CHEMICAL REACTIONS IN SUPERCRITICAL WATER WITH DENSITY-DEPENDENT RATES

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INTRODUCTION

Supercritical water (T_c = 374°C, P_c = 218 atm) is an attractive medium for organic chemistry, in part because it is considered to be a "green" or environmentally benign reaction medium. Using SCW instead of organic solvents in chemical processes is a pathway for pollution prevention. Moreover, water near its critical point possesses properties very different from those of ambient liquid water. The dielectric constant is much lower, and the number and persistence of hydrogen bonds are both diminished. Consequently, SCW behaves as many organic solvents in that small organic compounds enjoy very high solubilities.

The rates of organic chemical reactions conducted in supercritical water can be sensitive to the water density, but the causes of density-dependent rates are not always clear. In some cases, this influence arises from water molecules serving as reactants, catalysts, or catalyst precursors. In other cases, water is simply a solvent but its density-dependent properties influence reaction rates. It is also possible that physical processes (solvent cage effects, water as a collision partner) are responsible. Akiya and Savage recently reviewed this field [1]. This present paper presents experimental results from our laboratory regarding the influence of water density on different reactions in supercritical water. The reactions considered include phenol oxidation, methylamine hydrothermolysis, and benzoic acid decarboxylation. Mechanistic modeling has been used to examine some of the possible roles of water in these reactions. Modeling complements the experiments and provides access to potential molecular-level explanations for the observed, and in some cases, striking, effect of water density on the rates of these reactions.

EXPERIMENTAL

All batch experiments (benzoic acid decarboxylation, methylamine hydrothermolysis) were done isothermally in constant-volume mini batch reactors made from stainless steel Swagelok tube fittings. Each reactor comprised two caps and one port connector (nominal size 1/4 or 3/8 in). All chemicals were purchased commercially at high purity and used as received. For a given reaction, we changed the water loading over a sufficiently wide range to determine their effects on the product yields. We performed multiple experiments at each set of conditions so we could determine the uncertainties in the experimental results. All results reported herein represent mean values.

All reactants were weighed to within ± 0.1 mg on an analytical balance after they were added to the reactors. After the reactors were loaded and sealed they were weighed and then placed in a preheated, isothermal fluidized sand bath. We determined experimentally that the reactor contents reach the temperature of the sand bath within three minutes and then remain at that temperature. After the desired reaction time elapsed, the reactors were removed from the sand bath and cooled to room temperature. The cooled reactors were then opened and their non-gaseous contents were collected by successive additions of a suitable solvent. We made no attempt to collect or analyze gaseous products. Additional details are available [2,3].

All flow reactor experiments (phenol oxidation) were done in a nominally isothermal, isobaric, tubular reactor operating at steady state. The coiled reactor, fashioned from Hastelloy tubing, was immersed in a temperature-controlled, fluidized sand bath. The reactor feed streams (phenol in water, hydrogen peroxide in water, and at times helium) were preheated to the reaction temperature before mixing together at the reactor entrance. The hydrogen peroxide decomposed completely to oxygen and water before reaching the mixing tee. The reactor effluent was collected and subsequently analyzed. Additional details are available [4,5].

Regardless of the type of reactor used for the experiment, product analyses were by HPLC, GC, and GC-MS. To facilitate the quantification of product yields, standards containing the compounds relevant to a given reaction were analyzed chromatographically to generate response factors and calibration curves. Molar yields were calculated by dividing the number of moles of each product present after the reaction by the initial number of moles of reactant loaded into the reactor.

PHENOL OXIDATION

Supercritical water oxidation (SCWO) is a chemistry and process technology that can be used for the complete mineralization of organic wastes. The chemistry can be thought of as analogous to incineration (complete oxidation), but done at lower temperatures and higher pressures and in the presence of water. Phenol has been widely used as model compound in SCWO kinetics and reaction studies. Water density is known to influence the phenol SCWO rate, but there are conflicting reports regarding whether its influence is to inhibit or accelerate the rate. A more detailed discussion of these apparently contradictory results appears in a recent report [4] from our laboratory. In none of these previous reports was there a thorough and systematic investigation of the effect of the water density. Rather, the experiments more typically involved sampling only a small number of water densities and then assuming that the unsampled portion of the parameter space behaved similarly. We have completed sets of experiments at different temperatures wherein the water density was the sole manipulated variable (1.6 – 22 mol/liter). The goal in these experiments was to determine more precisely the effect of water density (or concentration) on phenol SCWO kinetics.
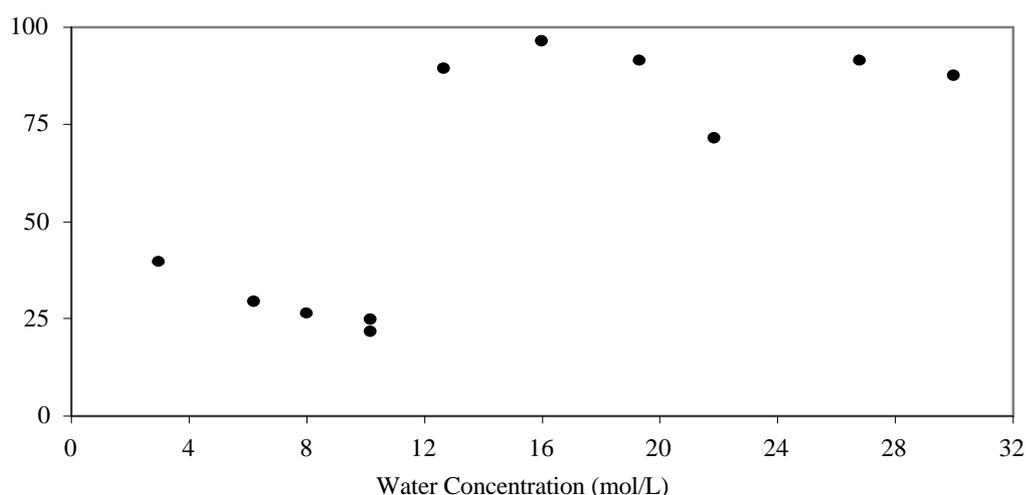
Figure 1: Effect of Water Concentration on Phenol Conversion at 380°C and 40 sec.

Figure 1 provides representative experimental results. These data were obtained from reaction at 380°C and a residence time of 40 sec. The concentrations of phenol and oxygen at the reactor entrance (at reaction conditions) were about 0.2 and 6.6 mmol/liter in all runs. These data show that the qualitative and quantitative influence of the water concentration changes as the water density changes. At low concentrations (< 10 mol/L), increasing density decreases the rate. At about 10 mol/L, there is a sharp increase in rate within a very narrow density window. Further increases in density appear to decrease the rate, but this declaration remains equivocal. This complicated and remarkable variation of conversion (and hence rate) with the water density could explain why previous investigators, who sampled only a portion of the parameter space we explored and did so with fewer data points, obtained seemingly contradictory results.

The striking behavior in Figure 1 begs for an explanation in terms of the underlying physics and chemistry. One avenue we explored to secure this explanation was consideration of the role of water as a reactant, product, and collision partner in elementary reaction steps. The influence of water in these roles can be explored through use of a mechanism-based kinetics model for phenol SCWO. These models have as their basis the underlying chemistry in terms of a set of free-radical reaction steps. If the rate constants for each step are known or can be estimated, then the mechanistic model can be used to predict the outcome of experiments. We updated some of the kinetics parameters in a previously published mechanistic model [6] for phenol SCWO, and used this model to determine whether the known roles of water as a reactant, product, or energy-transfer agent in elementary steps could account for the effect of water density observed for phenol SCWO. Figure 2 compares the model results with experimental results at 420°C. The experiments showed a pronounced effect of water density on the conversion, whereas the mechanistic model predicts essentially no effect. Therefore, if the model has accurately captured the chemistry (which is not certain), then water is influencing the kinetics in some way other than through its direct, molecular participation in free-radical reaction steps.
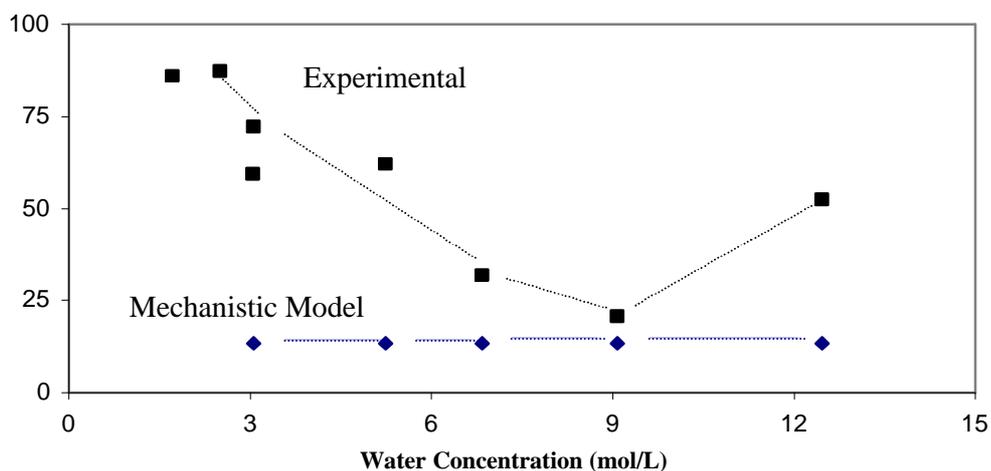
Figure 2: Model and Experimental Results for Phenol SCWO at 420°C and 40 sec.
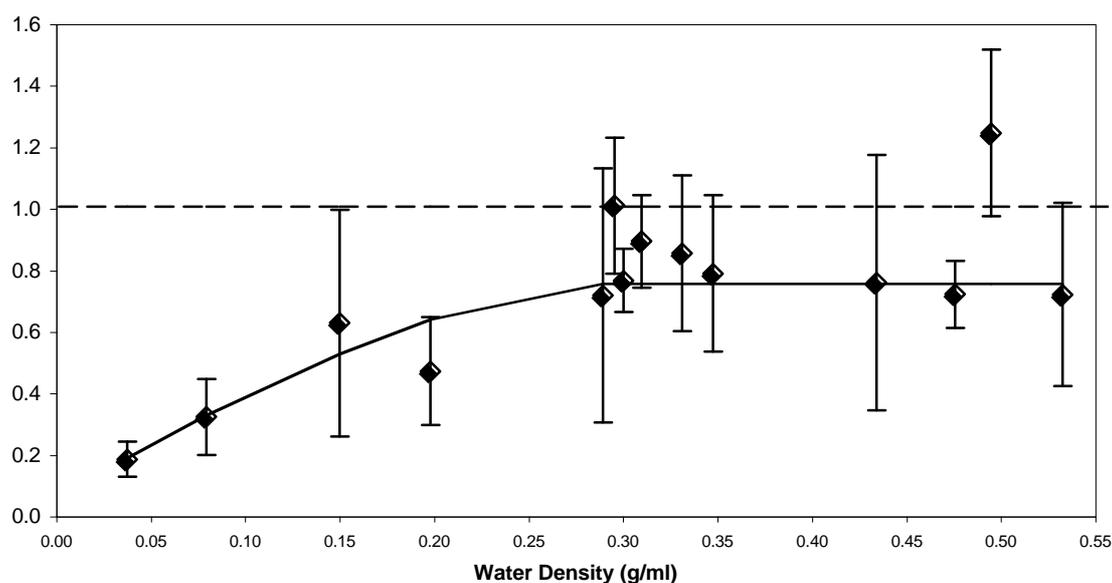
METHYLAMINE HYDROTHERMOLYSIS

The literature concerning hydrothermal reactions deals largely with hydrocarbons. Much less information is available regarding the chemistry of heteroatom-containing molecules, and especially those containing nitrogen atoms. To help fill this void, we have examined the reactivity of a model nitrogen-containing molecule, methylamine, in supercritical water. There have been no previous reports on the hydrothermal reactions of methylamine. The goal of this investigation is to resolve the reactivity of methylamine in supercritical water with respect to the possible pyrolytic and hydrolytic components of the reaction pathways. Methylamine may hydrolyze to form methanol and ammonia, while the pyrolysis of methylamine likely leads to products such as methane, ammonia, HCN, and H_2CNH. Examining the reactivity of methylamine in supercritical water at different water densities was the experimental approach we chose to obtain data that would enable us to resolve the relative importance of the competing reaction paths at different reaction conditions.
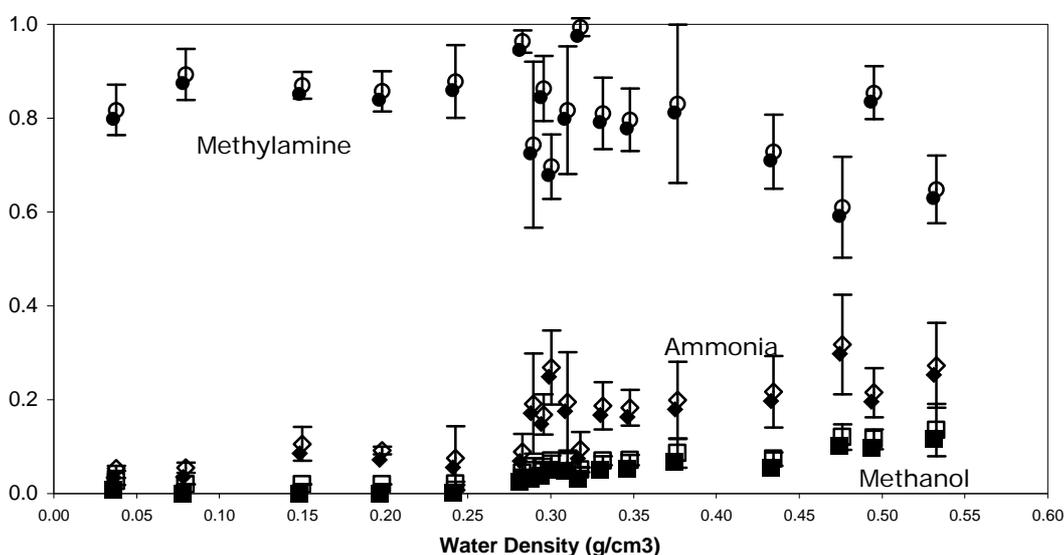
Figure 3: Product Yields from Methylamine Hydrothermolysis at 410°C

Figure 3 displays the molar yields of methylamine, ammonia, and methanol as a function of water density from reactions at 410°C, an initial methylamine concentration of 33.3 mmol/L, and a reaction time of 2 hours. These data suggest that there are two distinct regions of reactivity. At water densities less than 0.3 g/ml, the methylamine yield, or conversion, is constant, and therefore not affected by water density. This insensitivity to water density is consistent with what Lee and Gloyna [7] observed for acetamide hydrolysis between 400-525°C and with water densities from 0.1 - 0.26 g/ml. In this low water density region, ammonia is a major product, but very little methanol is formed.

At water densities greater than 0.3 g/ml, overall reactivity increases and methylamine yield decreases with water density. Simultaneously, the ammonia and methanol yields increase with water density in the region. This feature indicates that more direct hydrolysis of methylamine occurs at water densities greater than 0.3 g/ml than it did at water densities less than 0.3 g/ml. The ammonia selectivity increases with water density, too, as shown in Figure 4.

Figure 4: Ammonia Selectivity from Methylamine Hydrothermolysis

BENZOIC ACID DECARBOXYLATION

The stability and decarboxylation of organic acids in high-temperature and supercritical water is important in the synthesis of aromatic acids, which are used in large quantites as monomers, in waste treatment, and in fuel processing. The behavior of benzoic acid in supercritical water has been studied previously, but only to a limited extent. One group [8] reports 45% conversion after 60 min at 400°C, whereas another [9] reports 3% conversion after 30 min at 450°C. The higher conversion was obtained at a water density of 0.21 g/cm^3 whereas the lower one was at 0.01 g/cm^3. These seemingly counterintuitive results (lower conversion at higher temperature) might be due to the influence of the water density on the reaction. To test this hypothesis, we performed experiments [2] wherein all conditions were identical except for the water density. One set of experiments was done at a density of 0.3 g/cm^3 and the other at 0.01 g/cm^3. Figure 5 displays the results from these experiments. It is clear that both at 400 and 450°C, the conversion is higher in the experiments with the higher water density. These results show that benzoic acid does decarboxylate in supercritical water, and that the decarboxylation rate is sensitive to the water density. The reason for this density dependence is currently under investigation.

SUMMARY

This article has provided representative experimental results for three chemical reaction systems. Each system possesses a conversion and/or product selectivity that exhibits a response to changes in the water density/concentration. Collectively, these data add to the growing literature in this area, which shows that water density is an important variable for different types of reactions in SCW. In none of these cases has the precise cause of the density dependence been elucidated, in large part because the precise chemistry taking place has not yet been established definitively.
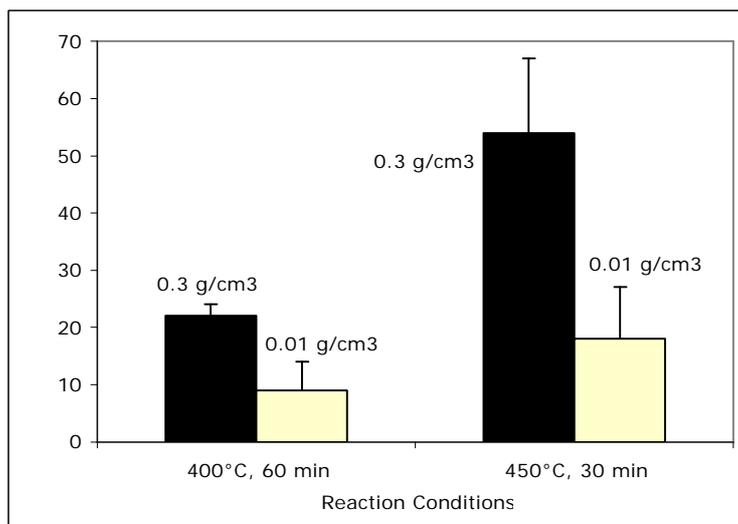
Figure 5: Conversion of Benzoic Acid in Supercritical Water

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