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SHORT COMMUNICATION

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Surface tension of mixed surfactant systems: lignosulfonate and sodium dodecyl sulfate

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Abstract The association between lignosulfonate (LS) and an anionic surfactant, sodium dodecyl sulfate (SDS) has been investigated by surface tension measurement. Three different LS samples were used in this study. In every case, the critical micelle concentration (CMC) value was close to about 4 mmol/l for mixed systems whereas the CMC value for SDS alone is about 8 mmol/l. Surface tension measurements at different concentrations of LS indicated that LS alone behaves as a polymeric surfactant. In the mixed LS/SDS surfactant system however, it appears that LS behaves primarily as a polyelectrolyte.

Keywords Surface tension · Lignosulfonates · Sodium dodecyl sulfate · Mixed surfactant

Introduction

Lignosulfonates (LS) are water-soluble polydisperse polymers, anionic surface-active derivatives of lignin. They have attracted both academic and industrial interest in terms of new materials with improved properties, particularly with applications in enhanced oil recovery, drilling additives, adhesives and other areas. In the field application of surfactant flooding in partially depleted oil reservoirs, LS have been used as an inexpensive preflush material to block adsorption sites, which would otherwise scavenge the more costly surfactant [1, 2, 3, 4, 5, 6, 7]. In another application, modified lignosulfonate can be used as a polymeric thinning agent for aqueous bentonite muds in oilfields drilling [5]. Oxidized lignosulfonate with increased carbonyl group content has been found to be effective as a wood adhesive [6].

Recently, the association behavior between lignosulfonate as one component, and cationic and non-ionic surfactant as the other, was studied by electrophoretic measurements as well as by surface tension and viscosity measurements. It was established that while a strong interaction exists in the former system, there is no interaction in the latter system. Although LS are relatively strong electrolytes, they differ from conventional electrolytes because of their high molecular weight, polydispersity and because of different possible distribution of ionizable groups attached to the polymer backbone. It has been asserted that LS behaves as a polyelectrolyte, and is capable of forming polyelectrolyte-surfactant complexes. The reduced viscosity of the LS solution decreases with increasing concentration which indicates that LS behaves as a flexible polyelectrolyte [7].

Past research in this laboratory has focused mainly on LS as additives to petroleum sulfonates (PS) in enhanced oil recovery [8, 9, 10, 11, 12, 13, 14, 15, 16]. Using a spinning drop tensiometer, Son et al. found that ultralow interfacial tensions (<0.01 mN/m) against crude oil could be achieved when using mixed PS/LS solution [10]. Chiwetelu et al. obtained data showing clearly that PS/LS mixed surfactant solutions were potentially effective in mobilizing residual oil from petroleum reservoirs [11]. In an attempt to ascertain the mechanisms underlying the high interfacial activity of PS/LS mixed systems, Manasrah et al. have shown that supramolecular aggregates involving liquid crystalline structures are formed in the mixed surfactant solution as revealed by viscosity, electrical conductivity, and phase studies [12, 13]. With the help of an inclined spinning drop tensiometer [14], Kumar et al. found that mixed surfactant systems containing divalent cations also showed faster coalescence behavior compared to the univalent cation [14].

The research described above was carried out using commercially available LS samples without any purification or modification. The present work is conducted with better-characterized LS materials for which quantitative information, e.g., % of sulfur, % of sugar, % of salt, and molecular weights, are available. The purpose of this study is to investigate the surface tension behavior of such LS samples in combination with a simple anionic surfactant, sodium dodecyl sulfate (SDS).

Experimental

Sodium dodecyl sulfate (SDS) of high purity grade was obtained from BDH Chemicals Ltd and was used as received. Aldrich Chemical Company supplied three different types of sodium lignosulfonates. The characterization data including the sulfur content percentage, salt content, as well as the number- and weight-average molecular weights of the samples are shown in Table 1. Sodium lignosulfonates were used without further purification. The Wilhelmy plate apparatus (Krüss Process Tensiometer Model K-12) was used to measure the surface tension. The measurements were conducted at 25 °C and at atmospheric pressure. Distilled water was used in the preparation of all SDS and LS solutions. The LS solution was placed in the tensiometer cell and SDS solution was added using a Hamilton micro-syringe.

Results and discussion

Figure 1 shows the surface tension as a function of the concentration of sodium dodecyl sulfate (SDS) surfactant in water. It is well known that there is a distinct break of the physical properties with respect to concentration which is associated with the formation of supramolecular aggregates (namely, the critical micelle concentration (CMC) in the case of a surfactant, or the critical association concentration (CAC) in the case of a polyelectrolyte). From the curve, the critical micelle concentration of SDS can be estimated to be approximately 8 mmol/l. This is in good agreement with the published value of the CMC for pure SDS surfactant [16].

Table 1. Characterization data of lignosulfonate samples

Sample	$M_n \times 10^{-3}$	$M_w \times 10^{-4}$	Sulfur (wt %)	Other characteristics
LS-1	7	5.2	5.2	8.2 wt% sodium
LS-2	6	5.4	4.9	4.6 wt% sodium Reducing sugars (sugared)
LS-3	5	1.2	3.1	7.8 wt% sodium Partially desulfonated

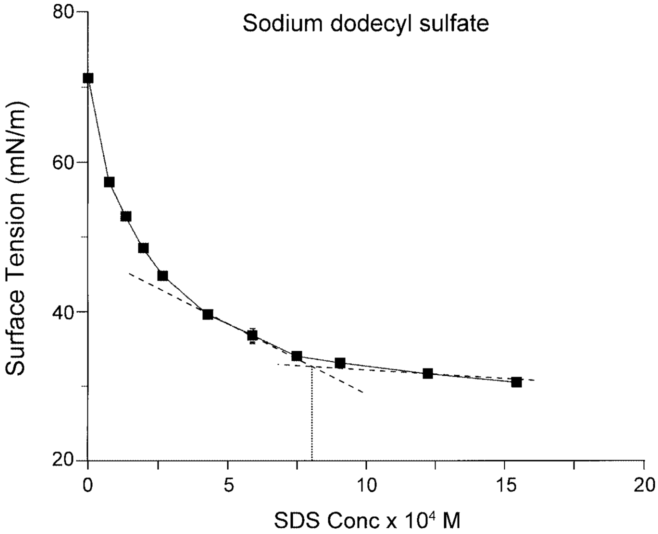


Fig. 1. Surface tension as a function of sodium dodecyl sulfate (SDS) concentration in water

Figure 2a,b shows the surface tension with respect to dilution in water for two different LS solutions in the absence of SDS. From the above figure, both LS samples are found to be surface-active, as indicated by a distinct break observed on the surface tension vs concentration plot. The CAC values correspond to 10 and 19 wt% for sodium lignosulfonate LS-1 and sodium lignosulfonate ("sugared") LS-2, respectively. In the presence of sugar, the carbohydrate component seems to hinder the aggregation of the polyelectrolyte portion of the macromolecule. It is expected that LS containing sugar will need a higher concentration for micelle formation compared to the LS without sugar. According to dyestuff adsorption measurements carried out by Gardon and Mason [17], LS can be considered as a flexible polyelectrolyte whose behavior is analogous to micelle formation in ordinary colloidal electrolytes. In the presence of cationic dyestuff (namely pinacyanole), the LS solution forms a dyestuff-discharge aggregate complex as indicated by the new adsorption peak at 630 nm. The adsorption or incorporation of the dyestuff onto or into the micelle alters the color of the dyestuff. It can be concluded from the surface tension measurements that all LS samples in an aqueous solution behave as polymeric surfactants.

Figure 3a–c shows the surface tension as a function of sodium dodecyl sulfate (SDS) surfactant concentration in three different lignosulfonate solutions. In every case, the estimated CAC value is close to about 4 mmol/l for mixed LS/SDS systems. LS, a water-soluble polyelectrolyte, appears to enhance the micellization process in comparison to the pure surfactant. Here, the surfactant/polymer interaction leads to a synergistic cooperative interaction that indicates the formation of mixed

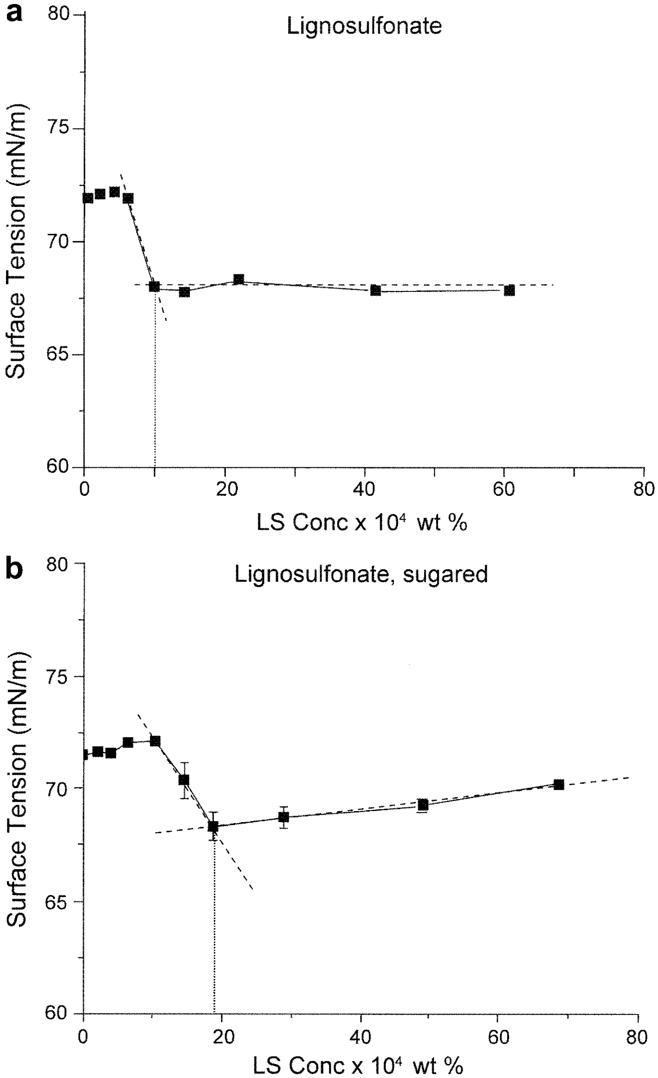
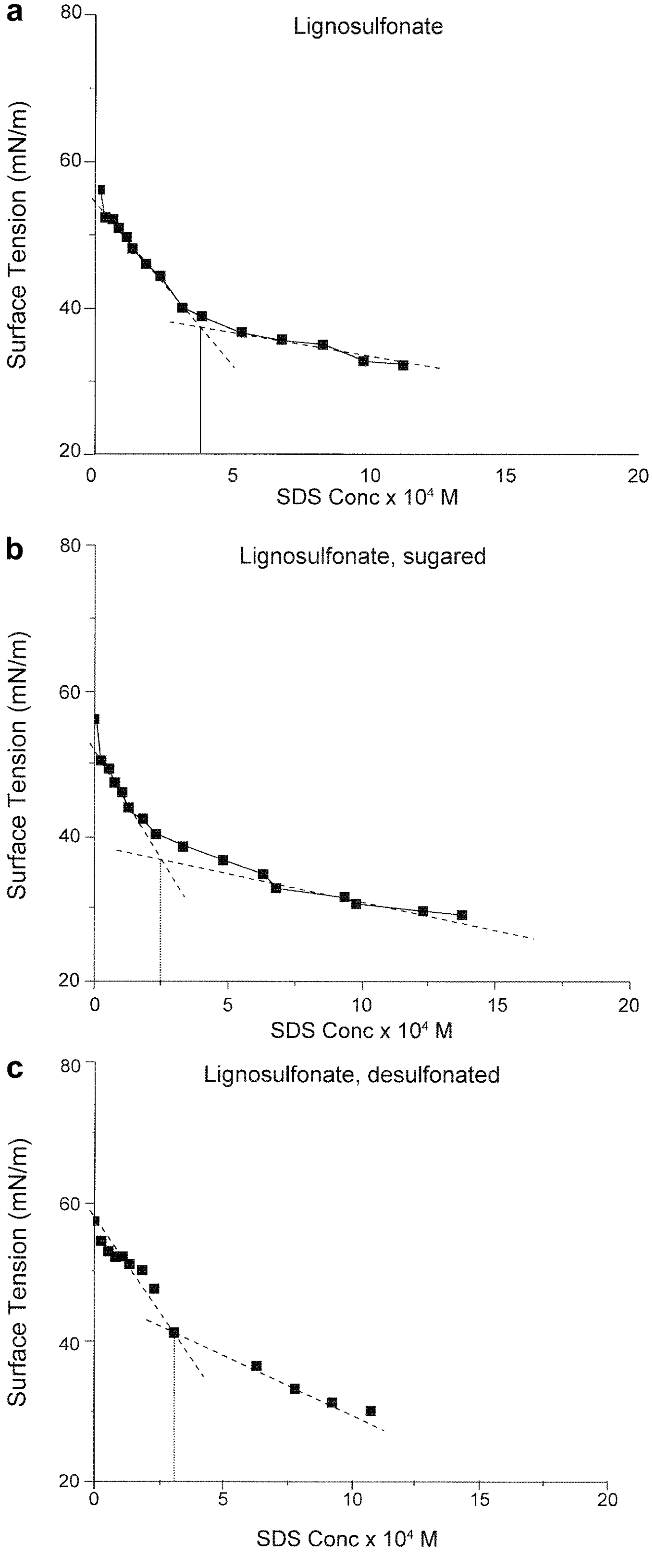


Fig. 2. **a** Surface tension as a function of lignosulfonate (LS-1) concentration in water. **b** Surface tension as a function of lignosulfonate, sugared (LS-2) concentration in water

micelles. Recently, Askvik et al. studied the association behavior between a lignosulfonate, and cationic or nonionic surfactant using surface tension measurements [7]. They found that a strong interaction existed in the LS/cationic surfactant system whereas no interaction was observed for LS/nonionic surfactant system. The present work shows that LS/anionic surfactant systems also exhibit a strong interaction. As has been mentioned before, earlier work in this laboratory has shown that LS as well as other water-soluble polymer additives affected



▶

Fig. 3. **a** Surface tension as a function of sodium dodecyl sulfate (SDS) concentration in presence of aqueous lignosulfonate (LS-1) solution. **b** Surface tension as a function of sodium dodecyl sulfate (SDS) concentration in presence of aqueous lignosulfonate, sugared (LS-2) solution. **c** Surface tension as a function of sodium dodecyl sulfate (SDS) concentration in presence of aqueous lignosulfonate, desulfonated (LS-3) solution

strongly the interfacial tension behavior of oil-water systems containing anionic surfactants [11, 12]. Similarly, the dynamic interfacial tension (IFT) behavior of reacting oil-water system (in which an anionic surfactant is formed in situ by a reaction between an oil-based acid and a water-based alkali) was also affected by the presence of a polymer cosurfactant although this effect was rather complex [18]. The dynamic interfacial tension decreased as the concentration of water-soluble polymer (polyvinyl alcohol or polyacrylamide) additive increased in the case of linoleic acid in paraffin oil mixture against distilled water, whereas the IFT increased as the concentration of water-soluble polymer additive increased in the case of linoleic acid in paraffin oil mixture against aqueous NaOH solution.

In conclusion, the surface tension measurements carried out in this work give a clear indication that LS, water-soluble polyelectrolytes, are surface-active on their own. In the presence of the SDS surfactant, the observed surface tension behavior characteristics are typical of a mixed surfactant system. There is relatively little difference in how the three different types of lignosulfonate affect the surface tension behavior of SDS solution. There is essentially no difference between lignosulfonate LS-1 and desulfonated lignosulfonate LS-3. Lignosulfonate (sugared) yields somewhat lower surface tension values below the CMC. After the CMC has been reached, the slope of the surface tension vs SDS concentration curve is very similar for all three lignosulfonates.

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