Derivatives of glutamic acid as new surfactants

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Summary. Starting from glutamic acid, different types of surfactants have been synthesised by using original trimodular strategies. Monosubstituted zwitterionic amides of glutamic acid obtained with excellent yields show good surface activity.

The grafting of a second hydrophobic side-chain leads to bicatenar cationic surfactants or to disubstituted nonionic cyclic compounds. In order to reduce the hydrophobic character of the bicatenar surfactants, a second synthetic method has been developed, allowing the introduction of a polar sugar group into these molecules.

The surfactant properties of several of the products have been determined by physico-chemical methods such as surface tension measurements and compression isotherm studies by means of a Langmuir balance.

Keywords: Amino acids – Glutamic acid – Surfactant – Amide – Imide – Critical concentration

Introduction

The synthesis of molecules with properties suitable for specific applications is one of the important objectives of modern organic chemistry. In this context we have been concerned for several years with the preparation and characterisation of new surfactants (Larpent, 1995).

These compounds are amphipathic molecules, generally characterized by the presence of two distinctly different regions in the same molecule: a lipophilic part (restrictively called hydrophobic) and a lipophobic or hydrophilic portion. The existence in the same molecule of two moieties, one with an affinity for the solvent and the other antipathetic to it, is termed amphiphily or amphipathy. Surface active agents constitute a versatile class of natural or synthetic compounds. They may contain a large variety of polar ionic or nonionic parts (called head) and apolar moieties (named tail), the latter consisting generally of long hydrocarbon chains (Attwood et al., 1983).
This dual nature is responsible for the phenomenon of surface activity, and of micellisation, formation of Molecular Organised Systems (Mittal, 1984) (lamellar phases, liquid crystals, vesicles, etc.), and their capacity of solubilisation by forming emulsions and microemulsions (Schick, 1987).

Our approach respects as much as possible the constraints of environmental compatibility as well as those imposed by the applications concerned. Therefore we have developed synthetic methods for surfactant molecules based on amino acids (Seguer et al., 1994, 1996; Allouch et al., 1996) or peptides (Selve et al., 1989, 1992).

In this paper we present a novel family of compounds derived from glutamic acid. For certain compounds, a sugar plays the role of the polar headgroup, and the apolar parts consist either of long-chain alcohols or fatty amines.

**Results and discussion**

*I. Syntheses*

We have prepared the surfactant molecules following the trimodular pathway (Emmanouil et al., 1998; Rico-Lattes et al. 1997) shown in Scheme 1.

a) Strategy I

We have tried to prepare the surfactants by methods avoiding all the reactions necessitating protective groups. In analogy to the synthesis of ε-alkyl-lysine (Takizawa et al., 1975) we have synthesized the monoammonium salts of glutamic acid in a first step.

Since the pK values of the two carboxyl groups of glutamic acid differ by more than two units (pK\(_a\) = 2.19, pK\(_b\) = 4.25) a good selectivity for the α-position during salt-formation is observed and the dehydration of the salt leads to a majority of the α-monoamide (>95%) with good yields (Table 1). The structure obtained (Scheme 2) is confirmed by comparison with authentic

**Strategy I**: (1) junction of Glu and hydrophobic chain and (2) addition of a polar headgroup

**Strategy II**: (1) junction of Glu and polar head and (2) addition of hydrophobic chain

**Scheme 1.** Synthetic strategies for the preparation of surfactants