HCW during heating process. 2,4-Dichlorotoluene is at the left of the FSCR.

The images are of 2,4-dichlorotoluene and water in the FSCR under the microscope at temperatures of (a) 24.4°C, (b) 102.5°C, (c) 196.5°C, (d) 248.9°C, (e) 265.8°C, (f) 272.1°C, (g) 274.0°C, and (h) 274.2°C. The 2,4-dichlorotoluene swelled at 196.5°C (c), and dissolved totally at 274.2°C (g-h).

volume of the injected liquid was measured with a micrometer (OLYSIM, accurate to ± 1 μm), and then converted to mass. Water was then immediately injected into the FSCR, and centrifuged to the closed end. In order to reduce evaporation of 2,4-dichlorotoluene and water in the space above the liquid phase, the void was 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 an FSCR. The volume of injected water was measured with a micrometer at ambient temperature and then converted to mass. The phase behavior change images of the sample during heating were recorded in a computer using a digital camera (JVC, TK—C9501, Japan), and the dissolution temperature of 2,4-dichlorotoluene identified for each sample.

The sample was allowed to equilibrate for 20–35 h until the solute was totally dissolved in the HCW. The sample changes during heating were observed under a microscope and recorded using a digital camera and a computer. The homogeneity of the solution in the FSCR during HOCs dissolution was checked using an *in situ* Raman system. Raman spectra were acquired using a JY/Horiba LabRam HR Raman system (Horiba Jobin Yvon, Villeneuve d'Ascq, France) equipped with a 531.95 nm frequency-doubled Nd:YAG and a charge-coupled device (CCD) detector (multichannel, air cooled). Analyses were carried out with a 10× Olympus objective with a 0.25 numerical aperture, and a 600 grooves mm^{-1} grating with a spectral resolution of 1 cm^{-1}. An approximately 50 mW laser light was focused on a central level of the horizontal FSCR to acquire Raman signals in the

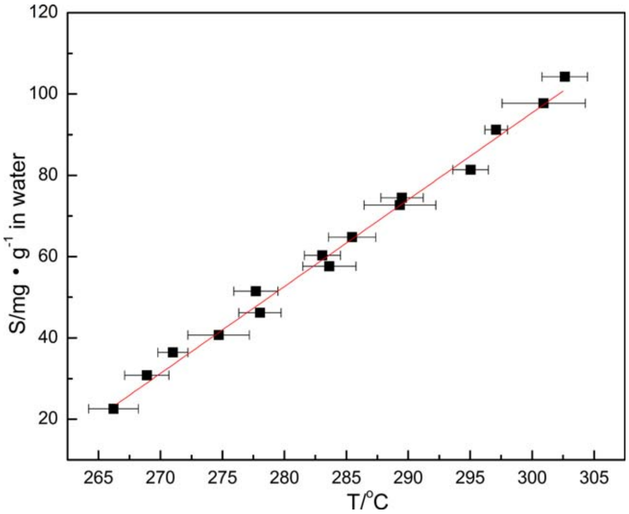

Figure 4. Solubility of 2,4-dichlorotoluene in water at temperatures between 266.3 and 302.4°C: (■) experimental data; (—) least-squares fit of the data.

The error bars show the maximum and minimum dissolution temperatures obtained in three tests for each sample.

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liquid phase. Spectra were collected in the range 100–4000 cm^{-1}, which covers the Raman peaks of benzene, 2,4-dichlorotoluene, and water (characteristic peaks: benzene, 990.43 cm^{-1} and 3069.09 cm^{-1}; 2,4-dichlorotoluene, 457.04 cm^{-1} and 828.54 cm^{-1}; water, 3533.1 cm^{-1}). The integration time was 30 s, with three accumulations per spectrum. The experimental details were presented online in the Supporting Information.

In order to ensure that the solubility apparatus was viable; the solubility of benzene in water was measured at specific temperatures. A comparison of our experimental data with the literature[32–34] data is shown in Figure 1; the maximum difference is 18#, and our data are in good agreement with those reported by Chandler et al.[34]

In this study, the Raman spectra of liquid benzene and 2,4-dichlorotoluene were collected from four different positions in the FSCR at 226.8°C, 28 h, and 220.0°C, 20 h, respectively. The image of benzene and 2,4-dichlorotoluene and the Raman spectra of benzene and 2,4-dichlorotoluene are shown in Figure 2.

As shown in Figure 2b, the Raman spectra collected from four different positions in the FSCR showed the same relative band intensities at 990.43 cm^{-1} and 3069.09 cm^{-1}, indicating that benzene diffused uniformly when it dissolved totally in the FSCR at 226.8°C, 28 h. The Raman signals of 2,4-dichlorotoluene were weak and disappeared at higher temperatures as a result of fluorescence, so the Raman spectra of 2,4-dichlorotoluene were recorded at 220.0°C. Figure 2d shows that the Raman spectra of 2,4-dichlorotoluene also had bands with the same relative intensities at 457.04 cm^{-1} and 828.54 cm^{-1}. It can be concluded that the solute diffused uniformly and the system reached phase equilibrium within a certain time, proving that the apparatus is viable.

The solubility of 2,4-dichlorotoluene in HCW was measured at several temperatures. Sample images were obtained during heating from 24.4 to 274.2°C, as shown in Figure 3; the concentration was 40.7 mg/(g·H_2O). These images show that 2,4-dichlorotoluene dissolved gradually during heating and dissolved completely at 274.2°C.

The solubility data of 2,4-dichlorotoluene are shown in Figure 4 in terms of solubility (S) and temperature (T). The results indicate that the solubility of 2,4-dichlorotoluene increased from 22.6 to 104.2 mg/(g·H_2O) when the temperature rose from 266.3 to 302.4°C; the effect of temperature can be represented by the linear equation

$$S=2.137T-545.725 \tag{1}$$

with $R^2=0.989$. The maximum relative error between the experimental data and the values calculated from Eq. 1 for the solubility is 4.52%.

This experimental method has great potential for determining the solubilities of HOCs in sub- and supercritical fluids, and for theoretical studies of fluids and chemical reactions under elevated pressure−temperature conditions.

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Literature Cited

1. Kruse A, Dinjus E. Hot compressed water as reaction medium and reactant: Properties and synthesis reactions. *J Supercrit Fluids.* 2007;39:362–380.
2. Tollbäck J, Bigatá MB, Crescenzi C, Ström J. Feasibility of analyzing fine particulate matter in air using solid-phase extraction membranes and dynamic subcritical water extraction. *Anal Chem.* 2008;80:3159–3167.
3. Herrero M, Cifuentes A, Ibanez E. Sub-and supercritical fluid extraction of functional ingredients from different natural sources: Plants, food-by-products, algae and microalgae: A review. *Food Chem.* 2006;98:136–148.
4. Stucki S, Vogel F, Ludwig C, Haiduc AG, Brandenberger M. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. *Energy Environ Sci.* 2009;2:535–541.
5. Brunner G. Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. *J Supercrit Fluids.* 2009;47:373–381.
6. Huang Y, Liu S, Pan Z. Effects of plastic additives on depolymerization of polycarbonate in sub-critical water. *Polym Degrad Stability.* 2011;96:1405–1410.
7. Sato O, Masuda Y, Hiyoshi N, Yamaguchi A, Shirai M. Chemical recycling process of poly(ethylene terephthalate) in high-temperature liquid water. *J Chem Eng Jpn.* 2010;43:313–317.
8. Vander KM, Cid F, Woerlee G, Veugelers W, Witkamp G. Dyeing of natural and synthetic textiles in supercritical carbon dioxide with disperse reactive dyes. *J Supercrit Fluids.* 2007;40:470–476.
9. Schubert M, Regler JW, Vogel F. Continuous salt precipitation and separation from supercritical water. *Part 1: Type 1 salts. J Supercrit Fluids.* 2010;52:99–112.
10. Miller DJ, Hawthorne SB. Solubility of liquid organic flavor and fragrance compounds in subcritical (hot/

liquid) water from 298 K to 473 K. *J Chem Eng Data.* 2000;45:315–318.

11. Kayan B, Yang Y, Lindquist EJ, Gizir AM. Solubility of benzoic and salicylic acids in subcritical water at temperatures ranging from (298 to 473) K. *J Chem Eng Data.* 2009;55:2229–2232.
12. Carr AG, Mammucari R, Foster NR. Solubility, solubility modeling, and precipitation of naproxen from subcritical water solutions. *Ind Eng Chem Res.* 2010;49:9385–9393.
13. Khuwijitjaru P, Adachi S, Matsuno R. Solubility of saturated fatty acids in water at elevated temperatures. *Biosci Biotechnol Biochem.* 2002;66:1723–1726.
14. Srinivas K, King JW, Howard LR, Monrad JK. Solubility and solution thermodynamic properties of quercetin and quercetin dihydrate in subcritical water. *J Food Eng.* 2010;100:208–218.
15. Srinivas K, King JW, Howard LR, Monrad JK. Solubility of gallic acid, catechin, and protocatechuic acid in subcritical water from (298.75 to 415.85) K. *J Chem Eng Data.* 2010;55:3101–3108.
16. Zhang DF, Montañés F, Srinivas K, Fornari T, Ibáñez E, King JW. Measurement and correlation of the solubility of carbohydrates in subcritical water. *Ind Eng Chem Res.* 2010;49:6691–6698.
17. Karásek P, Hohnová B, Planeta J, Šťavíková L, Roth M. Solubilities of selected organic electronic materials in pressurized hot water and estimations of aqueous solubilities at 298.15 K. *Chemosphere.* 2013;90:2035–2040.
18. Takebayashi Y, Sue K, Yoda S, Hakuta Y, Furuya T. Solubility of terephthalic acid in subcritical water. *J Chem Eng Data.* 2012;57:1810–1816.
19. Pereda S, Awan JA, Mohammadi AH, et al. Solubility of hydrocarbons in water: Experimental measurements and modeling using a group contribution with association equation of state (GCA-EoS). *Fluid Phase Equilib.* 2009;275:52–59.
20. Fonseca J, Dohrn R, Peper S. High-pressure fluid-phase equilibria: experimental methods and systems investigated (2005–2008). *Fluid Phase Equilib.* 2011;300:1–69.
21. Dohrn R, Peper S, Fonseca J. High-pressure fluid-phase equilibria: Experimental methods and systems investigated (2000–2004). *Fluid Phase Equilib.* 2010;288:1–54.
22. Guigard SE, Hayward GL, Zytner RG, Stiver WH. Measurement of solubilities in supercritical fluids using a piezoelectric quartz crystal. *Fluid Phase Equilib.* 2001; 187:233–246.
23. Stenger VA, Van Effen RM, Walker LC. Solubility of calcium bromate in water. *J Chem Eng Data.* 2002;47: 618–619.
24. Karásek P, Hohnová B, Planeta J, Roth M. Solubility of solid ferrocene in pressurized hot water. *J Chem Eng Data.* 2010;55:2866–2869.
25. Reza J, Trejo A, Elena Vera-Ávila L. Determination of the temperature dependence of water solubilities of polycyclic aromatic hydrocarbons by a generator column-on-line solid-phase extraction-liquid chromatographic method. *Chemosphere.* 2002;47:933–945.
26. Bremholm M, Jensen H, Iversen SB, Iversen BB. Reactor design for in situ X-ray scattering studies of nanoparticle formation in supercritical water syntheses. *J Supercrit Fluids.* 2008;44:385–390.
27. Frezzotti ML, Tecce F, Casagli A. Raman spectroscopy for fluid inclusion analysis. *J Geochem Explor.* 2012; 112:1–20.
28. Pan ZY, Dong Z. Determination of chlorobenzene solubilities in subcritical water in a fused silica capillary reactor from 173 to 267 C. *Ind Eng Chem Res.* 2011;50: 11724–11727.
29. Pan ZY, Chou IM, Burruss RC. Hydrolysis of polycarbonate in sub-critical water in fused silica capillary reactor with in situ Raman spectroscopy. *Green Chem.* 2009; 11:1105–1107.
30. Liu H, Pan Z. Visual observations and raman spectroscopic studies of supercritical water oxidation of chlorobenzene in an anticorrosive fused-silica capillary reactor. *Environ Sci Technol.* 2012;46:3384–3389.
31. Chen Y, Jin Z, Pan Z. In situ Raman spectroscopic study of hydrolysis of carbon tetrachloride in hot compressed water in a fused silica capillary reactor. *J Supercrit Fluids.* 2012;72:22–27.
32. Connolly J. Solubility of hydrocarbons in water near the critical solution temperatures. *J Chem Eng Data.* 1966; 11:13–16.
33. Miller DJ, Hawthorne SB. Solubility of liquid organics of environmental interest in subcritical (hot/liquid) water from 298 K to 473 K. *J Chem Eng Data.* 2000;45:78–81.
34. Chandler K, Eason B, Liotta CL, Eckert CA. Phase equilibria for binary aqueous systems from a near-critical water reaction apparatus. *Ind Eng Chem Res.* 1998;37: 3515–3518.

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