Benign Separations and Recycle by CO2-Enhanced Aqueous Extraction

Separation and product purification is crucial for environmentally benign and economically attractive chemical processes. We propose to use CO2 to enhance aqueous extractions of highly polar and ionic species from organic solvents into aqueous media. Typical of these would be catalysts, such as the quarternary ammonium salts used as phase transfer catalysts (PTCs), hydrophilic organometallic catalysts, and reaction products such as amines, which become salts on contact with CO2.

Introduction

CO2 is miscible with most organics, but is virtually immiscible with water; also it acts as a powerful antisolvent. CO2 is readily absorbed into an organic liquid as a gas expanded liquid phase - Figure 1. The composition and properties of this GEL vary continuously, from the high solvent power of an organic like acetone (shown on the ET scale in Figure 2) to the very weak solvent power of liquid CO2.

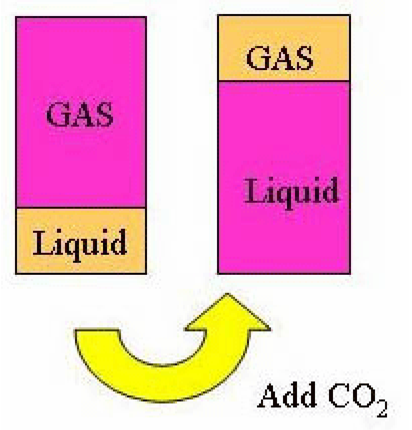

Figure 1. Gas-expanded liquid (GEL) from the addition of CO2 to most organics.

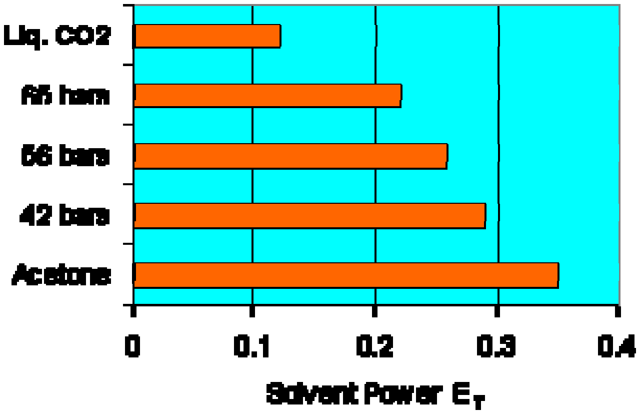

Figure 2. Relative solvent power of CO2-Acetone GELs - ET scale.

It has often been used in this manner for particle production or for fractional crystallization, but these applications require a saturated solution. We use it in conjunction with aqueous extraction to enhance recovery from more dilute organic solutions. We have demonstrated that its use can greatly alter the distribution coefficients of two PTCs between organics solvents and water. In the systems studied, CO2 enhanced aqueous extraction provides the potential to reduce the washwater typically used for PTC recovery by more than an order of magnitude, with concomitant energy savings in catalyst recovery. This would permit the recycling of toxic or expensive catalysts and the environmentally benign and economical purification of many dilute reaction products.

Results

Many potential industrial applications of this method are in phase transfer catalysis (PTC). PTC is widely used as a method for reacting nonpolar organics with ionic species, immiscible in the same solvent. It uses large "greasy" counterions, such as quaternary ammonium cations, to drag anions into a nonpolar phase to react, and then to transport the product anion back to the aqueous phase for re-equilibration. In essence, the quaternary ammonium cations can transfer anions from aqueous to organic solvents as well as activate anions for reactions. More than 500 chemical products are currently made by such techniques in the U.S. at a value in excess of $10 billion/year.

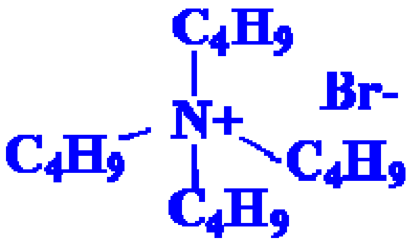

Figure 3. Tetrabutyl ammonium bromide, TBAB, a common PTC catalyst

After reactions are complete the moderately expensive and mildly toxic organic salt catalysts require separation and recycle from the organic product mixture. Organic salts may be recovered from organic product mixtures by distillation, but this separation technique is limited to systems with low boiling product mixtures as many organic salts thermally decompose at temperatures higher than 90°C. More often, organic salts are recovered from the organic product mixture by extraction with water, but extracting the more hydrophobic organic salts may require very large quantities of wash water. In addition, recovering expensive and potentially toxic organic salts from dilute aqueous solutions requires enormous amounts of energy and becomes prohibitively expensive.

In addition to PTC, many other examples exist where the recovery of hydrophilic catalysts by similar techniques would be valuable. We are also studying the application of this method for the separation of organometallic catalysts with hydrophilic ligands and, augmented by the complexing power of CO2, for the recovery of some reaction products.

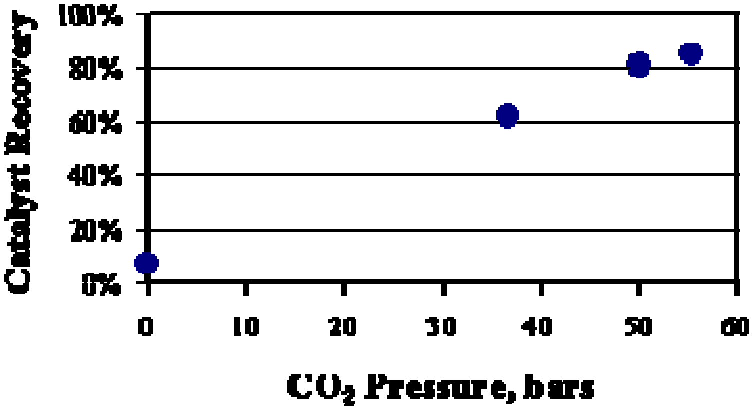

Figure 4. CO2-assisted aqueous recovery of BTEAB catalyst at 25 °C. 11.5 g NaCl solution (20 wt%), 20 ml acetonitrile, 0.0068g (2.5x10-5 mole) BTEAB.

We have measured the effect of CO2 on the distribution (ratio of solute concentrations in aqueous to organic phases in mol/liter) of these salts between immiscible aqueous and organic phases at room temperature. We determined the effect of CO2 on the distribution of triethylbenzylammonium bromide (BTEAB) between acetonitrile and an immiscible aqueous phase containing 20 wt % NaCl, Figure 4.

The effect is even more dramatic if viewed in terms of the distribution coefficient, K - the ratio of the aqueous phase concentration/organic phase concentration. The distribution coefficient can be changed by more than 2 orders of magnitude, Figure 5.

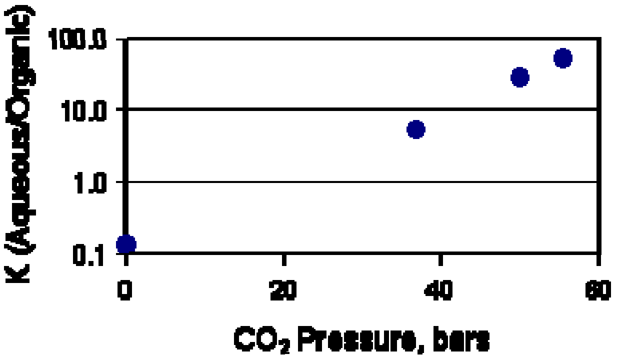

Figure 5. Distribution coefficient of BTEAB catalyst between aqueous and acetonitile phases at 25 °C. 11.5 g NaCl solution (20 wt%), 20 ml acetonitrile, 0.0068g (2.5x10-5 mole) BTEAB.

We have also measured the distribution of another organic salt, tetrabutylammonium picrate (TBAP) between water and several immiscible organic solvents was also measured. For butyl acetate, methyl isobutyl ketone (MIBK), and methylene chloride, distribution coefficient changes of substantially more than 1 order of magnitude were observed, Figure 6 below.

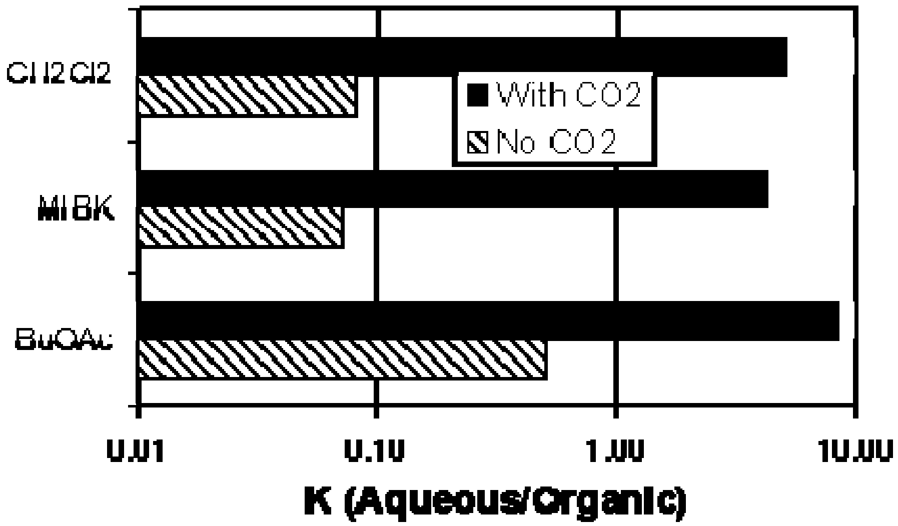

Figure 6. The effect of CO2 (volume expansion of 90%) on the distribution coefficient K for TBAP between aqueous and organic phases at 25 °C. Solvents are methylene chloride (CH2Cl2), methyl isobutyl ketone (MIBK) and butyl acetate (BuOAc). 20 ml of 8.77 x 10-5 M TBAP aqueous solution, 20 ml organic solvent.

Reduction of Wash Water

These large changes in the distribution coefficients of these two organic salts in immiscible aqueous/organic systems could allow substantial reductions of wash water required for the organic salt extraction. The water usage of a conventional aqueous extraction at atmospheric pressure and a CO2 enhanced aqueous extraction with 50 bar CO2 pressure are compared in Table I for equal volume and countercurrent modes. Reduction of wash water volumes of more than 95% are possible.

	Equal volume	Countercurrent
Atmospheric pressure	60L	20~30L
50 bar CO_2 pressure	2.7L	0.3~0.5L

Vaporization of water at 25 °C requires 2440 kj/kg of energy (Harvey and Klein 1996). The CO2 compression cycle at 40 °C from 30 to 100 bar requires 65 kj/kg (Brunner 1994), and the heat of vaporization of CO2 at 25 °C is only 120 kj/kg (Bush 2001). In the example above with one liter of methylene chloride, the evaporation of ~25 L of water would require ~ 60,000 kj of energy. The same separation could be achieved with ~ 4 kg of CO2 requiring a compression energy of less than 740 kj of energy-a > 98% reduction in the energy required.

CO2 enhanced extraction may be applicable to multiple solutes, and in some instances may serve to actually improve the selectivity of an extraction. The decrease in polarity caused by the addition of CO2 may drive one solute into the aqueous phase while simultaneously extracting another into the organic phase. Based on the results of the CO2 enhanced extraction of single solutes, more opportunities to enhance the selectivity of systems with multiple solutes are being identified.

Economic Analysis

We are also demonstrating efficient separations of products and catalysts. For our results to have the most impact and greatest likelihood of industrial application, it is necessary to include comparisons of energy use and capital expenditure between our proposed processes and current industrial technologies. Our goal is to provide industrial users with a means of choosing a solvent system for catalyst recycle based on reduced separations cost. We are making preliminary process designs with economic calculations to compare CO2 enhanced aqueous extraction with current processes. We find that while working with pressurized carbon dioxide may require some additional capital expenditure for pressurized equipment, the pressure requirements for efficient separation with CO2 enhanced extraction were relatively low in the preliminary work (less than 60 bar). This cost may be more than offset by the reduced energy cost of less water evaporation and the lower capital cost of smaller / fewer separation units.

Conclusion

We have demonstrated that CO2 can dramatically change the partitioning of some hydrophilic solutes between organic and aqueous phases even in dilute quantities. This provides the potential to significantly reducing the amount of water required for an aqueous extraction and decreasing the loss of organic solute in the aqueous extract. A more concentrated extract solution facilitates separation of products and catalyst recycle. Specifically, this technique should be most effective with immiscible aqueous/organic systems with organic solutes with some hydrophilicity or that react reversibly with CO2 to form hydrophilic products.