

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 stabilize 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 emul-

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. The emulsion was composed of 18% hexadecane and 82% water.

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