

$L = 4.0 \times 10^{-11}$ N, $W = 1.0 \times 10^{-2}$ J/m². The diameter of the colloids was 1.0 μ m and the cell thickness was 2.0 μ m. For this particular choice of parameter values, both configurations are stable. The quadrupole is metastable with respect to the dipole, and therefore by only changing the initial conditions for the relaxation algorithm, either dipolar

or quadrupolar defect structures were generated. Periodic boundary conditions in x and y directions were used.

Supporting Online Material

www.sciencemag.org/cgi/content/full/313/5789/954/DC1
Materials and Methods

Fig. S1
References

8 May 2006; accepted 6 July 2006
10.1126/science.1129660

Switchable Surfactants

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Many industrial applications that rely on emulsions would benefit from an efficient, rapid method of breaking these emulsions at a specific desired stage. We report that long-chain alkyl amidine compounds can be reversibly transformed into charged surfactants by exposure to an atmosphere of carbon dioxide, thereby stabilizing water/alkane emulsions or, for the purpose of micro-suspension polymerization, styrene-in-water emulsions. Bubbling nitrogen, argon, or air through the amidinium bicarbonate solutions at 65°C reverses the reaction, releasing carbon dioxide and breaking the emulsion. We also find that the neutral amidines function as switchable demulsifiers of an aqueous crude oil emulsion, enhancing their practical potential.

Surfactants are designed to stabilize emulsions during certain stages in cleaning, manufacturing, oil recovery, and other processes. Temporary emulsions (emulsions that are desired only during one stage of a process) are of practical interest in many areas, including (i) emulsion and micro-suspension polymerizations, because of the low viscosity and efficient heat transfer compared with bulk polymerization; (ii) cleaning and metal degreasing of equipment; (iii) viscous oil transportation through pipelines, because the emulsion is far less viscous than the oil itself (1, 2); (iv) enhanced oil-recovery (EOR), because surfactants help labilize oil by lowering the oil/water interfacial tension (3, 4); (v) separation of oil from oil sands (5); and (vi) even some cosmetic emulsions which are intended to separate upon use (6). In these applications, an emulsion is only useful during one stage of a process, after which the surfactant becomes a liability that hinders separation of the components. The problem of how to break surfactant-stabilized temporary emulsions has not been resolved satisfactorily in the literature.

Cleavable or switchable surfactants could be used to address this problem, but they still have several drawbacks. A cleavable surfactant can be irreversibly converted, typically by application of a chemical or photochemical trigger, into one or more molecules with greatly reduced surface activity. This ability is usually conferred on the surfactant by

incorporating a cleavable functional group such as an ester between the hydrophilic headgroup and the hydrophobic tail (7). A switchable surfactant, by contrast, can undergo fully reversible interconversions between active and inactive forms. Emulsions stabilized by either type of surfactant can thus be broken by application of the appropriate trigger. Solid materials such as particles that are temporarily protected by surfactants during synthesis can be deprotected and purified. Switchable surfactants have the additional advantages that their activity can be delayed until needed, they can be recovered and reused afterward, and their removal from the product stream can be facilitated by switching the surfactant to the form least soluble in the relevant medium.

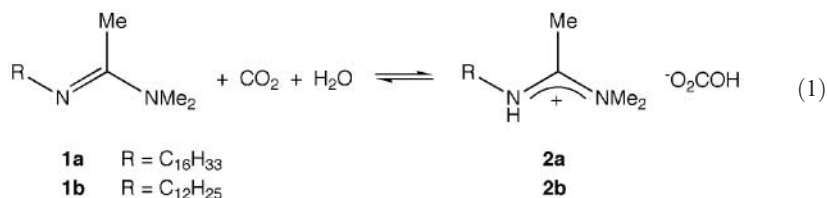
At the same time, the nature of the trigger can limit the practical viability of cleavable and switchable surfactants. Triggers based on the addition of acids, bases, oxidants, or reductants suffer from economic and environmental costs, as well as the potential for product contamination or modification by these reagents. Mild and inexpensive triggers are therefore preferable. Photochemical approaches are hindered by the opacity of many emulsions. Surfactants in which the head-group functionality or the polarity of the tail can be switched electrochemically have been reported (8–14), but they contain

expensive ferrocenyl groups, highly toxic viologen groups, or groups sensitive to O₂.

Here, we report switchable surfactants that use benign gases (CO₂ and air) as the triggers to switch them “on” and “off”. The chemistry behind the transformation was uncovered during our earlier studies of amidine reactivity: On exposure to 1 atmosphere of gaseous CO₂, amidines mixed with water (15) or an alcohol (16) react exothermically to form the bicarbonate or alkylcarbonate salts. The reaction can be reversed by bubbling N₂ or Ar through the neat liquid salt, or else through a solution if the salt is a solid. We reasoned that an amidine with a long alkyl chain should be a poor surfactant but would become an effective surfactant on conversion to the charged amidinium bicarbonate by exposure to water and CO₂. A further benefit of the amidine systems is that the product generated by switching off the surfactant has negligible surface activity and water solubility—a substantial environmental advantage.

To evaluate this hypothesis, two such amidines, **1a** and **1b**, were prepared and characterized. Their reaction with CO₂ and water to produce amidinium bicarbonate salts (**2a** and **2b**) was confirmed by bubbling CO₂ through wet ether or wet acetonitrile solutions of **1a,b** and collecting and characterizing the precipitate (Reaction 1). The bicarbonate salts can be reconverted to the amidines by bubbling argon through solutions of **2a,b** in tetrahydrofuran; the products were isolated and their structures confirmed by ¹H nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. Thermogravimetric analysis of solid **2a** (fig. S1) showed that the CO₂ and water are driven off between 50 and 63°C (17).

The reversibility and repeatability of the process were confirmed by monitoring the conductivity of a solution of **1a** in wet dimethyl sulfoxide (DMSO) while CO₂ and then argon were bubbled through the solution over three cycles (Fig. 1). The conductivity rose when CO₂ was bubbled through the



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Fig. 1. The conductivity of a DMSO solution of **1a** at 23°C as a function of time during three cycles of treatment with CO₂ followed by argon.

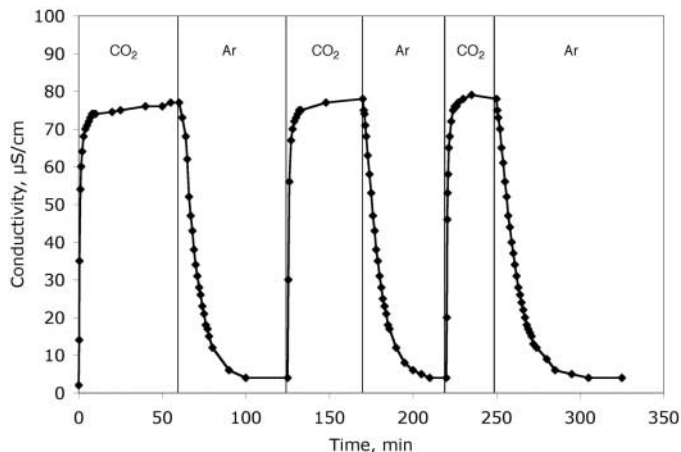
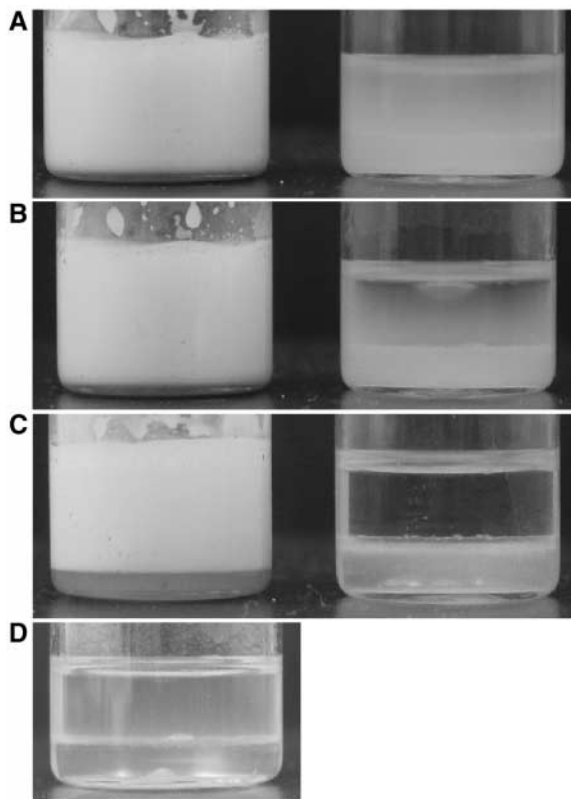


Fig. 2. Photographs of 2:1 (v/v) hexadecane/water mixtures containing **1a** and either CO₂ (left) or argon (right) after 10 min of shaking followed by a waiting period of (A) 5 min, (B) 30 min, and (C) 24 hours. (D) Photograph of the CO₂-induced emulsion after treatment with argon at 65 to 70°C for 2 hours (26).



solution, and it dropped upon argon addition. Air was found to have the same effect as argon.

The capacity of the amidines for stabilizing an emulsion was evaluated by automated shaking of mixtures of hexadecane and water containing **1a** (90 mg). Although an emulsion formed, it clearly separated into two layers within 5 min after the cessation of shaking (Fig. 2). However, if the solution was treated with CO₂ for an hour before the shaking, the emulsion was much more stable. It showed no evidence of separation for 3 hours, at which point a very thin layer of cloudy liquid began to appear at the bottom of the flask. After one day, the emulsion still

occupied 82% of the liquid volume (Fig. 2C). Bubbling argon through the emulsion at 65°C resulted in a complete separation of the hexadecane and water into two clear layers.

Similar experiments were performed with crude oil, but with notably different results (Fig. 3). Light crude oil, when shaken with water but without any additive, was able to form a fairly stable emulsion, presumably as a result of naturally occurring surfactants in the oil (18, 19). A stable emulsion also resulted from treatment of the same oil/water mixture with compound **1a** and CO₂. However, addition of compound **1a** under argon does not lead to a stable emulsion; the mixture separates into two layers within 30 min,

revealing that the uncharged amidine functions as a demulsifier (20). This demulsifying effect suggests that variations of these switchable surfactants may be useful in oil production for such applications as the breaking emulsions after EOR, oil-sands separations, and even cleaning of equipment. Although demulsifiers are known, including some that contain closely related head groups such as cyclic amidines (21), reversible switching between surfactant and demulsifier is, to our knowledge, unprecedented. Application of this technology to oil industry operations may depend on modifying the structure of the switchable demulsifier so that it will demulsify emulsions of heavy crudes.

Surfactants are also used to protect the surfaces of nanoparticles, colloids, latexes, and other particulates during their synthesis; in the absence of a coating of surfactant, these particles tend to agglomerate into undesirably large particles. In many cases, once the synthesis is complete, protection by the surfactant is no longer needed. For some applications, such as the preparation of supported metal catalysts, the complete removal of the surfactant is desired but difficult because the surfactant binds too strongly to the surface. For other applications, mere deactivation of the surfactant is desired and not necessarily removal. In either case, a switchable surfactant would be advantageous. As a preliminary demonstration that the amidine-based switchable surfactants can be used to protect growing particles during synthesis and then can be switched off, we tested their use in a microsuspension polymerization (Reaction 2) (22, 23). Microsuspension and emulsion polymerizations, techniques very commonly used for polymerizations involving radical mechanisms, require surfactants to protect the growing polymer particles during the synthesis. The product is a latex, meaning a surfactant-stabilized dispersion of polymeric particles in water. Isolation of the polymer from the suspension is facilitated if the surfactant can be switched off. The current industrial method to isolate the polymeric product is the addition of salts to coagulate the dispersion, followed by filtration and removal of the surfactant and added salts by washing (24). The washing step is often ineffective in removing the surfactants, resulting in polymers that are unnecessarily hydrophilic, which can be undesirable in many applications. An alternative route is to perform the polymerization in an organic solvent, but this approach is undesirable for two reasons. First, the removal of the solvent from the product is hindered by the high viscosity of the product mixture. More important, the use of the solvent increases emissions of volatile organic compounds (25). Although many polymers are made by surfactant-stabilized

methods, styrene polymerization was chosen as a test example. The radical polymerization of styrene, initiated by thermal decomposition of an azo-based free radical initiator, was performed in a styrene-in-water emulsion stabilized by **2b** under CO₂. Switching the surfactant off by bubbling argon or nitrogen through the system at 65°C and then cooling to room temperature and adding more water allows the polymer to settle. The settling is accelerated if the sample is

centrifuged. However, without the argon/nitrogen treatment, the polymer failed to settle within an observation period of 3 days or with centrifuging (Fig. 4).

Future work in this area will include quantitative measurement and improvement of the rate of surfactant switching and optimization of the surfactant designs for specific applications, especially in nanoparticle synthesis, polymerization, and the oil industry applications that we have described.

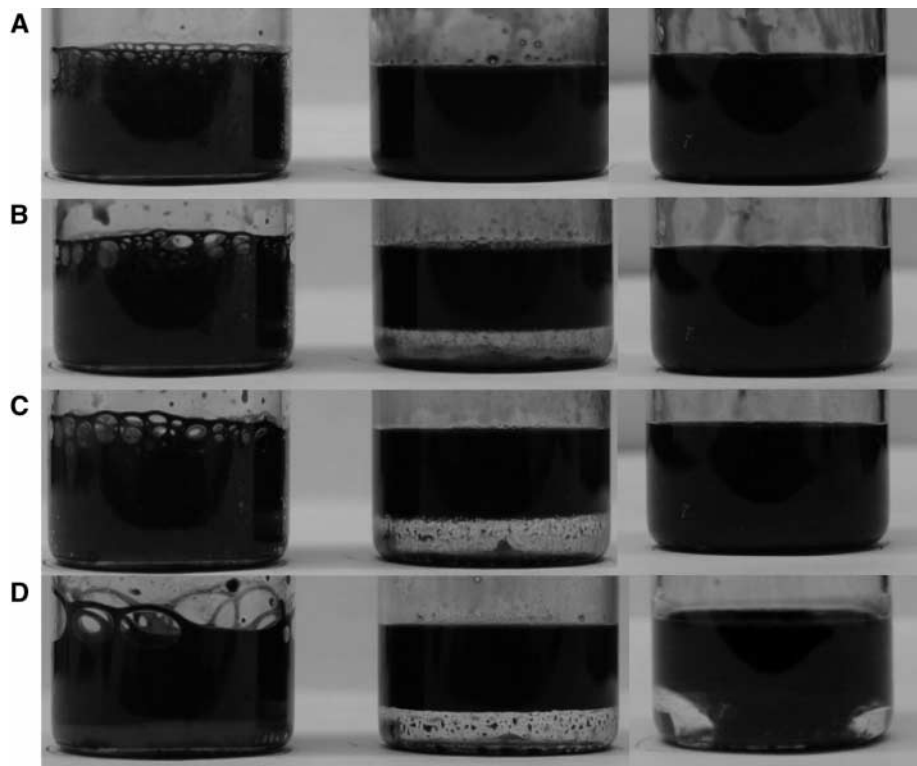


Fig. 3. Photographs of 2:1 (v/v) crude oil/water mixtures containing either **1a** and CO₂ (left), **1a** and argon (center), or only argon (right) after 10 min of shaking followed by a waiting period of (A) 5 min, (B) 30 min, (C) 60 min, and (D) 15.5 hours.

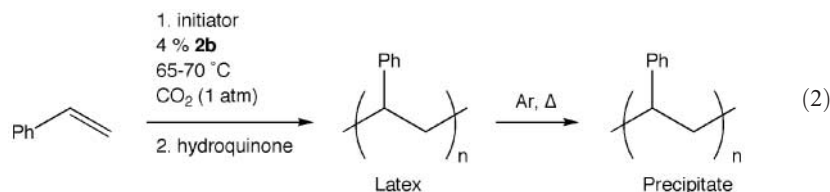
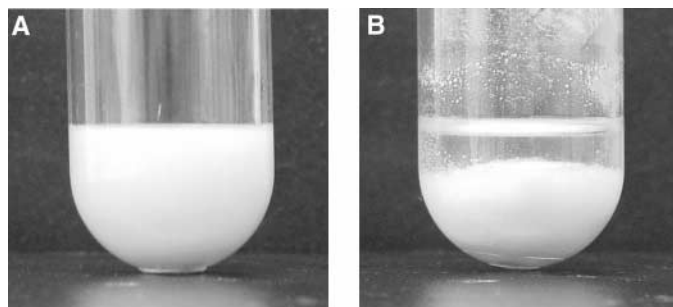


Fig. 4. Photographs of a latex suspension of polystyrene particles after polymerization in the presence of **2b** and (A) after centrifugation or (B) after argon treatment followed by centrifugation.



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- The rates of, and minimum times required for, the conversion of **1** to **2**, the conversion of **2** to **1**, and the transport of the surfactant to the liquid-liquid interface have not yet been quantified.
- We thank Shell and Imperial Oil for gifts of crude oil, and the Canada Research Chair program and the Natural Sciences and Engineering Research Council of Canada for funding the work.

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Materials and Methods

SOM Text

Figs. S1 to S3

Table S1

References

30 March 2006; accepted 6 July 2006

10.1126/science.1128142

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Science, 313 (5789), • DOI: 10.1126/science.1128142

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