

THE USE OF REACTION INTERMEDIATES TO PROBE SUPERCRITICAL FLUID SOLVENT EFFECTS

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ABSTRACT

Reactions of free radicals and other reaction intermediates in supercritical fluids (SCFs) have proven to be excellent mechanistic probes of the influence of SCF solvation and SCF solvent effects on a variety of categories of chemical reactions in SCFs. This presentation will focus on mechanistic studies of reaction intermediates and, in particular, free radical reactions in SCFs and their relationship to our overall understanding of reaction chemistry under sub-critical and supercritical conditions. Three categories of reactivity that may be influenced in different fashions by SCF solvation and solvent effects will be described. The categories are: 1) diffusion-controlled reactions; 2) activated processes; and 3) reactions that may be influenced by solvent cage effects. The importance of solute-solute, solute-solvent and solute-cosolute interactions to these categories of reactivity will be addressed.

I. INTRODUCTION

Experimental, (1-9) theoretical (10-13) and simulation (7,14-24) investigations have now clearly documented that the local solvent density of SCFs about a dilute solute may be significantly greater than the bulk density of the fluid. This effect of enhanced solvent-solute interaction is often referred to as local density augmentation or SCF solvent clustering. Spectroscopic techniques and solvatochromic probes (1-9) have been particularly useful in the identification and quantification of local density enhancement about dilute solutes. Solvatochromic shifts and fluorescence intensity ratio measurements in a variety of SCFs have shown significant density dependent deviations in behavior from normal liquid solvents, and from behavior predicted from solution based theory. For example, *Kajimoto et al.* (5) have investigated the charge-transfer (CT) emission of (N,N,-dimethylamino)benzotrile in SC CHF₃. Bathochromic shifts of the CT emission are expected to vary linearly with solvent polarity, according to Onsager reaction field theory. (5) While *Kajimoto* found reasonable agreement with liquid data in high density SCF, large deviations from expected values occurred in the medium and low fluid density regimes. These deviations were attributed to solvent aggregation around the dilute solutes. Similar results have been observed for solvatochromic absorption probes where plots of the solvent polarity parameter, ET, versus density were also found to deviate from *McRae-Bayliss* theory at moderate to sub-critical densities. (4)

The physical and chemical properties of free radicals have also played an instrumental role in understanding local density enhancement about dilute solutes in SCFs. *Randolph* and coworkers (9,19-23) have demonstrated that electron paramagnetic resonance (EPR) spectroscopy of stable nitroxide free radicals may be used as an extremely versatile probe to simultaneously measure reaction kinetics and local solvent density augmentation. The nitrogen hyperfine splitting constants of nitroxides (AN) are known to be sensitive probes of solvent polarity and probe the cybotactic region of the solvent, i.e., probes the immediate volume around the nitroxide that has been

affected by the nitroxide radical. Therefore, AN values may be used to reflect degrees of solvation. The experimental data of Carlier and Randolph (9) for di-tert (9, 19-22) have clearly demonstrated that local density augmentation (solvent-solute clustering) does not generally correlate with kT . This indicates that local density enhancements are short-range effects and not related to long-range fluctuations that are responsible for the maximum in kT , and other phenomenon related to criticality, such as very large negative partial molar volumes of dilute solutes in SCFs. Therefore these results indicated that "supercritical fluid clustering" is not a long-range critical effect, but rather a result of short-range structural effect of solvation. This supports previous interpretations by Kajimoto, et al. in 1988, (5) and Knutson, et al. in 1992. (7) To date, several different methods of investigation of solvent-solute interactions have demonstrated that local density augmentation may be as much as two to three times the bulk solvent density and exhibits a maximum at fluid densities of one third to 0.8 of the critical density.

In addition to solvent-solute interactions in SCFs, it is also known that addition of small quantities (1-5 mol %) of cosolvent greatly enhances solubility of organic solutes in SCFs. This methodology is routinely used to enhance SC extraction and chromatography performances. Spectroscopic studies have indicated that this phenomenon is a result of enhanced solute-cosolvent interactions and may result in local composition enhancements in the cybotactic sphere as large as 8 to 10 times the bulk composition. (1-2, 7-8) Cosolvent enhancements are observed to increase from high to low mixture densities approaching the critical pressure in the compressible region of the SC solvent mixture. However, local compositions significantly greater than the bulk have been observed at temperatures and pressures well removed from the critical temperature. This indicates that changes in the local environment are not direct functions of the proximity of the critical point but, as with local density, are also controlled by short-range solvation interactions. Therefore, a second form of SCF "clustering" exists, local composition enhancement.

II. RESULTS

We have used several different types of reaction intermediates, including free radicals, electronically excited states, carbocations and radical anions to probe the influence of the above mentioned solvation effects on various categories of chemical reactions in supercritical fluids. (25-31) For example, we have examined the solvent density dependence of the non-geminate diffusion-controlled reactions of benzyl free radical and the triplet-triplet annihilation reaction of benzophenone (measured by second order kinetics). (25-26) In both cases these reactions were found to be influenced only by changes in the bulk physical property of change in diffusivity, and not by local solvent density enhancements. We have also found that this is true for diffusion-controlled reactions that are measured by pseudo-first-order kinetics. (27) However, for reaction that contain some activation, i.e., not fully diffusion-controlled, the influence of local composition "cosolvent enhancements" can appear as significantly enhancing absolute rate constants when bulk reactant concentrations are used in the kinetic analysis. (28-31)

III. CONCLUSIONS

Several examples of these types of reactions will be presented in order to demonstrate that factors that drive chemical reactions in supercritical fluids are often predictable and can be better understood when the specific reaction mechanisms under consideration are carefully examined.

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