Alkyl triazole glycosides (ATGs)—A new class of bio-related surfactants

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**Article Info**

**Abstract**

A series of glucose based surfactants varying in chain length and anomeric configuration were synthesized and investigated on their surfactant properties. The synthesis applied glycosylation of propargyl alcohol followed by cycloaddition with alkyl azides in CLICK chemistry fashion. This approach enables a homogeneous coupling of hydrophilic unprotected sugars and hydrophobic paraffin components in low molecular weight alcohols without solvent side reactions, as commonly found for APGs. The combination of alcohols as inert medium with practically quantitative coupling of the surfactant domains avoids particularly hydrophobic contaminations of the surfactant, thus providing access to pure surfactants. ATGs with chain lengths up to 12 carbons exhibit Krafft points below room temperature and no cloud points were detected. The values for the CMC of ATGs with 12 carbon alkyl chains and above were in good agreement with those of corresponding alkyl glucosides. However, lower homologues exhibited significantly smaller CMCs, and the trend of the CMC upon the chain length did not match common surfactant behavior. This deviation may be related to the triazole that links the two surfactant domains.

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**1. Introduction**

The global demand for biocompatible materials has created considerable interest in surfactants based on natural resources rather than petrochemical precursors. With respect to considerable advantages of non-ionic surfactants, due to pH neutrality and ion-insensitive behavior, sugar-derived surfactants are most promising. The chemical instability of ester bonds disfavors sugar esters for applications involving higher temperature treatments at non-neutral pH. Glycosides, on the other hand, provide excellent stability, while maintaining the requested feature of biological degradability. Despite considerable higher costs compared to standard industrial surfactants, alkyl poly-glycosides (APGs) [1,2] have gained market share. Their usage is focused on both high-end life-science [3,4] or critical environmental applications, like drilling fluids [5,6].

APGs are commonly obtained by acidic reaction of fatty alcohols with glucose at high temperature. The reaction provides a complex mixture of oligomers and diastereomers based on a random condensation of sugar molecules with limited stereoselectivity for glycosidic bonds. Fig. 1 provides an overview on the chemical reactions. Due to insufficient miscibility of the hydrophilic sugar and the hydrophobic fatty alcohol, homogenizers have to be added during the process. Usually medium chain alcohols are applied. However, competing reactions between the homogenizer and fatty alcohols lead to remaining homogenizer as chemically bonded non-surfactant impurity inside the product. Moreover, the fatty alcohol is incompletely converted, thus leaving ‘oil-impurities’ inside the product, which affect the surfactant properties. The removal of the latter is difficult, requiring an extraction process with supercritical CO2 [7], due to the surfactant nature of the product, which has reasonable affinity for the fatty alcohol impurity.

The compound diversity of ATGs makes them unfavorable for pharmaceutical applications, as every component needs to be biologically tested on efficiency and toxicity. Better chances are found for pure alkyl glycosides. However, high production costs disfavor these. In order to obtain economic glycoside surfactants with high chemical purity and low chemical diversity for potential life science applications, we aimed for a different surfactant synthesis. Although the approach intends to preserve the generic alkyl glycoside structure, chemical modifications arise out of the demand for an effective coupling of the two surfactant domains, i.e. paraffin chain and sugar. A promising method for the coupling of the hydrophilic and the hydrophobic surfactant domain is found in CLICK chemistry [8–10], because the method is effective and applicable for a wide range of solvents. The concept has already been applied for the preparation of glycoside surfactants [11], but it suffers from the tedious and costly preparation of glycosyl azides. Instead of using a glycosyl azide and a propargylated fatty alcohol, we used the reverse approach, i.e. an alkyn on the sugar and the azide on the hydrocarbon chain, following a concept that has been used for the preparation of glycopeptides [12]. The resulting structure type has been reported before for a galactoside involving a C12–chain [13], but was not investigated as a surfactant.
surfactants of short chain length, including the lamellar ($L_\alpha$), the bicontinuous cubic ($V_1$), the hexagonal columnar ($H_1$) and the micellar phase ($L_\beta$). The lyotropic phase diversity for several ATGs is summarized in Table 4.

5. Conclusion

The synthesis of ATGs provides easy access to chemically pure surfactants based on natural resources, comprising of only two stereoisomers, whose surfactant behavior does not differ significantly. The process is reasonable economic, but the costs exceed those of common APGs due to one additional reaction step, i.e. the preparation of an alkyl azide. While the surfactant behavior of long chain ATGs more or less reflects the one of corresponding APGs, shorter homologues exhibit significantly reduced CMCs, indicating a reduction of molecular water solubility due to the heterocyclic linkage of the hydrophilic and the hydrophobic surfactant domains.

6. Supporting information

Detailed experimental procedures and chemical characterization data for anomerically pure ATGs as well as an example of a contact penetration scan image are provided in supplementary material.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfb.2012.03.030.

References