

What are the surfactants?

Surface-active agents (surfactants) belong to a group of substances that at low concentrations are adsorbed onto the surface or interfaces of a system altering the free energy of those systems (Rosen, 2004). In the case of water as solvent, surfactant consists of a hydrophilic head and a hydrophobic tail. In water, surfactant molecules concentrate at the water–air interface, with the hydrophilic heads oriented towards the water and the hydrophobic tails oriented away from it (West and Harwell, 1992). When surfactants arrange themselves along the water–air interface, the surface tension of the solution decreases with increasing surfactant concentration until the surface tension is below a critical point. The concentration at which the critical point occurs indicates the formation of micelle structures and it is defined as the critical micelle concentration (CMC) (Haigh, 1996). A hydrophobic molecule in contact with an aqueous solution containing surfactant tends to arrange itself within the core of the micelles. Therefore the hydrophobic core of the micelle structure enables the surfactant to enhance the aqueous solubility of hydrophobic organic compounds, increasing their apparent solubility (West and Harwell, 1992)

Humic acids molecules as natural surfactants

Humic acids (HAs), one of the most important fraction of humic substances are composed of hydrocarbon chains that come from a relatively unchanging segments of plant polymers, and hydrophilic fraction, which mainly consist of ionic groups such as carboxylic acids, and the non polar compounds such as phenols, alcohols, aldehydes, ketones, amides and amines. These characteristics indicate that humic acids have amphiphilic properties, and can act as natural surfactants, i.e. can reduce the surface tension of water forming at high concentrations similar to micelle structure.

The ability of HAs to arrange themselves so as to have their internal hydrophobic groups (hydrocarbon) and hydrophilic portions outwards, such as carboxyl, phenols and hydroxyl groups, depends on the length and flexibility of their constituent chains. Intramolecular aggregation of HAs plays an important role in the micelle formation, and long flexible HA polymers are considerably the best sequestering agents (Engelbreton and Von Wandruszka, 1997). The presence of nitrogen compounds in HAs seems, also, to affect CMC (Quadri et al., 2008), in agreement with what was reported for the synthetic surfactant. Amides have been reported to be incorporated in the aggregate/micelle lowering CMC. Amide molecules are probably adsorbed at the outer portion of the micelle, close to the water–micelle interface reducing the work required for micellization, as a consequence of the reduction of the mutual repulsion of the polar groups (COO⁻) of HA (Rosen, 2004).

Chemical characterization of humic acids

Surface tension and CMC values for HA-surfactants extracted from different raw materials [Quadri et al. (2008), Savarino et al. (2010), Adani et al. (2010)]

Type of HA's	Atomski odnos			¹³ C NMR				Hb/Hl	CMC* (mg L ⁻¹)	Surface tension (mN m ⁻¹)
	C/H	C/H	O/C	% Alkyl-C 0-45 ppm	% OIN Alkyl-C 45-110 ppm	% Aromatic-C 110-160 ppm	% Carbonyl-C 160-220 ppm			
From biomass	13,9	0,75	0,4	40	30,7	18,1	10,9	1,4	712	43,5
From municipal and green waste	13,7	0,8	0,3	46,5	28,4	14,7	10,6	1,61	750	38
From plants	18	0,7	0,4	24	45	22	9	0,86	1986	43

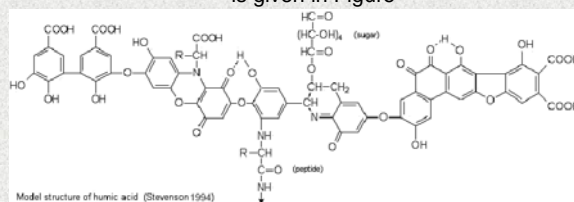
* CMC value experimentally determined

Legend

CMC – Critical micellar concentration

Hb/Hl – ratio between hydrophobic vs. hydrophilic C, in which, Hl = percentage of hydrophilic carbon calculated as the sum of the ¹³C CP MAS NMR area of [(45–110)+(160–220) p.p.m.] and Hb = percentage of hydrophobic carbon calculated as the sum of the ¹³C CP MAS NMR area of [(0–45)+(110–160)] p.p.m.

Hypothetical structure of humic acids by Stevenson is given in Figure



Model structure of humic acid (Stevenson 1994)

Humic acids as natural surfactants: technological applications

Remediation of soil consisting of detoxification of polluting agents. In recent years the use of bioremediation is rising, which uses microorganisms to *in situ* degradation, but this technique has some limitations in terms of appropriate soil conditions for their activity. To be rehabilitated contamination of persistent organic pollutants, recent attention has focused on the possibility of desorption of contaminants from contaminated soil *in situ* technologies (irrigation area) or *ex situ* (soil washing). These technologies are based on the principle of separation of adsorbed pollutants from land to water with added surfactants.

The ability of HAs to increase the solubility of contaminants was tested directly on the soil. Humic acids at a concentration of 10 mgL⁻¹, were able to remove a similar amount of pollutants and polycyclic aromatic hydrocarbons (PAH), thiophene, as same as SDS and Triton X-100.

HAs exhibit the properties of surfactants and can be used as substitutes for synthetic surfactants for various applications. However, to fully realize the idea of using humic acids as natural surfactants, it is necessary to establish adequate procedures for quality control, certification and labeling. Without this it would be difficult to promote as the substituents on the competitive market.

Our research results in connection with HAs, during *ex situ* bioremediation, also included in this paper.

References

- Rosen MJ. Surfactants and interfacial phenomena. 3rd ed. New York: John Wiley & Sons Interscience; 2004.
- West CC, Harwell JH. Surfactants and subsurface remediation. Environ Sci Technol 1992;26:2324–30.
- Haigh SD. A review of the interaction of surfactants with organic contaminants in soil. Sci Total Environ 1996;185:161–70.
- Stevenson FJ. Humus chemistry. 2nd ed. New York: John Wiley & Sons 1994
- Engelbreton RR, Von Wandruszka R. The effect of molecular size on humic acid associations. Organic Geochem 1997;26:759–67.
- Quadri G, Chen X, Jawitz JW, Tambone F, Genevini P, Faoro F, et al. Biobased surfactantlike molecules from organic wastes: the effect of waste composition and composting process on surfactant properties and on the ability to solubilize tetrachloroethene (PCE). Environ Sci Technol 2008;42:2618–23.
- Savarino P, Montoneri E, Musso G, Boffa V. Biosurfactants from urban wastes for detergent formulation: surface activity and washing performance. J Surfact Deterg 2010;13:59–68.
- Adani F, Tambone F, Davoli E, Scaglia B. Surfactant properties and tetrachloroethene (PCE) solubilisation ability of humic acid-like substances extracted from maize plant and from organic wastes: a comparative study. Chemosphere 2010;78: 1017–22