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ORIGINAL CONTRIBUTION

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Influence of 1-decanol on the surface tension and wetting power of a new anionic surfactant derived from sugar

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Abstract We studied the adsorption behaviour at the liquid/air and liquid/solid interface of a new anionic surfactant derived from sugar, the sodium decyl galacturonate. The surface tension of aqueous solutions, measured in equilibrium and as a function of time, is particularly affected by the presence of decanol, synthesis residue, which amount ranges between about 0 and 13%. The surface tension lowering is accelerated in presence of decanol, owing to its rapid diffusion to the interface or/and because it affects the mobility and adsorption process of the anionic surfactant molecules. The wetting power of surfactant solutions were also investigated in relation with textile treatment applications. We measured the kinetics of absorption of surfactant solutions in a piece of standard cotton and compared it to the absorption of pure decanol, a completely wetting liquid and to the absorption of an alkylpolyglucoside. The time at which the fabric piece is saturated appears to be related to the adsorption of surface-active molecules on the fibers at the advancing liquid front/fabric contact line. Decanol was found to promote absorption and micellar life-time seem to reflect the differences observed at high concentration. This study shows the importance of controlling the amount of surface-active residues which may alter the kinetics of surfactant adsorption, particularly in industrial processes where equilibrium conditions are not reached.

Key words Sugar-based surfactant – surfactant-alcohol mixtures – surface tension – textile wetting

Introduction

New surfactants, synthesized from agricultural raw materials are much sought after provided they combine efficient interfacial propertie and softness.

Since now, most sugar-based surfactants are non-ionic surfactants as alkylpolyglucosides and sucroesters. Preliminary studies on functionalisation of these nonionic surfactants for the obtention of anionic or cationic derivatives have been done quite recently [1]. In this paper, we present results concerning a new soft anionic surfactant derived from sugar, i.e. the sodium decyl galactoside uronate (GA C10). The system studied, of industrial interest, is a well-defined mixture of four stable isomers. It contains decanol as a synthesis residue.

The surface tension of aqueous solutions, which reflect surface-active material adsorption at the solution/air interface, was measured as a function of surfactant concentration for various decanol amounts. A strong time-dependence of surface tension is observed making difficult the determination of the critical micellar concentration by this method. This behaviour is emphasized by the presence in solution of several isomers characterized by different equilibrium and dynamic surface-active properties.

The wetting power of aqueous solutions was also investigated in relation with textile treatment applications. In the experimental procedure we propose, a vertical piece of fabric is put into contact with the liquid surface. The mass of the liquid-absorbing fabric is measured as a function of time. In the case of pure liquids, this experiment allows to determine the wetting force of the liquid on the bottom edge of the solid, the retention properties and eventual swelling of the fabric [2, 3] and the kinetics of imbibition [3]. It was shown that liquid absorption of the fabric arises from two simultaneous mechanisms: capillary rise inside the fibers, described by the classical Washburn law [4], and capillary rise along the surface, filling the pores resulting from the woven structure of the fabric. The kinetics is controlled by the slower process, i.e. the capillary rise into the fibers. Modeling the fiber as an assembly of capillaries of radius r^*, it is then possible to relate the time t_s at which the fabric piece of height h_0 is saturated to r^* through the Washburn law [4, 5]:

$$h_0^2 = 1/2\, r^* V^* t_s \tag{1}$$

V^* being the penetrating velocity of the liquid: $V^* = \gamma\cos\theta/\eta$, where γ is the liquid surface tension, θ the advancing contact angle of the liquid on the solid, and η the liquid viscosity.

In the case of surfactant solutions the interpretation of imbibition kinetics is more complicated owing to the kinetics of surfactant adsorption on the solid surface [5–8]: equilibrium conditions are not reached. In the case of strong adsorption, depletion of surfactant at the liquid front level is so important that the wetting time appears to be related to the rate of supply of surfactants [8], i.e. the surfactant diffusion to the liquid front, and above the critical micellar concentration to the micellar life-time [7]. We investigated the absorption kinetics of surfactant solutions in a standard cotton, for various surfactant concentrations and decanol amounts, and compared it to the absorption of a pure wetting organic liquid, decanol, and to the absorption of alkylpolyglucoside (APG) solutions.

Experimental procedures

Sodium decyl galactoside uronate sample has been provided by AgroIndustries Recherches at Développement (Pomacle, France). It is composed of four stable isomers: α-pyrano (38%), β-pyrano (43%), α-furano (3%) and β-furano (16%). The synthesis of this compound is described in [9]. The structure of the α-pyrano form is shown on Fig. 1. The critical micellar concentrations of pure α-pyrano, α-furano and β-furano are respectively 21 g/l, 7 g/l and 8 g/l [9]. A cmc determination has not been possible for the β-pyrano, which is less hydrosoluble than the other isomers, since not enough pure compound was available so far. Such difference in the cmc of isomers has also been observed with decyl galactosides [10].

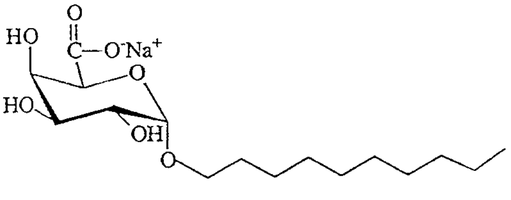

Fig. 1 Molecular structure of the sodium (decyl galactoside) uronate α-pyrano isomer

The GA C10 system was found to be efficient in real detergency conditions. The detergent power was evaluated through colorimetric measurements (pH = 8, 9). From the results, GA C10 appears to have a detergent power similar to Lauryl Ether Sulfate 12/16 and APG 12/16 samples. GA C12/14 appears to be a better detergent [11]. Toxicity tests have been performed showing that the decyl galacturonate is not dangerous in case of ingestion, not irritating for the eye (Draize test), and not irritating for the skin [11].

The unpurified compound contains 13% of decanol, synthesis residue. After washing the sample in ethanol, different amounts of decanol could be obtained: ~0%, 2%, 5% weight of surface active material.

Concentrations are expressed in grams of surface-active material by liter of solution. Ultra-pure water (sation 9000-Scientinor, France) is used to prepare the solutions. 1-Decanol (purity > 97%) is obtained from Fluka. Its physical characteristics are: density $\rho = 0.83$, surface tension $\gamma = 28.8$ mN/m, $\eta = 14$ mPa.s at $T = 20\,^\circ$C.

The alkylpolyglucoside sample is Oramix NS10 (obtained from Seppic). The hydrocarbon chain contains ten carbon atoms as for the decyl galacturonate.

Surface tension measurements

Surface tension of aqueous solutions were measured through the Wilhelmy plate method as a function of time (Krüss K12) at 20 °C. The solution surface is cleaned before the experiment starts. The first value is obtained

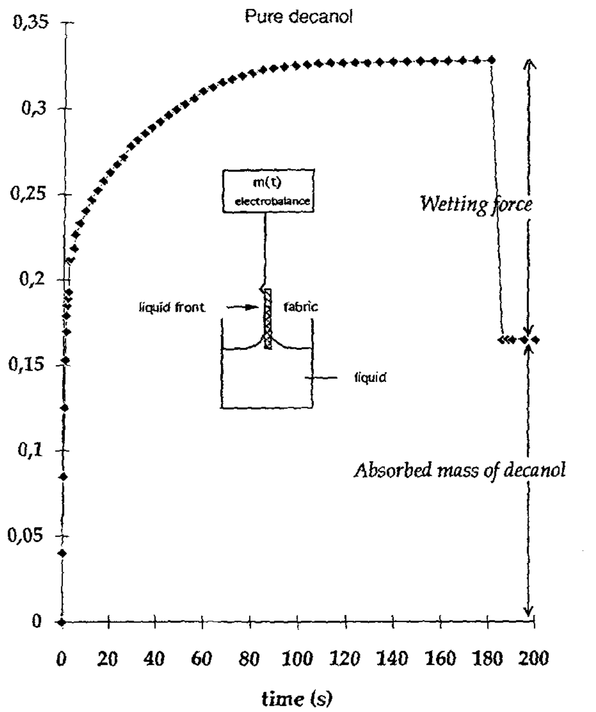

Fig. 2 Mass recorded as a function of time during the absorption process of decanol in a piece of fabric. The experimental procedure is schematically represented

100 s after the begining of the experiment which lasts at least 30 minutes.

Fabric imbibition

A vertically suspended piece of fabric is placed in the fixing clamp of the K12 tensiometer. The fabric is put into contact with the liquid surface so that it just touches it. Then the mass of the fabric is recorded, as liquid is absorbed into it, until the top of the sample is reached. Then the fabric is saturated and its mass does not vary anymore (Fig. 2).

The corresponding force can be divided into two components [2, 3]: the wetting force on the bottom edge of the fabric and the weight of liquid absorbed. Raising the fabric slowly out of the liquid so that the fabric does not touch the liquid anymore allows to determine the mass of liquid absorbed by the fibrous system. The fabric is a standard cotton used in the normalized wetting power test (ISO 8022), obtained from Mortelecque (France). Each sample is 2.5 cm wide, 1.5 cm high (h_0 = 1.5 cm) and 0.75 cm thick. This material is highly hydrophobic, thus unwetted by water but wetted by organic liquids as decanol. Each experiment is reproduced three times leading to a good reproducibility.

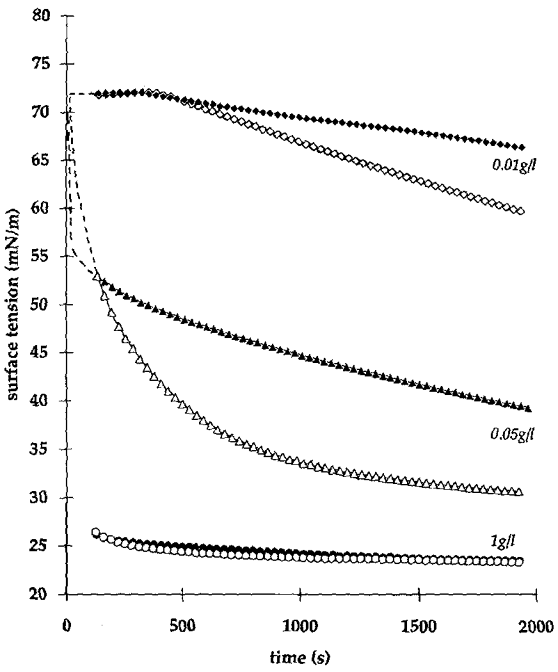

Fig. 3 Surface tension reduction as a function of time for the 2% (white dots) and 13% (black dots) decanol samples for different surfactant concentrations: ◇: 0.01 g/l; △: 0.05 g/l; ○: 1 g/l. The dotted lines represent the instantaneous surface reduction as measured with the Langmuir Balance Technique

Surface tension of GA C10-decanol aqueous solutions

Surface tensions of GA C10-decanol mixtures were measured as a function of time over at least 30 minutes. Figure 3 displays the time-dependence of surface tension for different concentrations of the 2% and 13% decanol samples.

In the low concentration range, i.e. $c \leq 0.01$ g/l a plateau is observed before surface tension starts to decrease with time. Such an induction time has already been observed in the case of large molecules as proteins [12] and attributed to orientation effects of the molecules at the interface. It may come in our case from sugar head-group orientation at the interface.

In the intermediate concentration range, i.e. $0.01 \leq c \leq 0.1$ g/l, a strong time-dependence of surface tension is observed, much more important than in the case of classical anionic surfactants as sodium dodecylsulfate (SDS). This behaviour, which was also noticed on a single isomer [9] and emphasized by the occurence of several isomers in solution, arises from the hydrophilic group structure: sugar parts lead to strong interactions with water through hydrogen bonds which may slower the adsorption process. We may notice here that sugar molecules are water-structuring molecules. Their strong interaction with water is also shown by the cloud point phenomena [13]. A marked time-dependence of surface tension is also observed for ethoxylated nonionic surfactants, particularly at low concentrations and explained by the occurence of an energy barrier for adsorption [14].

The equilibrium surface tension obtained in the high concentration range i.e. $c \geq 1$ g/l, is particularly low: $\gamma = 23$ mN/m to be compared to about 35 mN/m in the case of SDS, 27 mN/m in the case of APG C10 and 28.8 mN/m for pure 1-decanol. As a comparison, for decyl galactosides a surface tension of about 28 mN/m is found [10] and 30 mN/m for C_8C_{10} and $C_{10}C_{12}$ APG samples (at 25°) [13]. The surface tension γ_{cmc} of α-pyrano and β-furano is around 30 mN/m [9].

Such important surface pressures ($\Pi = \gamma_{H_2O} - \gamma_{solution} \sim$ 50 mN/m) are generally obtained in the case of nonionic surfactants with small hydrophilic head-groups and for anionic-cationic salts [15]. These hydrophilic group structures allow a close packing of the molecules at the interface. In the case we study, synergism effects of the mixture could explain such a low surface tension. The low value of the equilibrium surface tension at high concentration does not significantly vary with the decanol amount. Such an effectiveness in surface tension reduction is important indeed in process where the liquid/air area increases as in wetting and foaming [16].

Differences in surface tension reduction kinetics were observed varying the decanol amount particularly in the intermediate concentration range. If the magnitude of equilibrium surface tension reduction is more important for the 2% decanol sample, the instantaneous surface tension reduction (dotted lines on Fig. 3) is significantly higher in the case of the 13% decanol sample. This behaviour has been confirmed by surface tension measurements through the Langmuir balance technique, which allows instantaneous determination of the surface pressure. The instantaneous surface tension decrease in the case of the 13% sample can result either from rapid adsorption of decanol molecules at the interface, or because decanol affects the surfactant mobility. It was shown indeed that the addition of non-ionic amphiphilic molecules increase the mobility of anionic surfactants and reduces the mobility of cationic surfactants [17].

Variations of surface tension versus concentration (at $t = 20$ minutes) allow to deduce an order of magnitude of the critical micellar concentration. Their values range between 0.1 g/l and 0.2 g/l for the 0%, 2% and 5% decanol samples and around 0.5–1 g/l for the 13% sample. In the conditions of our experiments, the cmc appears to increase at high decanol content. The cmc obtained for the 0% sample is much lower than the cmc of single isomers (except for the β-pyrano for which the cmc is not known) and could also result from synergism effects of the mixture.

As described in the literature the effect of organic additives on the surfactant cmc may occur in two ways [18].

- incorporation in micelles of the organic molecules, generally in a small quantity, leads to a reduction of the cmc due to hydrophobic interactions favoring the micelle formation.
- the presence of a water-soluble organic compound, generally in higher quantity than for the previous case, may induce a modification of the solvent-surfactant and solvent-micelle interactions. A modification of the water solubility parameters, increasing the surfactant solubility, will lead to an increase of the cmc.

Owing to these two mechanisms a minimum cmc can be observed varying the additive concentration, as it is observed in the case of short-chain alcohols [19].

We are currently undertaking Small-Angle Neutron scattering experiments on these systems to characterize the micelle structure and evidence the decanol effect on these structures.

Fabric imbibition

We will first describe the absorption kinetics of a pure liquid, decanol. As observed on Fig. 2, the recorded mass first increases rapidly due to the wetting contribution of the liquid on the bottom edge of the fabric ($m_{wetting} = 0.163$ g). Then, as absorption proceeds, the recorded mass progressively increases during about two minutes until the fabric saturation where $m_{abs} = 0.165$ g of decanol have been absorbed. We will not discuss here the detailed analysis of fabric imbibition which is treated in [3]. Nevertheless, the absorption curve of decanol allows to determine the characteristic capillary radius r^* using Eq. (1) supposing complete wetting. The penetrating velocity of decanol is then $V^* = 2.04$ m/s. Taking $h_0 = 1.5$ cm and $t_s = 100$ s gives $r^* = 2.2$ μm, which is in agreement with the fiber structure as determined by electronic microscopy [3].

In the case of surfactant solutions, the observed behaviour strongly depends on their concentration.

First no absorption is observed below 0.1 g/l. Between 0.1 and about 1 g/l, no spontaneous wetting occurs and the absorption process is very slow as shown on Fig. 4 for 0.5 g/l solutions (white dots). There is no marked dependence on the decanol amount.

At higher concentrations, higher than the cmc of all compounds, the absorption curve strongly depends on the decanol amount (the results for 2.5 g/l solutions are

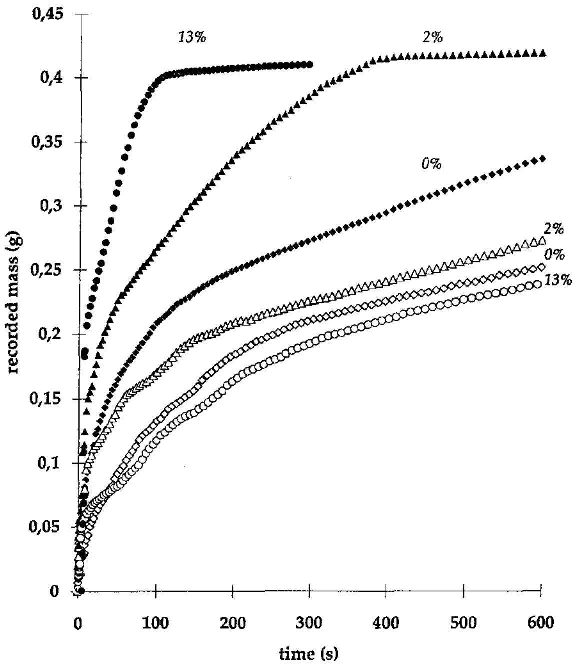

Fig. 4 Mass recorded during absorption in a fabric piece of surfactant solutions of concentration: 0.5 g/l (white dots) and 2.5 g/l (black dots) and different decanol amounts: ◇: 0%; △: 2%; ○: 13%

represented with black dots on Fig. 4). Spontaneous wetting is only observed at high decanol amount (for 5% and 13%) and the time at which saturation occurs decreases as the decanol amount increases. The penetrating velocity of these surfactant solutions, owing complete wetting is obtained, would be $\gamma/\eta \sim 23$ m/s, the solution viscosities being close to pure water viscosity (about 1 mPas). Then, for the same fabric height, the time of saturation should be ten times shorter for the surfactant solutions than for decanol. However, this time t_s measured are about 120 s, 220 s and 400 s, respectively for the 13%, 5% and 2% samples (see Fig. 4), then higher than for pure decanol ($t_{s=100\,s}$). In the case of a APG C10 solution of the same concentration (2.5 g/l) a value of $t_s = 35$ s is found. This shows, as expected [5, 6], that the system is far from equilibrium and that the advancing contact angle of the liquid front must be considered. Using Eq. (1), with $\gamma = 23$ mN/m, we obtain respectively 85°, 87° and 89° for the 13%, 5% and 2% samples, and 75° for the APG C10 sample, values which are very high. These values depend on the extent of surfactant and decanol adsorption on the fabric fiber surface and on the supply of surfactant at the liquid front. If the contact angle is very close to 90°, the pressure gradient leading to capillary rise will be close to zero and the fabric saturation will even never be reached, as it is the case for low concentration surfactant solutions.

Different factors may explain the better wetting behaviour observed with high decanol content. First, we showed that instantaneous surface tension reduction with time was faster in presence of decanol, so that surface-active material diffusion and adsorption at the liquid/air interface is faster: the same behaviour might be observed at the hydrophobic fiber/liquid interface. Moreover it has been showed that alcohol incorporation into the micelles results in a decrease of the micellar life-time [20] leading to a faster surfactant supply by the micelles. Then, we know that pure decanol completely wets the fabric, so that decanol molecules may better adsorb onto the fabric.

Another characteristic of fabric impregnation by surfactant solutions may be noticed: the retention of surfactant solution by the fabric ($m_{abs} = 0.26$–0.27 g or about 0.26–0.27 cm^3 for both GA C10 and APG C10 samples) is more important than the retention of pure organic liquids as decanol ($m_{abs} = 0.165$ g or 0.20 cm^3). Moreover a visible swelling is obtained making even more difficult the modelisation of the absorption process since the geometric characteristic of the fibrous assembly may be affected.

Conclusion

We studied the adsorption behaviour at the liquid/air and liquid/solid interface of a new anionic surfactant derived from sugar. The system is characterised by slow adsorption times, as deduced from surface tension decreasing behaviour as a function of time. The presence of decanol, synthesis residue, induces a faster instantaneous decrease of the surfactant tension. Concerning fabric imbibition, important differences are observed between pure liquids and surfactant solutions. The surfactant aqueous solutions absorption in the fabric is very slow and evidences that adsorption at the fabric surface/dvancing liquid front is not enough to induce a marked decrease of the contact angle. The influence of decanol on the kinetics of surfactant adsorption and micellar lifetime seem to reflect the differences observed at high concentration. A significant swelling of the fabric after surfactant solution absorption was also observed, which may modify the geometric parameters of the fabric, as the characteristic capillary radius, and complicate the imbibition mechanisms.

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