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Phase-transfer catalyst separation by CO_2 enhanced aqueous extraction

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CO_2 is used to enhance the environmentally benign and efficient recovery of phase transfer catalysts with aqueous extraction; this method can alter the distribution of phase transfer catalysts so dramatically that even in dilute organic solutions they can be separated selectively from an organic reaction mixture with only a small fraction of the water required in a traditional aqueous extraction.

Phase transfer catalysis is a technique for conducting reactions between reaction partners located in separate, contiguous immiscible phases employing a phase transfer catalyst (PTC) such as a quaternary salt.[1] After reaction is complete, the moderately expensive and mildly toxic catalyst must be separated from the product and recycled.[2] This is usually accomplished by one of four separation methods: extraction, distillation, adsorption, or binding to an insoluble support.[1] Nanofiltration has also been used in a recent publication.[3] Extraction is probably the most common method used to separate phase transfer catalysts in commercial processes; however, many lipophilic catalysts, though water soluble, require a large amount of wash water to be removed from the organic phase. This then requires the evaporation of large amounts of water to concentrate the catalyst for recycling or results in the loss of catalyst plus treatment and disposal of many gallons of waste water per pound of product produced.

CO_2 is miscible with most organic solvents at elevated pressure.[4] Since it is nonpolar and a very weak solvent, the addition of a significant quantity of CO_2 can reduce the ability of polar organic solvents to dissolve ions and polar organic solutes. One application of this principle is the gas anti-solvent process (GAS) where ions or polar organic solutes are crystallized from polar organic solvents by the addition of CO_2 as an antisolvent.[5] Although CO_2 is a reasonable antisolvent for normal PTC–solvent systems, the concentration of PTC in an organic phase is generally not high enough to reach the supersaturation required for crystallization without the addition of enormous amounts of CO_2.

Alternatively, this work investigates the effect of CO_2 on the partitioning behavior of lipophilic phase transfer catalysts between organic and aqueous phases. CO_2 may be added to an immiscible aqueous–organic mixture to enhance aqueous extraction by driving more PTC into the aqueous phase to alter the aqueous–organic distribution coefficient. Unlike antisolvent crystallization, CO_2 enhances extractions even when a PTC is present in low concentration. Further, the addition of CO_2 reduces the mutual solubility of organic solutes and water. The net result of the process is to reduce the amount of wash water required, to reduce the loss of organic solvent in the aqueous extract, and to facilitate product recovery and catalyst recycling.

To demonstrate the principle of CO_2 enhanced aqueous extraction, two model quaternary ammonium salts were used in several biphasic systems. One model salt was benzyltriethylammonium bromide (BTEAB), which is quite widely used as a phase transfer catalyst. The biphasic system comprised acetonitrile and an aqueous solution with 20 wt% NaCl.[6] Distribution coefficients[7] of benzyltriethylammonium cation at different CO_2 pressures, shown in Fig. 1, were calculated from the measurement of phase volumes and benzyltriethylammonium cation concentration in the aqueous phase.[8] At pressures less than 60 bar, CO_2 drove the BTEAB into the aqueous phase, altering the distribution coefficient by about 200 fold. Another finding of practical interest was that the acetonitrile concentration in the aqueous phase decreased by 5 fold with the addition of CO_2.

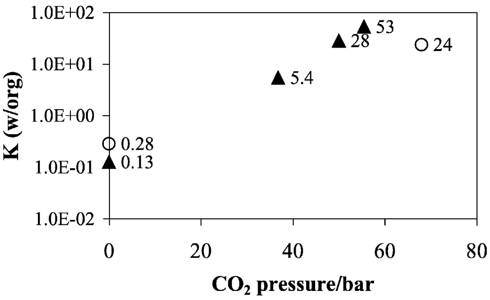

Fig. 1 BTEAB distribution coefficient as a function of CO_2 pressure at room temperature (23–25 °C). Data (○): 50 g NaCl solution (20 wt%), 20 ml acetonitrile, 0.3 g (0.0011 mole) BTEAB. Data (▲): 11.5 g NaCl solution (20 wt%), 20 ml acetonitrile, 0.0068 g (2.5×10^{-5} mole) BTEAB.

A second model salt, tetrabutylammonium picrate (TBAP), is an analog of tetrabutylammonium bromide (a common industrial PTC) that may be conveniently analyzed by UV-vis spectroscopy.[9] Three common solvents for PTC, butyl acetate, methyl isobutyl ketone (MIBK), and methylene chloride, were each used as the organic phase in the aqueous biphasic system.

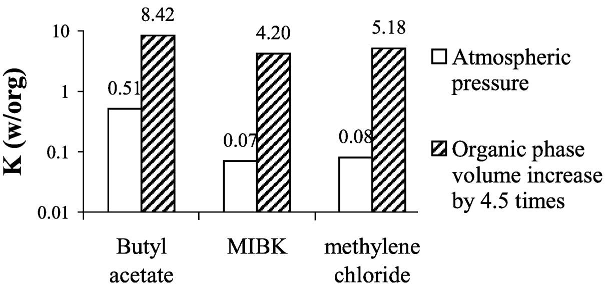

Fig. 2 TBAP distribution coefficient as a function of CO_2 pressure at room temperature (23–25 °C). Organic solvents used respectively: butyl acetate, methyl isobutyl ketone and methylene chloride. 20 ml 8.770×10^{-5} M TBAP aqueous solution, 20 ml organic solvent. For the three solvents used, CO_2 pressures are less than 60 bar to achieve 4.5 times volume expansion of the organic phase.

Table 1 Comparison of the water usage of a conventional aqueous extraction at atmospheric pressure and a CO_2 enhanced aqueous extraction with 50 bar CO_2 pressure for equal volume batch and countercurrent modes. The calculation is based on the data for the CH_2Cl_2–H_2O system in Fig. 2 and concentration reduction by 100 fold in 1 litre of organic solvent.

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

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The measurement of distribution coefficient was as described previously. Distribution coefficients were again significantly changed as a consequence of added CO_2 (Fig. 2).

These large changes in the distribution coefficients of organic salts in immiscible aqueous–organic systems can result in substantial reductions of wash water required for the organic salt extraction. The water usage of a conventional aqueous extraction at atmospheric pressure and an aqueous extraction enhanced with 50 bar CO_2 pressure are compared in Table 1 for equal volume batch and countercurrent modes. Reductions of wash water volumes of more than 95% are possible.

In conclusion, CO_2 enhanced aqueous extraction has been demonstrated as an efficient and environmentally benign technique to separate BTEAB and TBAP in several systems; further, this technique has the potential to separate other water-soluble but lipophilic substances.

Notes and references

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6 High concentration salt solutions are commonly used in PTC reactions. In this case, the salt makes acetonitrile and water less miscible.

7 Distribution coefficient is used instead of partition coefficient because: (1) only one or two concentrations are investigated; (2) other ionic equilibria exist.

8 Measurement of the distribution coefficients was performed in a 150 ml windowed pressure vessel (Jerguson) at room temperature (23–25 °C). Known amounts of organic salt in aqueous solution and organic solvent were introduced into the windowed pressure vessel before sealing. Then CO_2 was metered into the vessel with a syringe pump (ISCO 260 D). Pressure in the vessel was measured to ± 0.07 bar (Druck DPI 260). The volume changes of the two liquid phases were estimated by the relationship between fiduciary marks on the outside of the vessel and the menisci at the aqueous organic interface and the organic–vapor interface. After rocking the vessel to reach equilibrium, we took water phase samples from the bottom of the pressure vessel through a sampling valve. A HP 8453 UV/Vis spectrometer was used to measure the concentration of triethylbenzylammonium cation (λ_{max} = 265 nm, ε = 342 between 3.351×10^{-4} M and 4.600×10^{-3} M).

9 Picric anion (λ_{max} = 356 nm, ε = 1.561×10^4 between 1.754×10^{-6} M and 8.770×10^{-5} M).

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