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Historical perspective

## Amino acid-based surfactants – do they deserve more attention?

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## ABSTRACT

The 20 standard amino acids (together with a few more that are not used in the biosynthesis of proteins) constitute a versatile tool box for synthesis of surfactants. Anionic, cationic and zwitterionic amphiphiles can be prepared and surfactants with several functional groups can be obtained by the proper choice of starting amino acid. This review gives examples of procedures used for preparation and discusses important physico-chemical properties of the amphiphiles and how these can be taken advantage of for various applications. Micelles with a chiral surface can be obtained by self-assembly of enantiomerically pure surfactants and such supramolecular chirality can be utilized for asymmetric organic synthesis and for preparation of mesoporous materials with chiral pores. Surfactants based on amino acids with two carboxyl groups are effective chelating agents and can be used as collectors in mineral ore flotation. A surfactant based on cysteine readily oxidizes into the corresponding cystine compound, which can be regarded as a gemini surfactant. The facile and reversible cysteine-cystine transformation has been taken advantage of in the design of a switchable surfactant. A very attractive aspect of surfactants based on amino acids is that the polar head-group is entirely natural and that the linkage to the hydrophobic tail, which is often an ester or an amide bond, is easily cleaved. The rate of degradation can be tailored by the structure of the amphiphile. The ester linkage in betaine ester surfactants is particularly susceptible to alkaline hydrolysis and this surfactant type can be used as a biocide with short-lived action. This paper is not intended as a full review on the topic. Instead it highlights concepts that are unique to amino acid-based surfactants and that we believe can have practical implications.

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## 1. Motivation and scope

The pressure from legislation as well as from consumers to move towards more environmentally benign chemicals has had a strong impact on surfactants during the last decades. Some established surfactant classes such as linear alkylbenzene sulfonates, alkylphenol ethoxylates and dialkyl quats have almost entirely been phased out in Europe and the US and have been replaced by surfactants that are less toxic to the marine environment and/or undergo faster biodegradation.

The trend towards more environmentally benign surfactants continues. Besides the constant challenge of finding ways to minimize the manufacturing cost for existing surfactants, the market pull for 'greener' products is the overriding driving force for surfactants development. Some general trends are

- to synthesize the surfactant from *natural building blocks*; this is a central issue for this article. Peptide-based surfactants will not be reviewed, however.
- to use starting materials – natural or synthetic – that give *proper rate of biodegradation*; this point is also applicable to the present article

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- to insert one or more *weak bonds into the structure* in order to speed up the degradation; such surfactants are sometimes referred to as 'cleavable surfactants'; also this issue is brought up in the article
- to make *more efficient surfactants*, i.e., surfactants that can be used in lower amounts; gemini surfactants are examples of that approach. Gemini surfactants can be made from amino acids, as will be shown in this paper.

Polyols such as glycerol, glucose and other simple sugars are examples of natural compounds that have become established as natural building blocks for surfactants. They constitute the polar head-group of the amphiphile and since the majority of the polyols used for the purpose are non-charged, they are primarily used for making nonionic surfactants. Alkyl polyglucosides, fatty acid esters of glucose and sorbitan, and fatty acid esters of glycerol and polyglycerol are all examples of nonionic surfactants that have an established position on the market since long back.

Amino acids are another natural building block that can constitute the polar head-group of amphiphilic compounds. Compared to polyols, amino acids are much more versatile with respect to type of surfactant that can be prepared. Many of the 20 standard amino acids (the  $\alpha$ -amino acids that are used in the biosynthesis of proteins) have been explored as surfactant raw material. A number of amino acid-based surfactants are established on the market but the volume of such surfactants produced is still relatively small.

All  $\alpha$ -amino acids have a carboxyl group and a primary amino group. A surfactant can be prepared by attaching the hydrophobic moiety at either of these, as shown in Fig. 1. The carboxyl group may be derivatized by reaction with a fatty alcohol to give an amphiphilic esteramine (*path 1*) or with a long-chain amine to yield a surface-active amidoamine (*path 2*). In the latter reaction, care must be taken to avoid reaction with the  $\alpha$ -amino group of the amino acid. This can be accomplished by protecting the  $\alpha$ -amino group. Alternatively, the  $\alpha$ -amino group can be derivatized. This may be done by amidation with a fatty acid or more conveniently with a reactive derivative of a fatty acid. The product is an amido acid (*path 3*). The  $\alpha$ -amino group may also be alkylated with a long-chain alkyl halide, transforming it to a secondary (or tertiary) amine (*path 4*). The product is a long-chain *N*-alkyl amino acid.

Paths 1 and 2 give surface-active primary amines. Under neutral and acidic conditions they will be protonated and act as cationic surfactants. If the starting amino acid has a quaternary ammonium group instead of a primary amino group, as is the case for the amino acid betaine, a surfactant that is cationic also at high pH will be obtained. Path 3 results in the formation of an anionic surfactant under neutral and alkaline conditions and Path 4 gives a zwitterionic surfactant. Thus, several different classes of surfactants can be synthesized from the simple amino acid building block.

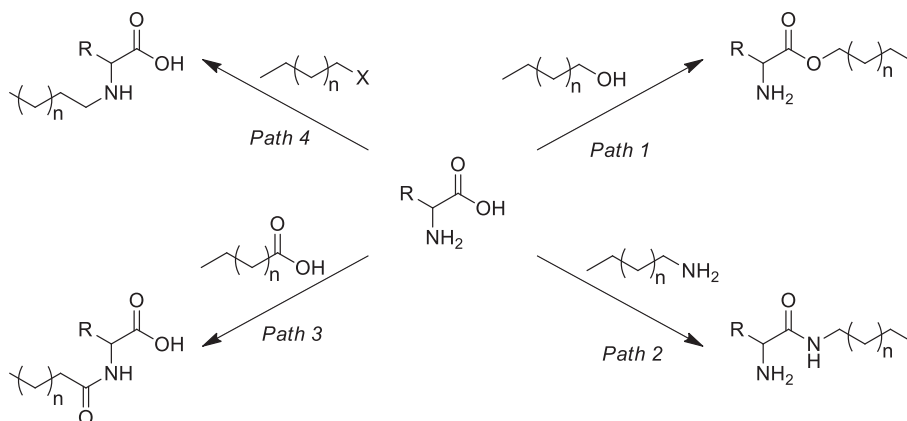


Fig. 1. Paths for synthesizing amphiphilic amino acid derivatives.

Two out of the 20 standard amino acids contain an extra carboxyl group: aspartic acid and glutamic acid. When derivatized via the  $\alpha$ -amino group (*paths 3 and 4*), dicarboxylic amino acid-based surfactants are obtained. Such amphiphiles have interesting chelating properties, as will be discussed below. The *N*-acyl amino acid derivatives, obtained by *path 3* are by far the most widely used. This surfactant class has been thoroughly investigated with respect to dermatological properties and is generally regarded as safe with respect to skin irritation and sensitization. The *N*-dodecanoyl (or cocoyl) derivative also exhibits good foaming properties, an important asset for surfactants used in personal care formulations [1].

There are also amino acids with more than one basic functional group: lysine, histidine and tryptophan. Derivatizing such amino acids via the carboxyl group (*paths 1 and 2*) gives surfactants with two cationic groups at low and neutral pH. In this respect they are alternatives to the established fatty diamine surfactants of the general formula  $C_nH_{2n+1}-NH-CH_2CH_2CH_2-NH_2$ , with *n* typically being 12–18. The group of Infante has explored this type of amino acid-based surfactants extensively [2,3].

In this paper we discuss the characteristic features of the different surfactants obtained from the synthesis routes shown in Fig. 1. We have relatively recently written a review on amino acid-based surfactants [4], and the present article is not intended as another comprehensive review. Instead, we highlight certain recent development routes that have taken place. The choice of issues is somewhat arbitrary. Some of them are mainly based on work from our group and some are from other sources. We believe that taken together they give a proper view of the current status and the potential of amino acid-based surfactants.

## 2. The amide bond contributes to the self-assembly process

*N*-acyl amino acid-based surfactants (prepared by *path 3* of Fig. 1) are anionic amphiphiles with an amide bond connecting the polar head-group and the hydrophobic tail. This structure raises the question about the role of this 'extra functional group' in the surfactant molecule for its self-assembly in bulk and at surfaces. Amide (peptide) bonds in proteins are known to be important for intra- and intermolecular interactions. Such amide bonds can act as both hydrogen bond donor (the N-H moiety) and hydrogen bond acceptor (the C = O group). Surfactants are known to self-assemble because of the so-called 'hydrophobic effect', which in turn is caused by the high cohesive energy of water [5–7]. This is the main driving force for all amphiphilic compounds to form self-assemblies in water (micelles) and at interfaces (monolayers at the air-water interface and at many solid-water interfaces; closely packed micelles or bilayers at some solid-water interfaces). This is certainly the case also for amino acid-based amphiphiles but here the question arises: does intermolecular hydrogen bonding

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