Interfacial properties of surfactant mixtures with alkyl polyglycosides

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Abstract: Alkyl monoglycosides and polyglycosides (APG) are characterized in terms of their interfacial properties which exhibit a dependence on alkyl chain length and degree of polymerization. A comparison is drawn to other nonionic and anionic surfactants. In hard water, clouding phenomena are observed for C8/10 and C12/14 APG. The critical micelle concentrations (CMC) of the alkylglycosides are similar to those of other nonionic surfactants and show a decrease with increasing alkyl chain length. The degree of polymerization has only a minor influence on the CMC. Above the CMC, alkylglycosides exhibit very low interfacial tensions against mineral oil compared to C12/14 fatty alcohol sulfate (C12/14 FAS). In contrast to C12/14 FAS and C12/14 fatty alcohol hexaglycol ether, respectively, C12/14 APG shows remarakbly high dynamic surface tensions even at a concentration far above the CMC. For mixtures of C12/14 APG and C12/14 FAS the static surface tensions and the CMC lie close to those of C12/14 APG, whereas the dynamic surface tension behavior is dominated by the anionic surfactant.

Key words: Alkyl polyglycoside; clouding behavior; static and dynamic surface tension; surfactant mixtures

1. Introduction

Alkyl polyglycosides (APG) are nonionic surfactants based on glycose and fatty alcohol. They can be extracted from renewable raw materials, and are non-toxic and readily biodegradable [1, 2]. Because their properties make them suitable for use as wetting agents, emulsifiers and hydrotropes, they are steadily gaining in importance for numerous technical appliations. The first systematic studies of their surface activity were made by Shinoda [3]. A more recent paper by Lüders and Balzer describes their synthesis and physicochemical properties [1]. Studies of the phase behavior of this class of surfactants are important with regard to their use in practical applications. The present paper aims to characterize these compounds and their mixtures with anionic surfactants. Specifically, we report on static and dynamic measurements of surface and interfacial tension. These properties, as exhibited by pure and technical grade surfactants, are described with particular reference to their dependence on alkyl chain length and degree of polymerization. A comparison is drawn with other nonionic and anionic surfactants.

2. Experimental

C8/10, C12, and C12/14 APG and C8, C10, and C12 monoglycosides were obtained by means of Fischer glycosidation with technical grade or pure fatty alcohols [4]. For the monoglycosides, distillation and fractional crystallization were also applied. In addition, C12/14 fatty alcohol sulfate (C12/14 FAS) and C12/14 fatty alcohol hexaglycol ether (C12/14 E6) were studied as technical grade surfactants. All of the substances were supplied by Henkel. The clouding behavior of APG was examined photometrically. Static surface tension was determined with an automatic tensiometer (Lauda). Dynamic surface tension was measured with a home-built appratus by means of the maximum bubble pressure method [6, 7]. Interfacial tension measurements were performed with a spinning-drop tensiometer (Krüss).

3. Results

3.1 Clouding behavior

The clouding behavior of C8/10 APG and C12/14 APG was studied as a function of concentration and temperature at a given water hardness. C12/14 APG behaves similarly to other nonionic surfactants in that it exhibits a concentration-dependent cloud point in distilled water. In contrast, C8/10 APG, which contains shorter chains, forms an isotropic liquid phase between 20° and 90°C in distilled water, even at high concentrations. However, when a mixture of Ca and Mg ions is added a narrow liquid/liquid coexistence region appears at low concentrations (Fig. 1).
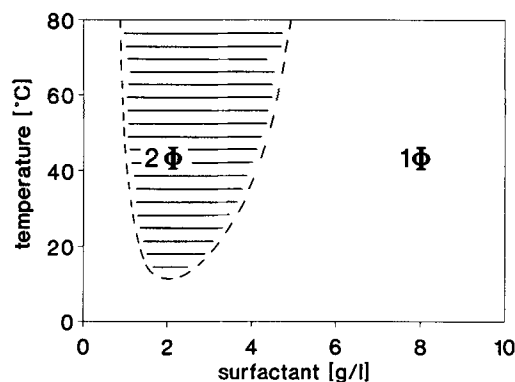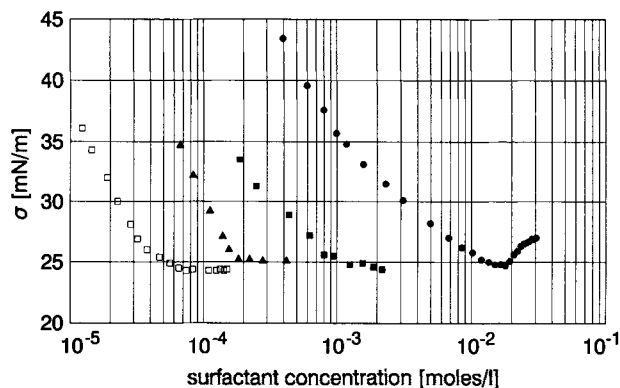

Fig. 2. Surface tension as a function of concentration for different alkylglycosides at 60°C in distilled water: (●) C8 monoglycoside; (■) C10 monoglycoside; (▲) C12 monoglycoside; (□) C12/14 APG

Fig. 1. Clouding behavior of C8/10 APG in water of 340 ppm hardness (Ca/Mg = 5/1)
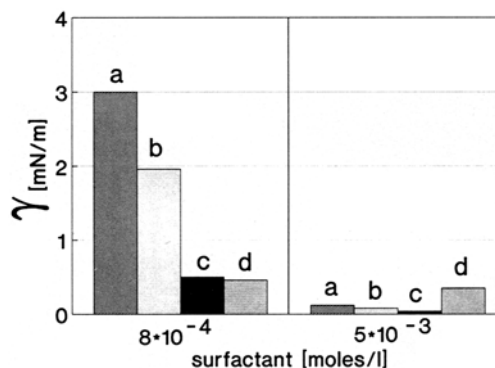

Fig. 3. Interfacial tension against mineral oil at 40°C for different concentrations: a) C8 monoglycoside; b) C10 monoglycoside; c) C12 monoglycoside; d) C12/14 FAS

3.2 Static surface tension

Figure 2 shows the dependence of surface tension on concentration of the pure and technical grade alkyl glycosides at 60°C. The critical micelle concentrations (CMC) are in the same region as those of conventional nonionic surfactants, and decrease markedly as the length of the alkyl chain increases. Compared with alkyl chain length, the number of glycoside groups of the APG exerts only a slight influence on the CMC.

3.3 Interfacial tension

Figure 3 shows the interfacial tensions against mineral oil of the three monoglycosides and C12/14

FAS obtained at two different concentrations and at 40°C. At the higher concentration (>CMC), low interfacial tensions (<1 mN/m) are measured in all cases. At the lower concentration the interfacial tension increases with decreasing alkyl chain length and increasing CMC (cf. Fig. 2). The alkyl glycosides therefore only exhibit marked interfacial activity at concentrations above or in the region of the CMC; with mineral oil, this activity is much higher than that exhibited by anionic surfactants.

3.4 Dynamic surface tension

Figure 4 exhibits the surface tension determined by the maximum bubble pressure method [5]. The
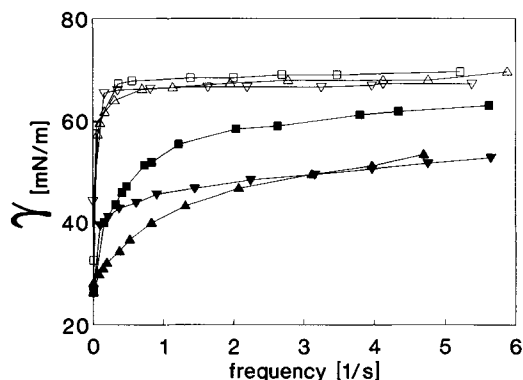
Fig. 4. Frequency dependence of dynamic surface tension of different surfactants at 40 °C for two concentrations: (□) $4 \cdot 10^{-5}$ moles/l C12/14 APG; (▽) $4 \cdot 10^{-5}$ moles/l C12/14 FAS; (△) $4 \cdot 10^{-5}$ moles/l C12/14 E6; (■) $8 \cdot 10^{-4}$ moles/l C12/14 APG; (▼) $8 \cdot 10^{-4}$ moles/l C12/14 FAS; (▲) $8 \cdot 10^{-4}$ moles/l C12/14 E6

3.5 Interfacial properties of APG/anionic surfactant mixtures

The interfacial properties of APG/anionic surfactant mixtures are of special importance for practical applications. Figure 5 shows the dependence of surface tension on concentration for C12/14 APG, C12/14 FAS and two mixtures at 60 °C. The values characterizing the mixtures lie close to the curve for APG, even when the anionic surfactant content is high. It may be concluded that the mixed micelle formation facilitates favorable interaction betweeen the nonionic and the anionic surfactant [8].

experiments were performed as a function of bubble frequency. With increasing frequency, there is a reduction in the time available for the surfactant to diffuse to the surface, i.e., there is less time available for the surface tension to be reduced [6]. In Fig. 4 the dynamic surface tensions at 40 °C for C12/14 APG, C12/14 FAS and C12/14 E6 are compared for two different concentrations. At lower concentration, chosen to be lower than the respective CMC, all of the technical grade surfactants exhibit slow and almost identical surface adsorption rates. At higher concentration, identical to the CMC for C12/14 FAS and exceeding it for C12/14 E6, the surface tension is markedly smaller over the whole frequency range. By comparison, C12/14 APG exhibits relatively high surface tension, especially at higher frequencies, so that diffusion to the surface must be slower, even though the concentration is above the CMC.

A comparison to the frequency dependence of dynamic surface tension obtained with the shorter chained alkyl glycosides at a concentration below the CMC shows that, at low frequencies, C8/10 APG occupies a position between the C8 monoglycoside which adsorbs slowly, and the C10 monoglycoside which adsorbs more rapidly. At higher frequencies the mixture approaches the behavior of the C8 monoglycoside. This effect is also observed at concentrations above the CMC, i.e., at lower static surface tensions.
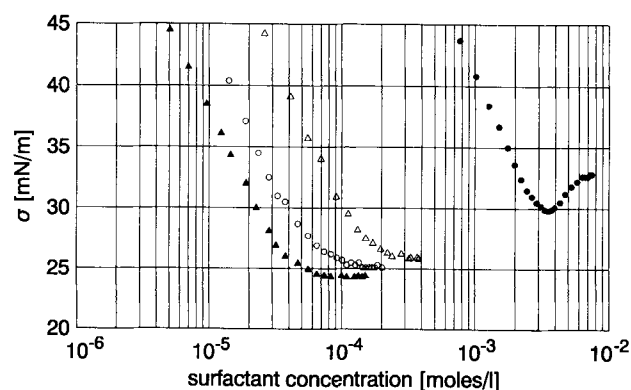

Fig. 5. Surface tension as a function of concentration for different mixtures of C12/14 APG and C12/14 FAS at 60 °C in distilled water: (▲) APG/FAS = 1/0; (o) APG/FAS = 4/1; (△) APG/FAS = 1/1; (●) APG/FAS = 0/1

Figure 6 shows the dynamic surface tension as a function of frequency measured at 40 °C by the bubble pressure method for the same series of mixtures as that in Fig. 5. In all cases, the concentration is above the CMC. In the rate-determining frequency range the behavior of the mixtures closely resembles that of C12/14 FAS, which adsorbs more quickly to the surface than that of C12/14 APG, which adsorbs more slowly. By contrast to the situation under static conditions, the change in surface tension of the surfactant mixture as a function of time seems to be dominated by the anionic surfactant. Both parameters, i.e., static and dynamic surface tension, indicate that mixtures of APG and anionic surfactants exhibit especially favorable interfacial properties.
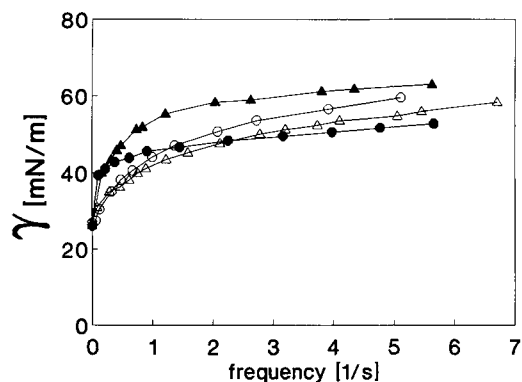
Fig. 6. Frequency dependence of dynamic surface tension of different mixtures of C12/14 APG and C12/14 FAS at 40°C: (▲) APG/FAS = 1/0; (o) APG/FAS = 4/1; (△) APG/FAS = 1/1; (●) APG/FAS = 0/1

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