

## Novel Solvents Systems for Catalytic Processes

### Part I: Supercritical Fluids and Nearcritical Water

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#### Introduction

A variety of tunable and smart solvent systems have been and are being developed for conducting green and sustainable catalytic processes. These solvent systems were designed to reversibly change physical and chemical properties upon application or removal of an external stimulus. The change can take place gradually (tunable solvent systems) or abruptly (smart solvent systems). The former systems include supercritical fluids, nearcritical water, gas-expanded liquids, and organic-aqueous tunable solvents. The latter systems include reversible ionic liquids and “volatile” DMSO substitutes. This presentation will include processes in supercritical fluids and nearcritical water. Part II, presented by my colleague Charles A. Eckert, will include processes in gas-expanded liquids, reversible ionic liquids, and “volatile” DMSO substitutes.

#### Results and Discussion

##### Supercritical Fluids and Phase Transfer Catalysis (1)

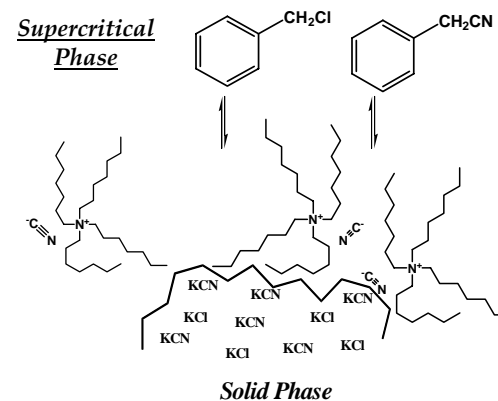
Phase transfer is a technique for conducting heterogeneous reaction processes between reactants located in contiguous phases. Generally the contiguous phases can be two immiscible liquids or a solid and a liquid. The phase transfer catalyst transports the reactant from the phase in which it resides to the phase containing the other reactant. Since the reaction partners are now located in the same phase reaction can take place. Phase transfer catalysts include quaternary ammonium salts and cyclic and linear multidentate ligands. Unfortunately, many phase transfer catalytic processes involve solvents which can be environmentally harmful. In addition, catalyst recycle is difficult and usually involves the expenditure of considerable amounts of energy. Supercritical fluids, such as supercritical carbon dioxide, have been successfully substituted for the organic solvent. Substitution reactions and alkylations reactions have been demonstrated in this unique solvent system (Figure 1). In addition, catalyst recycle is facile.

##### Nearcritical Water (2)

The physical and chemical properties of nearcritical water are substantially different from water at room temperature. Water at temperatures ranging from 250-300°C has a dielectric constant and a density similar to that of acetone. As a consequence it can dissolve both salts and organic molecules. In addition, the self-ionization constant,  $K_w$ , is approximately  $10^{-11}$ . Thus, the concentration of hydronium and hydroxyl ions has been increased by three orders of magnitude compared to water at room temperature. Acid and base catalyzed organic reactions can be conducted in near critical water and the isolation of the organic product can be achieved by simply cool the reaction system to room temperature to allow the product to phase separate. No neutralization of acid or base is needed. “Friedel-

Crafts” alkylations and acylation reactions and other condensation reactions have been successfully conducted in nearcritical water.

Figure 1: Mechanism of Supercritical Fluid Phase Transfer Catalysis



#### Significance

Industrial companies are striving to develop sustainable and green chemical processes especially for the production of fine chemicals. The systems described above and the systems described in Part II provide new and novel approaches to addressing the development of benign chemical processes.

#### References

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## Novel Solvents Systems for Catalytic Processes, Part II: Gas-Expanded Liquids and “Smart” Solvents

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### Introduction

For many chiral syntheses, homogeneous catalysts are used to improve rates and especially selectivity, but the catalyst removal and recycle is a problem. Also, often one must react species neither readily soluble in each other nor in a common solvent. Two types of novel solvents: gas-expanded liquids and “smart” solvents enable contact of dissimilar species for reaction and the recovery and recycle of homogeneous catalysts.

### Results and Discussion

**Gas-expanded liquids** are formed by the dissolution of a gas, usually CO<sub>2</sub>, into organic liquids. In general, liquid CO<sub>2</sub> is a poor solvent, whereas typical organics such as acetone and methanol are good solvents; thus a wide range of solvent properties are easily accessible through solvent expansion. At moderate pressures (generally 2-5 MPa), gaseous CO<sub>2</sub> has a considerable solubility in many organic solvents, thus providing the opportunity to alter the physicochemical properties of the liquid solvent – most notably the polarity, dielectric constant, and solubility – at much lower pressures than those required for supercritical fluid processing. Moreover, CO<sub>2</sub> is an ideal antisolvent, because it is environmentally benign, easily removed, and recyclable.<sup>1</sup> An example of the use of such a system for catalyst recycle was the improvement in the turnover frequency of a water-soluble catalyst system by a factor of 85 for the hydroformylation of 1-octene. The tunable solvent system increases substrate solubility and the reaction was run homogeneously in a miscible water-organic solution, and after reaction, CO<sub>2</sub> was used as a “miscibility switch” for efficient product and catalyst recovery. The rhodium catalyst was recycled three times with no loss of activity. Also we have shown the recycle of an enzyme *Candida Antarctica* lipase B (CALB) used for the hydrolysis of 2-phenethyl acetate to 2-phenylethanol in a dioxane-water miscible mixture. Here both the substrate and product are only sparingly soluble in water, but have good solubility in the mixture. After reaction, CO<sub>2</sub> splits the mixture, with the enzyme recycled in the (buffered) aqueous phase and with the dioxane gas-expanded liquid removing the product for purification, Figure 1. As another example with such a system

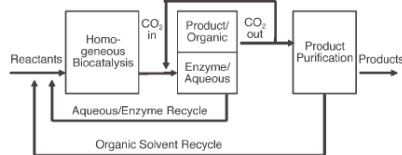


Figure 1. Catalyst recycle by OATS

We also use “**smart**” molecules – molecules that change properties to facilitate processing. Such molecules may change because of changes in temperature, pressure, pH, or adsorption of light. They may change from polar to nonpolar, involatile to volatile, or from surfactant to non-surfactant. We have used two types of such molecules specifically for homogeneous catalysis and facile catalyst recycle – reversible ionic liquids<sup>2</sup> and an easily

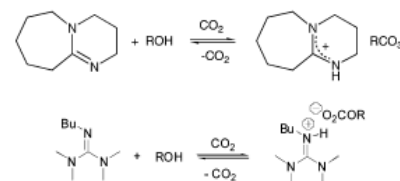


Figure 2. Reversible ionic liquids

retrochelotropic reaction of a diene with SO<sub>2</sub> to form a sulfone (Figure 3), reversible by modest heating. One example of the use of this solvent for catalyst recycle are aerobic oxidation of *p*-methoxy benzylalcohol with TEMPO. Another is ruthenium-catalyzed asymmetric transfer hydrogenation of benzophenones.

removable DMSO substitute<sup>3</sup>. The former is formed by the reaction (at ambient temperature and atmospheric pressure) of an amidine or guanidine to form an ionic liquid, with an enormous change in solvent polarity (Figure 2). It can be reversed by heat or by sparging with N<sub>2</sub>. An example of reaction in such a mixture was the Heck reaction of bromoacetophenone with butyl acrylate. The other example of a smart solvent switch is achieved by the

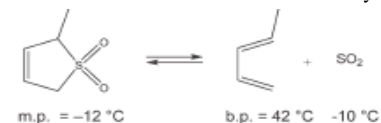


Figure 3. Formation of piperylene sulfone with reverse reaction at 110°C. Products

### Significance

Solvent management is the key to chemical processes, which invariably involve both reactions and separations. Solvents bring reactants and catalysts together and facilitate purification processes. In these two talks we have shown the synergistic combination of chemistry and engineering, using novel solvent systems to achieve homogeneous reactions and heterogeneous separations, with the goal of developing more benign and sustainable processes.

### References

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