Subsurface Transport Mechanisms

As described in 3-D Microemulsion Technical Bulletin 1.0 (Introduction), 3-D Microemulsion (3DMe)®, a form of HRC Advanced®, is a unique compound (patent applied for) which incorporates esterified lactic acid (the technology used in HRC) with esterified fatty acids. 3DMe's unmatched advantage is that is allows for the immediate and controlled release of lactic acid, which is among the most efficient electron donors, as well as the controlled release of proprietary fatty acids, providing a long-lasting, cost-effective source of hydrogen. This blend of organic acids rapidly stimulates reductive dechlorination and maintains activity for extended periods of time, up to 4+ years under optimum conditions (e.g. concentrated application in low-permeability, low-consumptive environments.)

3DMe is NOT Simple Emulsified Vegetable Oil

Vegetable oil is essentially insoluble. Thus, to make it amenable to injection into the subsurface, some vendors have added commercial emulsifying agents to simple vegetable oils and produced emulsions claiming that the "stable" emulsion will transport significant distances down-gradient from the injection point. Unfortunately, this is not the case.

When so-called "stabilized" oil-in-water emulsions are injected into a an aquifer, the emulsifying agents are rapidly stripped from the oil droplet due to the surface potential of the subsurface materials, causing adhesion of the hydrophilic "heads" of the emulsifying agents to soil and organic matter. Once the emulsifying agents have been stripped, the oil droplets rapidly coalesce in soil pores, creating a separate phase. When this coalescence occurs in the aquifer, further migration of any oil emulsion is retarded and groundwater flow can be halted. Use of emulsified oil products can result in significant lowering of the aquifer hydraulic conductivity within aquifer settings (Edible Oil Barriers for Treatment of Perchlorate Contaminated Groundwater, Environmental Security Technology Certification Program, US Department of Defense, November 2005.)

3DMe has a balanced HLB

The molecules composing 3DMe are surface active; they behave as surfactants, with a hydrophilic or "water-loving" end and a lipophilic or "oil-loving" end. As a result, the molecules will orient themselves with their hydrophilic ends in the aquatic matrix, leaving their lipophilic ends to interact with each other and to bind to organic compounds, such as the contaminant.

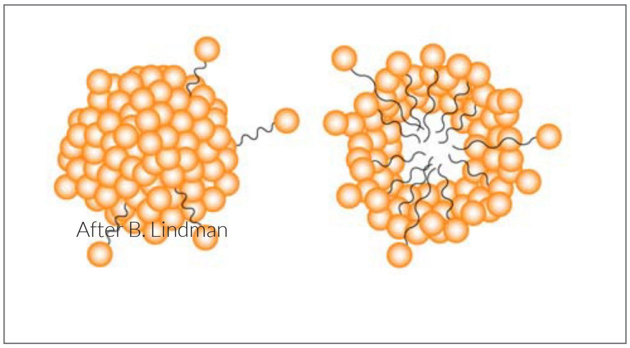
The Hydrophile/Lipophile Balace (HLB) is used by chemists to measure the degree to which a molecule is hydrophilic or lipophilic. The greater the HLB for a molecule, the higher its tendency to dissolve in water; conversely, low-HLB molecules generally separate from the water matrix and will preferentially sorb onto soil surfaces and organic compounds within an aquifer setting.

3DMe was designed to have a low, yet positive HLB, enabling it to sorb organic contaminants while maintaining significant solubility (and therefore transport) in an aqueous environment. 3DMe was designed to have a low, yet positive HLB, enabling it to sorb organic contaminants while maintaining significant solubility (and therefore transport) in an aqueous environment. A comparison of estimated HLBs for 3DMe and other reference substances is in the table below.

Substance	HLB
Sugars	30
Lecithin	20
3DMe	6
Vegetable Oil	-6

3DMe Forms Micelles

When 3DMe is in water in concentrations exceeding approximately 300ppm, dissolved molecules of 3DMe will spontaneously group themselves into forms called "micelles". In colloidal chemistry, this concentration is referred to as the "critical micelle concentration" or CMC. The grouping of the micellar structure is very orderly, with the charged or hydrophilic ends (heads) of the fatty acids oriented toward the water matrix and the hydrophobic ends (tails) oriented toward the center of the micelle. A depiction of a 3DMe micellar structure is shown below:



Depiction of 3-D ME Micellar Structure

The 3DMe micelles are very small, on the order of 0.02-0.05 microns in diameter and are generously spherical, but under certain circumstances, can become lamellar. These micelles allow 3DMe to travel further down-gradient from the injection point in an aquifer.

Mixing and Application

Concentrated Delivery

When applied to the subsurface in concentrated form, 3DMe will behave much like HRC. The material remains stationary at the injection point and slowly releases soluble lactic and fatty acids which diffuse and advect away from the point of application. The engineer is assured of a long-term, constant supply of electron donor emanating from the point of application for a period of up to 4+ years (under optimal conditions). This effect is particularly appealing when treating a flux of contamination from an up-gradient source or in any application in which a long-term supply of electron donor is required.

High Volume Delivery

3DMe can also be used to treat large areas in a short period of time by using a high-shear pump to mix the 3DMe with water prior to injection. Shear mixing generates a 3DMe colloidal suspension with micelles ranging from 0.02-0.05 microns in diameter or “swollen” micelles, termed “microemulsions,” which are 0.05-5 microns in diameter.

The colloidal suspension is injected into the subsurface in high volumes, followed by water, and will mix and dilute in existing pore waters. The micelles/microemulsions will begin to sorb onto the surfaces of soil particles due to the surface charge of the soil particles as well as any organic material present. As the sorption continues, the 3DMe will “coat” pore surfaces developing a layer of molecules (and in some cases a bilayer). This sorption continues as the micelles/microemulsion moves outward.

Unlike emulsified oil, the sorbed 3DMe has a significant capacity to move beyond the point of initial sorption. As the high concentration of 3DMe present in the initial injection volume decreases due to natural dilution, bound material desorbs. As long as the concentration exceeds the CMC, micelles will spontaneously form, carrying 3DMe further out in to the contaminated aquifer through diffusion and advection.

Additional Research Underway

REGENESIS is currently undertaking a series of laboratory studies and in-field research efforts to further define the extent to which 3DMe suspensions transport under various aquifer conditions. These studies will generate information which will aid in understanding the limitations to the transport of colloidal suspensions under realistic injection/aquifer dispersion conditions.