Rheological studies of aqueous alkylpolyglucoside surfactant solutions

Abstract Alkylpolyglucosides \((C_Y G_X)\) are industrial products of mixtures consisting of a hydrocarbon chain with \(Y\) carbon atoms linked to \(X\) sugar residues. Based on detailed analytical investigation of technical grade alkylpolyglucosides \((C_{8–10}G_X, C_{12–14}G_X\) and \(C_{8–16}G_X)\)/water systems using high-performance liquid chromatography in combination with a special kind of mass spectroscopy their rheological behaviour is discussed and compared to the rheological behaviour of pure alkyl monoglycosides \((C_8G_1\) and \(C_{10}G_1)\) in water. The rheological properties that exhibit a dependence on the alkyl chain length, \(Y\), and the degree of polymerisation, \(X\), are investigated by rotation and oscillation experiments over an extended concentration range. The Maxwell model fits the frequency dependence of the dynamic functions fairly well. The viscosity shows an Arrhenius-like dependence on temperature. A comparison is drawn between the monoglycosides and the polyglycosides, which shows that the rheological properties are more sensitive to the a change in chain length than in the degree of polymerisation. Phase transitions, especially liquid-crystalline to isotropic solutions, phase split into two coexisting liquid phases, and could be followed using visual observation and rheology. Depending on the difference in the rheological properties of the corresponding phases, viscoelastic measurements showed these transitions clearly. Additionally, the changes in viscosities were measured after addition of a second surfactant.

Key words Phase equilibria · Surfactant solution · Rheology · Alkylglucosides · Synergism

Introduction

Considering the wide range of applications of surfactant-containing systems, a detailed rheological characterization is quite important for the design of unit operation (pumping, agitation and mixing), quality control and optimization of formulations, establishing relationships with the microstructure. It has been known that such systems can have very complex flow properties, especially viscoelastic properties at high surfactant concentrations [1].

Alkylpolyglucosides (APG) [2, 3, 4], which are widely used as surfactants in commercial products, represent a complex mixture of \(C_Y G_X\) homologues with different hydrocarbon chain length \(Y\) and different number of glucose units \(X\). Although phase diagrams of two technical APG \((C_{8–10}G_X, C_{12–14}G_X)\) and pure \(n\)-alkyl-\(\beta\)-d-glucopyranosides \((C_8G_1, C_{10}G_1)\) in water have been the subject of considerable interest, only a few studies have addressed the rheological properties [5, 12, 15–19]. By combined analysis of dielectric properties and viscosities La Mesa et al. [15]...
found a slight and continuous dependence of micellar shape on surfactant content for the C₈G₁/water system. The rheological properties of the pure surfactant systems (C₈G₁/water, C₁₀G₁/water), obtained by oscillating measurements, can be described by a simple Maxwell model [12, 18] in the low-frequency range. Micellar aggregation, rheological properties, and phase behaviour of two systems (C₈–10G₊/water and C₁₂–14G₊/water) have been studied [5]. Light-scattering and viscosity experiments show that in water the short-chain C₈–10G₊ forms spherical micelles up to high surfactant concentrations that are highly hydrated, whereas the long-chain C₁₂–14 G₊ forms rodlike micelles in water [5]. The isotropic phase of C₈–10G₊/water which extends to 64 wt% above 298 K is a Newtonian liquid [5]. C₁₂–14G₊ solutions are viscoelastic even at low concentrations [5].

Starting from a quantitative analysis of the technical grade products according to their alkyl chain length, Y, and their number of glucose groups, X, the present paper gives a detailed comparison between the rheological properties of the technical grade surfactants (C₈–10G₊, C₁₂–14G₊ and C₈–16G₊) and two pure n-alkyl-β-D-glucopyranosides (C₈G₁, C₁₀G₁) [12, 18] in water over a large concentration range.

One method of decreasing the environmental impact of surfactants is to use mixtures of known surfactants that exhibit synergism in their interfacial properties. The requirements, in quantitative terms, for the existence of synergy in mixtures of surfactants have been elucidated for several interfacial phenomena [20, 21]. Shchipunov et al. [17] studied the change in the rheological properties by adding sugar surfactants to lecithin organogels, which consist of extended cylindrical lecithin micelles in an organic nonpolar solvent. However, to date, there has been relatively little work on the rheological properties [17] of surfactant mixtures containing sugar surfactants. In a way, this is very unfortunate because in many practical applications of such systems these properties are of fundamental importance. In this paper we direct our attention to the influence on the viscosity of adding a second surfactant to an aqueous APG solution.

Experimental

Materials

The n-octyl-β-D-glucopyranoside (C₈G₁) and n-decyl-β-D-glucopyranoside (C₁₀G₁) were purchased from Sigma Chemical Co. (USA), and were used without recrystallization. The water was double distilled over potassium permanganate. The technical grade alkylpolyglucosides (C₈–10G₊, C₁₂–14G₊ and C₈–16G₊) were gifts from Henkel, Düsseldorf, Germany. The other surfactants were supplied by the following companies: Aldrich Chemie (tetramethyliboxyphenol pentaethylene glycol ether [Igepal]), Merck, Darmstadt (sodium dodecylsulfate [SDS], Henkel (sodium tetradecylsulfate, sodium hexadecylsulfate and sodium octadecylsulfate [SOS]), Fluka (polyoxyethylene lauryl ether [Brij35]) and Ventron (dodecyl trimethylammonium bromide [DMAB]).

Methods

Rheological measurements

The rheological properties were determined by means of a stress-controlled rotational rheometer, Paar Physica LS100 low-stress rheometer, using a cone-plate measuring system (gap 50 μm, CP50/1 [cone angle 1°, cone radius 50 mm] or CP20/0.5 [cone angle 0.5°, cone radius 20 mm]). The experiments were carried out both at oscillating and constant stress. Care was taken to avoid evaporation. This was achieved by tightly enclosing the measurement system with a solvent trap and saturating the air in the system with water. The frequency range investigated was 0.001 Hz ≤ f ≤ 15 Hz. A Peltier system provided temperature control with an accuracy of ±0.1 K.

The rheological properties can be investigated if dynamic experiments are performed [22, 23]. From the phase angle between the stress and the strain and the amplitude of these quantities, the storage modulus, \( G' \), the loss modulus \( G'' \), and the magnitude of the complex viscosity, \( |\eta'| \), can be calculated. The simplest mechanical model that can describe the dynamic behaviour of a viscoelastic surfactant solution is called a Maxwell model. It consists of a spring and a dashpot connected in series. The behaviour of the Maxwell model under harmonic oscillations can be obtained from the following:

\[
G'(\omega) = \frac{G_0 \omega^2 \tau^2}{1 + \omega^2 \tau^2}
\]

\[
G''(\omega) = \frac{G_0 \omega \tau}{1 + \omega^2 \tau^2}
\]

\[
|\eta'| = \frac{\eta_0}{\sqrt{1 + \omega^2 \tau^2}}
\]

where \( \omega \) is the angular frequency, \( G_0 \) the zero-shear modulus, \( \eta_0 \) the zero-shear viscosity and \( \tau \) the structure relaxation time.

High-performance liquid chromatography (HPLC)

The samples were diluted with eluant and injected into a conventional HPLC apparatus provided by Bischoff, Germany. The analysing system consists of an RP-18 column and a 75 wt% methanol/water eluant. The signal was detected refractometrically.

Atmospheric pressure ionization – mass spectrometry (API-MS)

The experiments were carried out at the University of Leipzig, Institute of Analytical Chemistry, using a Perkin Elmer Sciex API 100 LC/MS system. The experimental conditions were as follows: orifice voltage 100 V and ring voltage 400 V. The eluant was 75 wt% methanol/water with a flow velocity of 0.6 ml/min.

Results and discussion

Characterization of the systems

Analytical composition of the technical grade surfactants

The technical grade surfactants are often synthesised from the corresponding long-chain alcohols. To produce such components on an industrial scale, mixtures of alcohols can be used and purification of the alkylglycosides obtained is difficult because their chromatographic