



Research review paper

Perspective on the use of humic acids from biomass as natural surfactants for industrial applications

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ABSTRACT

In the context of renewable vs. non-renewable sources of chemical compounds, the development of natural surfactants as a substitute for synthetic surfactants in technological applications is an important issue. In addition, as synthetic surfactants can persist in the environment causing toxic effects, the use of natural products presents a possibility to minimize impact on the environment. Nowadays, a promising new approach in surfactant-based technologies, consists of the use of humic acids (HAs) extracted directly from biomass that exhibit amphiphilic properties, and can be conveniently used as environmentally friendly surfactants. The raw material from which HAs are extracted and their macromolecular composition affect surfactant properties. Therefore fundamental data from more strictly qualitative aspects, needs to be investigated. This review highlights surfactant ability and chemical properties of HA substances coming from renewable sources in comparison to synthetic surfactants, and points out the capacity for HAs to be used effectively in this field of application.

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1. 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).

The molecular structure of surfactants consists of a group that has low affinity for the solvent (lyophobic group) and a group that has a strong affinity with the solvent (Rosen, 2004). This type of feature, i.e. to combine lyophobic group and lyophilic group components, is generally known as an amphiphilic property of a molecule. The particular molecular structure of surfactants enables them to adsorb and concentrate in liquid/gas, liquid/liquid and liquid/solid interphases establishing interactions with both phases in contact and reducing surface tension forces.

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

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the water and the hydrophobic tails oriented away from it (West and Harwell, 1992).

At high concentrations of surfactant, the free energy of the system can be reduced by the aggregation of the surfactants molecules into an assemblage with the hydrophobic groups located in the center (hydrophobic core) of the cluster and hydrophilic head groups toward the aqueous solvent (hydrophilic shell) (Chandler, 2005; Ying, 2006); this molecular aggregation is defined a “micelle”.

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 (Fig. 1). 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). As consequence of that, CMC is an important parameter, for hydrophobic molecule solubilisation in water, because lower CMC equates to a lower concentration of surfactant required to initiate solubilization of hydrophobic compounds due to micelle formation.

2. Natural surfactants vs. synthetic surfactants

Surfactants can be divided into two classes: those that are derived from petrochemical compounds i.e. “synthetic surfactants” and those that have a natural origin, i.e. “natural surfactants”.

Synthetic surfactants have a non-renewable nature and are chemically synthesized from feedstocks such as by-products of the oil refining industry, crude oil, natural gas and coal. Synthetic surfactants are of widespread use and have a high consumption rate: the world production of these compounds has been reported to be $7.2 \cdot 10^6 \text{ Mg y}^{-1}$ (Di Corcia, 1998).

Synthetic surfactants have many applications in different fields including industrial human health, food preparation, and environmental remediation applications (Ying, 2006).

Many synthetic surfactants are characterized by high retention rates in the environment (e.g. soil, water, sediment etc.) (Brownawell et al., 1997; John et al., 2000), and although most of them are degraded by microorganisms, many others are not biodegradable, and are toxic to the environment (Garcia et al., 2001; Krueger et al., 1998; Scott and Jones, 2000) and organisms (Ying, 2006). Several studies (Singh et al., 2002; Utsunomiya et al., 1997; Verge et al., 2000), focused on various aquatic organisms, showed acute and chronic toxicity caused by some synthetic surfactants. In particular, some researchers (Jobling et al., 1998; Soto et al., 1991) observed several

problems in the reproductive system of fish grown in waters heavily contaminated by surfactants. Few studies have been performed on soil fauna (Jensen, 1999; Kloepper-Sams et al., 1996) and there is still a lack of detailed information about the toxicity of surfactants to terrestrial organisms and plants (Litz et al., 1987; Mieux et al., 1990).

The use of surfactants taken directly from a natural source (called biobased surfactants or natural surfactants) (Holmberg, 2001) holds promise as a more sustainable and environmentally friendly practice (Diallo et al., 1994).

The use of the terms “natural” and “synthetic” to describe the origin of surfactants have led to some confusion in the past. Technically, surfactants coming from natural sources are obtained from substrates by using different separation procedures such as extraction, distillation or precipitation, and no organic synthesis should be involved in the preparation (Holmberg, 2001). Strictly speaking, natural surfactants comprise natural products obtained directly from raw materials without any chemical synthesis or modifications (von Rybinski, 2001). Nevertheless, many researchers use the term “natural surfactants” to include molecules coming indirectly from natural raw materials (Holmberg, 2001; von Rybinski, 2001). There are many examples of natural surfactants. Roy et al. (1997) identified as possible replacements for synthetic surfactants, molecules derived directly from plants of the genus *Sapindaceae*. These plants produce a substance called saponin that seems to have surfactant properties that are similar to those of common synthetic surface-acting agents. Natural surfactants, such as fatty acid esters of sugars and fatty acid esters or amides of amino acids, have been proposed for various applications (Holmberg, 2001; Johansson and Svensson, 2001).

Natural surfactants can be categorized by three different groups: i) prepared by fermentation, ii) based on a natural hydrophilic head groups and, iii) based on a natural hydrophobic tail (Holmberg, 2001).

Surfactants prepared by fermentation include molecules from different origins such as acylpolyols (hydroxy fatty acid linked to disaccharides by ester bonds) that have been identified as extracellular compounds of actinomycetes (Haferburg et al., 1986), glycolipids (hydroxy fatty acid linked to a sugar) produced by yeasts and bacteria, rhamnolipids extracted from by *Pseudomonas* (Clifford et al., 2007; Mulligan, 2005; Nitschke et al., 2005) and acylpeptides (hydroxy acid with a short peptide chain), that are extracted from *Bacillus subtilis*. Among surfactants based on a natural polar head group there are sugars, amino acids and short peptides. For this group of surfactants it has been indicated that CMC increased and surface tension at CMC decreased, with increasing carbon atoms in the chain. The last group of surfactants, i.e., those characterized by a hydrophobic tail, includes fatty acids and sterols. In fatty acid-based surfactants, especially fatty amid ethoxylates, surface tension at CMC increases when the amide bond is present, while CMC decreases. Sterols extracted from plants have a structure similar to cholesterol and can contain an ethoxylated group in which surface tension at CMC increases with an increasing of polyoxyethylene chain length. All of the molecules cited have surfactant performances comparable to those of conventional surfactants (Holmberg, 2001).

Lignocellulose raw materials can also be considered a source of biosurfactant, i.e. carbohydrates (cellulose and starch), which are used as hydrophilic surfactants, and lignin sulfonates, which show surfactant ability because of the hydrophobic head and hydrophilic sulfonate groups (Johansson and Svensson, 2001).

3. Humic acids

3.1. Humic acid: origin and chemical structure

Humic substances (HS) represent the most widespread pool of natural recalcitrant organic carbon occurring in the biosphere, constituting the most stable fraction of organic matter in soils, sediment and waters (Kelleher and Simpson, 2006).

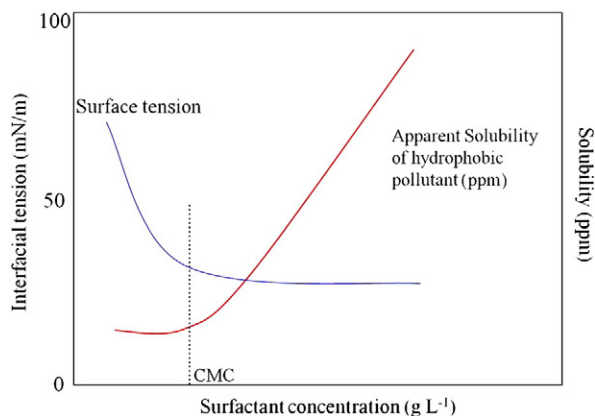


Fig. 1. Trend of organic pollutant apparent solubility and of water surface tension with surfactant concentration increases.

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