Switchable Solvents

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For many practical applications of solvents and surfactants, the ability to "switch" the material's properties during a process would be exceedingly useful. Imagine, for example, a solvent that is capable of dissolving a desired product during an extraction, and then afterwards can be "switched off" so that it is no longer capable of dissolving the product. The product would then precipitate and be easily collected, without any need for distillation. The author invented the first switchable solvents in 2004 and has been working with his students and collaborators to develop many more switchable liquid and solid materials since then.[1] There are three principal classes of switchable solvents:

a) "Switchable-polarity solvents" (SPS). These solvents have low polarity until they are exposed to an atmosphere of CO_2, which changes them into high-polarity solvents.[2-4] The process is reversed by removal of the CO_2 from solution. Amidine/alcohol mixtures, which convert to amidinium alkylcarbonate ionic liquids, were the first switchable solvents discovered, and have been successfully tested as reaction media, extraction solvents, and CO_2-capturing solvents. More recently, guanidine/alcohol mixtures, amidine/primary amine mixtures, and several single-component SPS have been discovered. The single-component SPS are secondary amines (giving $[R_2NH_2][R_2NCO_2]$ ionic liquids),[3] primary amines,[5] diamines,[6] hydroxy-amidines, and hydroxyguanidines.[6]

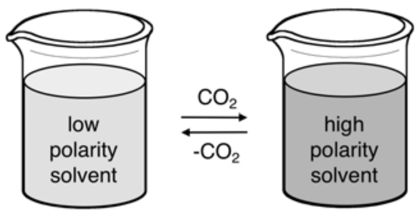

Fig. 1 – Switchable-polarity solvents, such as secondary amines or amidine/alcohol mixes, react with CO_2 to make a solvent of higher polarity than the original. Removal of the CO_2 reverses the process.

b) "Switchable-hydrophilicity solvents" (SHS) normally form a biphasic mixture when mixed with water but, when exposed to CO_2, these solvents become very hydrophilic and completely miscible with water (Figure 1).[7, 8] These solvents have applications in the area of solvent recovery. Industry normally uses distillation as the standard method for removing solvent from product, but distillation requires the solvent to be volatile and therefore flammable, smog-forming, and an inhalation risk to workers. If solvents could be removed from products and recycled without distillation, then nonvolatile organic solvents could be used, reducing the risk to the environment and the workers. SHS can be removed using carbonated water, rather than distillation. For example, imagine that the SHS is being used as a replacement for hexane or toluene for the extraction of some hydrophobic material like an oil. After the extraction, the solvent/product mixture is mixed with carbonated water, into which the SHS dissolves and the product does not. The product can be removed by decantation or filtration leaving behind the aqueous phase containing both the water and the SHS. Removing the CO_2 from that phase switches the SHS back into being hydrophobic, causing it to separate from the water. allowing both SHS and water to be used again. Such extractions have been demonstrated for soybean oil,[7] algae oil,[9] and bitumen from oil sands.[10]

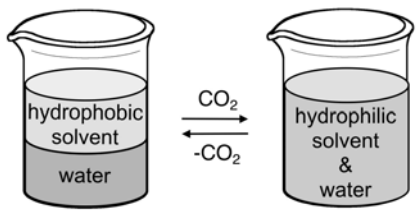

Fig. 2 – Switchable-hydrophilicity solvents, such as $CyNMe_2$, normally form a biphasic mixture when mixed with water, but will react with CO_2 to make a bicarbonate salt that is soluble in water, thus causing the two liquid phases to merge into one. Removal of the CO_2 reverses the process.

c) "Switchable water" (SW). An aqueous solution of a polyamine has a very low ionic strength. The solution can dissolve organic solutes well because the polyamine acts as a hydrotrope. However, if CO_2 is introduced, the polyamine changes to a salt, raising the ionic strength greatly. That change in ionic strength dramatically changes the properties of the water and its performance in many applications. In particular, the solubility of organic solutes drops greatly because the salt is not a hydrotrope and because organic compounds are generally not soluble in aqueous solutions of high ionic strength.[11, 12]

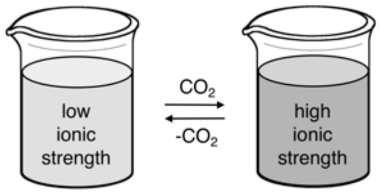

Fig. 3 – Switchable water is an aqueous solution of switchable ionic strength. The solution of an amine or polyamine in water has very low ionic strength, but if CO_2 is introduced the polyamine is converted into a bicarbonate salt (polyelectrolyte), causing the ionic strength of the solution to jump dramatically. Removal of the CO_2 reverses the process.

Switchable water can also be used to stabilize (without CO_2) and then destabilize (with CO_2) emulsions and suspensions.[13, 14] Switchable water makes ionic surfactants become CO_2-responsive, even if the surfactant would not normally be affected by CO_2.[14] With CO_2, switchable water is an excellent draw solution for forward osmosis, for the recovery of fresh water from wastewater or seawater.[15, 16] Once CO_2 has been removed, the amine can be easily recovered, leaving behind fresh water. Switchable water can also be used as the basis for aqueous solutions of switchable viscosity.[17]

The presentation will present a short summary of switchable solvents, followed by a more detailed description of recent developments in SHS and SW design and applications.

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