Surface activity of bagasse lignin derivatives found in the spent liquor of soda pulping plants

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ABSTRACT: Lignin compounds present in the black liquors from alkaline pulping of bagasse are separated by evaporation to dryness or precipitation by acidifying to pH 2. The separated lignin compounds exhibit the surface active characteristics of weak acid surfactant mixtures. Their surface tension versus concentration semi-log plot indicates a pattern similar to the break found at the critical micelle concentration of conventional surfactants. The surface activity of the lignin derivatives is strongly pH sensitive, and essentially vanishes under acidic pH conditions.

KEYWORDS: Alkali lignins, bagasse, bibliographies, black liquors, pH, soda pulping, spent liquors, surfactants.

Lignin is a natural polymer made up of phenylpropane units bearing hydroxyl and methoxyl groups. Lignin is found in varying amounts in softwoods and hardwoods, as well as in grass plants such as alfalfa, barley, oat, and sugar cane *(1, 2)*.

Bagasse is the fibrous by-product of the sugar cane milling; it typically contains 18–20% lignin *(3)*, which must be partially or totally removed from the cellulosic material to make the pulp.

In the chemical pulping processes, the lignin polymer is degraded into small fragments with molecular weights ranging from 4000, i.e., a few phenylpropane units, to 50,000 or more. These fragments are made soluble by modifying or forming anionic hydrophilic groups.

In the sulfite processes, the introduction of sulfonic acid groups leads to the production of lignosulfonates. In the other class of pulping processes, referred to as alkaline pulping, the hydroxyl groups are ionized and the aryl-ether linkages are cleaved; the result is the production of phenate anions, which are strongly hydrophilic and insure water solubility at high pH.

As a polymer containing aromatic rings with available reactive sites for electrophilic substitution, lignin derivatives can be modified and/or copolymerized with other materials to produce inexpensive binders, adhesives, fillers, etc. *(4)*.

Lignin derivatives contain a hydrocarbon backbone with hydrophilic groups "grafted" from place to place, a feature characteristic of some surfactants. Indeed, lignosulfonates are used as a clay dispersant in drilling fluids *(5–7)* and have been proposed as sacrificial adsorption agents *(8)* or low-cost co-surfactants in enhanced oil recovery processes *(9, 10)*. However, very few reports have been dedicated to the surface and interfacial properties of lignin derivatives, and all of them dealt with the water-soluble sodium lignosulfonates, either extracted from the sulfite process liquors *(11, 12)* or produced by sulfonating the lignin coming from other sources *(13, 14)*.

The present article deals with alkali lignin derivatives found in the black liquor of soda bagasse pulping. Since the water solubility of these products depends on the pH, the extraction process from the original black liquor will be discussed first as a function of the pH and other relevant factors. Then the surface activity of their aqueous solution will be analyzed in order to compare or contrast them with more conventional surfactants.

Lignin derivatives extracted from the spent liquor of a sulfite chemithermomechanical process will be dealt with similarly in a companion paper.

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Extraction of lignin derivatives from black liquors

Black liquors from different bagasse pulping mills are collected and filtered to remove any suspended solid materials. Typical liquor samples contained 3–4% of dissolved solids at pH 10, with a 2–9% span from mill to mill or from time to time in the same mill. Although these variations are appreciable, they have little effect on the results presented here. About 40% of the dissolved solids turned out to be lignin derivatives.

The solubilized lignin compounds are then extracted from the black liquor according to one of two methods:

The first method consists in concentrating the black liquor in a rotary evaporator (Buchi model 461) up to 15% solids, and then evaporating it to dryness in a flat pan placed in a convection oven. In the present study, two cases of this method will be reported, depending on whether the evaporation and drying take place at 100°C and atmospheric pressure or at 70°C under vacuum. These methods were selected, since they are more feasible on an industrial scale than freeze drying.

The second method consists in a controlled precipitation of the lignin compounds by acidifying the liquor with sulfuric acid. Since the lignin is solubilized at alkaline pH, its hydrophilic groups are mostly phenate and carboxylate anions. Both groups are the salts of a strong base and a weak acid, and their ionization decreases when the pH decreases. Since the undissociated form of the lignin derivatives is not water soluble, the decrease in ionization results in a decrease in solubility. As a consequence, these substances tend to precipitate as the pH is lowered and the nondissociated phenol or acid forms prevail.

Acid precipitation of lignin compounds from alkaline liquor has been studied by various investigators. Some authors used different acidifying reagents to precipitate over 50% of the lignin present in the soda bagasse liquor *(4, 15)*. Others reported that not only the pH, but also the temperature and the total dissolved solids content, can influence the precipitation *(4, 16–18)*.

In order to determine the effects of all these variables, the precipitation is carried out by acidifying with sulfuric acid according to a factorial design with three values of pH (7, 5, 2), three values of temperature (70°C, 80°C, and 90°C), and three values of total dissolved solids content (typically 15 wt.%, 25 wt.%, 35 wt.%).

The separation is carried out according to the following procedure: First, the original liquor is filtered and is diluted or concentrated (at 70°C under vacuum) to adjust the total solids content to the set value. Then a 250-mL sample is brought to the required temperature in a water bath and is acidified with a 2 *N* sulfuric acid solution until the preset precipitation pH is kept steady for 5 min. The sample is then removed from the hot water bath and placed in another water bath with running water at ambient temperature (22°C–25°C), in order to cool off and to induce the flocculation and coagulation of colloid size aggregates.

The separation of the precipitate is done in 50-mL polycarbonate tubes placed in a IEC model HN-SII centrifuge rotating at 2500 rpm for 2 h. The supernatant liquid is drained out and the precipitate is dried in a convection oven at 70°C until a constant weight is attained. The final lignin product is finely ground in a Siebtechnik ring crusher into a brown free-flowing powder, very similar to commercial ones. It is worth remarking that centrifugation allows for a lignin recovery slightly better than mere filtration.

The amount of lignin in the final powdered product is estimated by measuring the UV absorbance of a NaOH solution at 278 nm, in a Perkin-Elmer UV-VIS spectrometer; the concentration standards are lignin extracts prepared according to either the classical Klason determination *(19)* or the Kim *et al.* method *(20)*.

The lignin yield, Y_L, and total solids yield, Y_S, are taken as the dimensionless ratio between the weight of precipitated lignin or total solids, and the weight of total dissolved solids produced by evaporating to dryness an identical sample. The precipitation selectivity S, i.e., the ratio Y_L/Y_S, indicates the proportion of lignin in the precipitated solids. Thus, yields and selectivity are expressed as weight fractions.

1. Solids yield Y_S, lignin yield Y_L and selectivity in lignin precipitation S (all dimensionless weight fractions) at different pH, temperature and total solids content

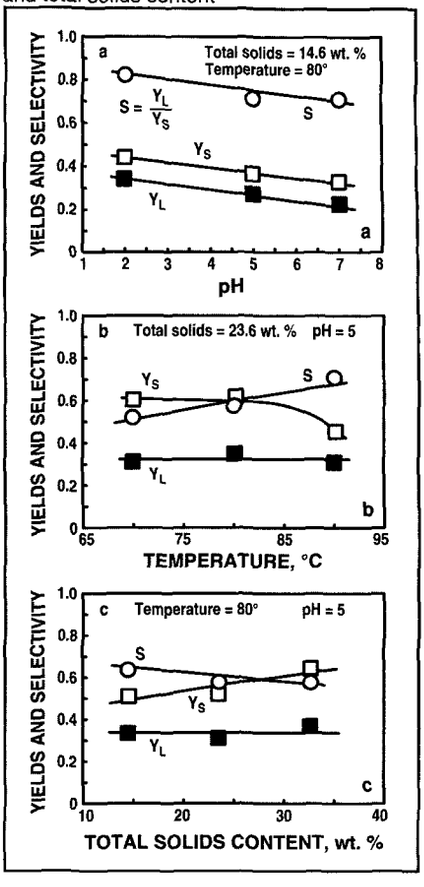
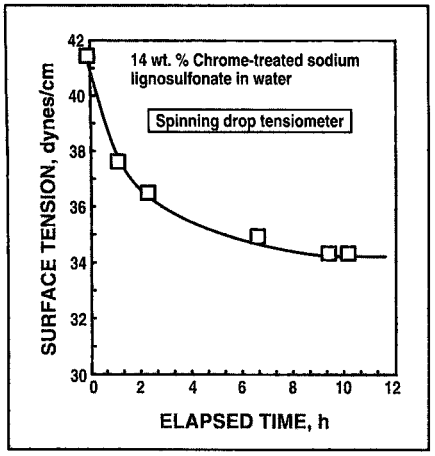


Figure 1 indicates typical variations of lignin and total solids yields versus different values of the pH, temperature, and total dissolved solids content. Figure 1(a) shows that the pH is the variable that most affects the result. A decrease in pH strongly increases both the lignin and total solids precipitation yields Y_L and Y_S. Selectivity also increases as pH decreases. As a matter of fact, the parallelism of the two yield lines means that their difference, i.e., the non-lignin precipi-

2. Variation of surface tension versus elapsed time



tated solids, is a constant amount over the considered range of pH. This indicates that only lignin derivatives are precipitated from pH 7 to pH 2.

This may be the basis for a selective separation of phenolic or weak acid lignin compounds, which are soluble at pH greater than 7 but insoluble at lower pH. The steady increase of lignin precipitation when the pH is lowered indicates that there exist different species, probably with a distribution in their hydrophilic-lypophilic balance (HLB) as suggested by Kudo and Kondo *(13)*. In effect, the lignin compound hydrophilicity is a function of two variables: on one hand the number of hydrophilic groups per phenylpropane unit, and on the other hand the ionization of these weak acid groups. The first depends upon the molecular structure, while the second depends upon the pH.

In carboxylic acid systems *(21)*, it was shown that the pH at which a given HLB value is attained, increases with the acid chain length *(21, 22)*. In the present case, the solubility threshold depends on the same variables. Thus, a lignin compound that precipitates at pH 5 has more hydrophilic groups per phenylpropane unit than the ones which precipitate at pH 7, and so forth. Since the hydrophilic groups often come from the cleavage of aryl ether linkages, a higher proportion of hydrophilic groups might be related to a higher degradation and a lower molecular weight, a point which will be dealt with in another study.

Figure 1(a) and (b) data show that the temperature and the total solids content do not affect significantly the precipitation yields, although larger variations have been reported for other kinds of lignin. In some of the tested systems, the increase in temperature produces a slight decrease in lignin yield. However, it is worth noting that an increase in temperature is always correlated with an increase in lignin precipitation selectivity S, as shown in Fig. 1(b), probably because it favors the coagulation of colloidal lignin. On the other hand, it seems that an increase in total solids tends to raise the precipitation yield at the expense of a slight decrease in the selectivity.

Surface activity estimation

Surfactants are known to be responsible for the reduction of the surface or interfacial tension, a property so characteristic that it resulted in the name tag meaning "tension-active" used in French, German, or Spanish to label surfactants.

As the surfactant concentration of an aqueous solution increases, the surface or interfacial tension starts decreasing and then levels-off at some concentration, so-called "critical micelle concentration" abbreviated CMC, above which it remains constant. Above the CMC, the surfactant molecules self-associate in aggregation polymers called micelles, as a way to reduce the free energy of the system *(23)*. If the surface or interfacial tension is plotted versus the logarithm of the concentration, a downward straight line variation is found just below the CMC for most surfactants, and the slope of this line can be linked with the surface concentration of the surfactant through the so-called Gibbs isotherm *(24)*:

$$\Gamma = -C/RT(\partial\gamma/\partial \ln C)_T$$

i.e., $$RT\Gamma = -(\partial\gamma/\partial\gamma \ln C)_T$$

where Γ is the excess surface concentration of surfactant or adsorption in mol/unit area, γ is the surface or interfacial tension and ln$C$ the natural logarithm of the concentration (dimensionless) in the bulk solution. R is the molar gas constant, and T is the absolute temperature.

In order to test the surface activity of a given product, the variation of γ as a function of log$C$ is plotted and the pattern and the numerical values are compared with those of conventional surfactants. For the sake of simplicity in the plot, the abscissa is usually taken as the decimal logarithm of the concentration in wt.% (log$C$), and a 2.3 factor has to be introduced in Gibbs formula. The surface tension decrease with increasing bulk phase concentration is an indication of surface activity, and a break in the γ-log$C$ plot is a hint that some change is occurring in the solution structure, maybe the formation of micelles or micelle-like structures.

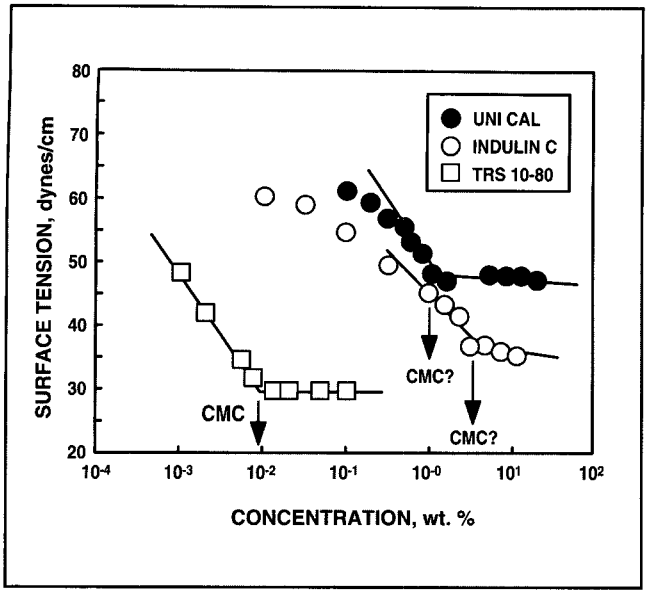
Finally the slope of the γ-log$C$ plot just before the tendency break, i.e., 2.3 $RT\,\Gamma$, is to be taken as an estimate of the adsorption.

The γ-log$C$ study is carried out for the lignin compounds which were separated by the different methods indicated in the previous section, as well as for some commercial lignin products.

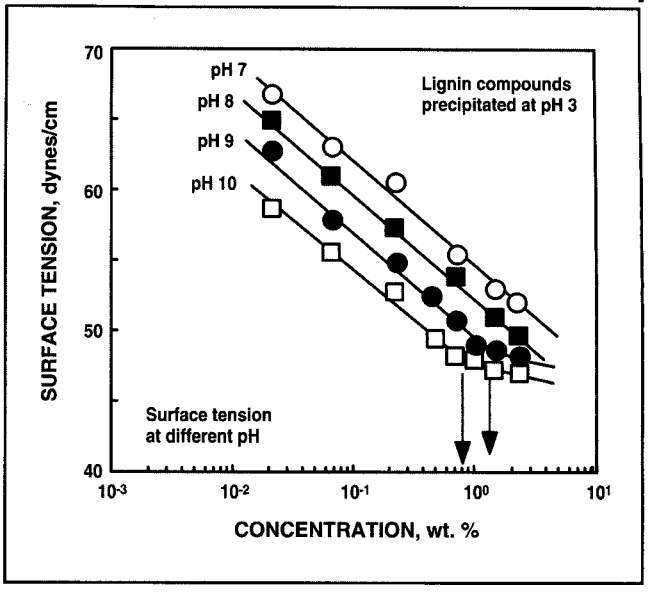
Unless otherwise stated, the surface tension is reported in dyne/cm, the conventional CGS unit (equivalent to mN/m), with a Whilhelmy plate apparatus (Biolar) with an accuracy of ± 0.1 dyne/cm. A concentrated solution of the tested product, say 10 wt.%, is prepared first; then this solution is diluted repeatedly with the proper aqueous diluent by a factor 2, 3, or other, so that the corresponding concentration sequence decreases according to a geometric progression; this is set in order to ensure equidistant data points with respect to the log$C$ scale.

The surface tension essentially depends upon the chemical species which are adsorbed onto the surface; it must be remarked that the adsorption-desorption equilibrium might not be reached at once, particularly if macromolecules with low diffusion coefficients, and/or electrical charges, are involved, as in the present case.

3. γ-log*C* plot for two lignin derivatives and a petroleum sulfonate surfactant



5. γ-log*C* plots for the lignin compounds precipitated at pH 3 and solubilized in different pH solutions



Whether equilibrium is reached or not, can be easily checked by monitoring the surface tension value versus the time elapsed since the surface was created in the first place. In this case, the surface tension measurements are carried out in a spinning drop tensiometer, developed at the University of Texas, which is found to be the most suitable equipment for the present purpose. In effect, the bubble-water interface cannot be contaminated from outside in this apparatus and the measurements are accurate.

Figure 2 indicates a typical plot of surface tension versus time measured in a spinning drop tensiometer for a 14 wt.% solution of Unical™, a commercial chrome-treated sodium lignosulfonate manufactured by Milpark Drilling Fluids as a deflocculant for use in water-based muds.

It is seen that the surface tension keeps decreasing for over 10 h before reaching a constant value. This case is particularly awkward because the concentration is very high and the substance is a polyelectrolyte of high molecular weight, which will last quite a long time to rearrange itself at the surface.

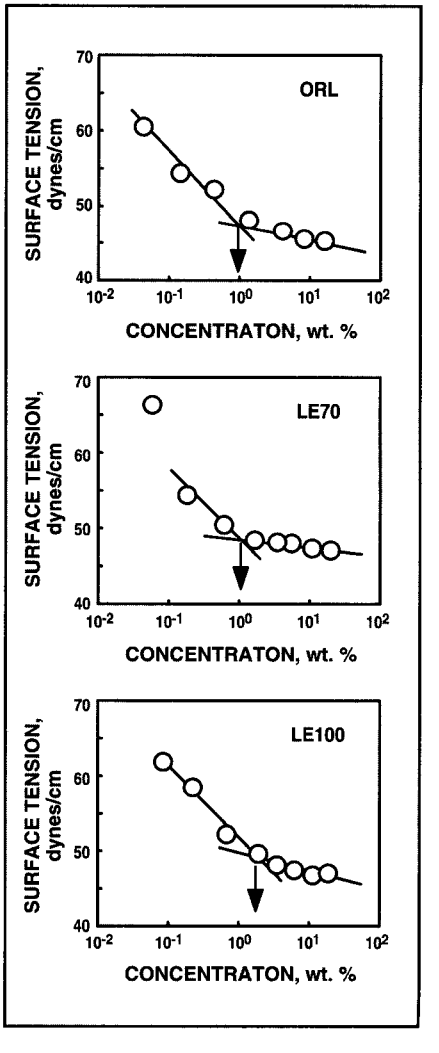
With most of the lignin compounds studied, the equilibrium is actually reached in much less time. However, and as a precaution, it is recommended that the system surface be pre-equilibrated, according to the following procedure, before measuring the surface tension by the Wilhelmy plate method.

First, a 10-mL solution sample is poured into a Petri dish the day before the tension measurement is to be carried out; then it is protected from outside dust with a glass cover, and it is stored in a constant temperature enclosure. In order to reduce any eventual evaporation, the enclosure also contains an open pan filled with water. The next day, the Petri dish is carefully moved to the tensiometer and the measurement is carried out on a surface which is at least 24 h old, and may be considered at equilibrium with the bulk solution.

The analysis of the results is carried out as follows: After plotting the surface tension versus the decimal logarithm of the concentration, expressed in wt.%, the straight lines which approximate the variations above and below the break, i.e., the CMC region if any, are extrapolated and their intersect is taken as the eventual CMC.

The surfactant efficiency is taken as the concentration required to reduce the surface tension to the minimum, i.e., the CMC.

4. γ-log*C* plot for the black liquor and the separated lignin derivatives



The surfactant effectivity is taken as the magnitude of the maximum effect, i.e., the maximum reduction in surface tension, that is the difference $\gamma_0 - \gamma_{CMC}$, where γ_0 stands for the surface tension of pure water, i.e., 72 dyne/cm.

The slope of the plot just below the CMC region is 2.3 *RT*, and gives an estimate of the adsorption, i. e., the surface packing *(24)*.

Figure 3 indicates the γ-log*C* plots for Indulin-C™, a commercial sodium salt of kraft pine lignin manufactured by Westvaco, for Unical™, and for TRS-10-80® a sodium petroleum sulfonate surfactant, equivalent molecular weight 425, manufactured by Witco Chemicals.

For the three samples the same characteristic pattern is exhibited, with a break in the trend at the CMC. However, it is seen that the commercial lignin derivatives plots exhibit some specific features.

First the straight line variation before the CMC is not as well defined as in the petroleum sulfonate TRS 10-80 surfactant plot; this results in some inaccuracy in determining the CMC.

The second difference is that the surface tension of the commercial lignin solutions is higher than the surface tension of the TRS 10-80 petroleum sulfonate solution, an indication of a lesser surface activity.

Third, the surface tension of the lignin solution does not remain absolutely constant above the CMC break, but instead it keeps decreasing slowly when the concentration increases. This means that the CMC has not exactly the same meaning for this kind of solution, probably due to a complex mixed micelle formation *(25)*.

Surface activity of the liquor and total solids solutions

The original liquor (ORL) as well as the solutions of dry powder produced by concentrating and evaporating at 70°C (LE70) or 100°C (LE100) are diluted and their γ-log*C* variations measured according to the above mentioned procedure.

Figure 4 plots show that the γ-log*C* relationship is essentially identical for the three products, which exhibit similar characteristics to the Fig. 3 plot for commercial lignin products. The three products come from the same liquor, and it is no wonder that they show identical patterns. This also means that the evaporation and drying does not produce any sizable modification in the surface activity of the lignin derivatives.

Surface activity of the solutions of precipitated lignin compounds

The same study is carried out with the powdered substances resulting from the acid precipitation of black liquor. Since the solubility of these substances depends upon the solution pH, the γ-log*C* measurements are carried out with solutions at different pH.

Figure 5 shows the γ-log*C* plots for the lignin compounds precipitated at pH 3 and solubilized in aqueous solutions at different pH. The substances came from the same original liquor as in Fig. 4 data, so that the efficiency and effectivity can be compared.

Figure 5 data show several things. First the γ-log*C* plots are better approximated by straight lines below the CMC than in the previous cases. This means that the adsorption remains constant over a larger range of concentration.

Secondly, the slope of this straight line (2.3 $RT\ \Gamma = 4.5$ dyne/cm) is the same in all cases; this indicates that the surface packing does not change with the pH of the solution.

Third, both the efficiency and effectivity increase as the solution pH increases; i.e., the substance becomes more surface active as the pH increases. The γ-log*C* plots at pH 9 and 10 are essentially similar to Fig. 4 plots, as expected, since the solution pH is alkaline in both cases.

Fourth, the precipitated product at pH 3 is a very poor surfactant when used at pH below 7; this is important because it was thought that the precipitated substances are good surfactants down to their pH of precipitation. This is not the case, probably because the precipitation threshold depends more on molecular weight than on ionization. In effect, it is clear that there is not enough ionization below pH 9 for these substances to be substantially surface active. No CMC-like break is observed at low pH conditions, a result mentioned with other lignin products *(12)*.

There is thus, probably, a wide distribution in molecular weight and hydrophilicity. Other data (not shown) indicate that the dispersant activity of the lignin compounds increases with the pH used for their precipitation, another hint pointing to the same direction.

Finally it is worth noting that although the efficiency of the precipitated products is slightly better than the efficiency of the dried ones or the original liquor, their effectivity and surface activity are essentially the same.

Conclusions

The lignin compounds extracted from the black liquors from the bagasse soda pulping mills, exhibit a surface activity similar to that of commercial lignin products. Their surface tension–concentration plot exhibits a break similar to a critical micelle concentration (CMC) pattern; it occurs in the 1 wt.% concentration range, with a surface tension reduction down to 45 dyne/cm.

This surface activity is exhibited in aqueous solution at high pH. At neutral and acid pH, the activity is reduced, and no CMC-like pattern is found. The lignin compounds exhibit essentially the same moderate surface activity whatever the method used to separate them from the black liquor.

The surface tension–concentration plot gives a good appreciation of the surface activity of this kind of product, and contains several characteristic data, such as the efficiency (CMC-like break concentration), the effectivity (tension lowering at CMC), the surface adsorption packing (slope of the γ-log*C* plot before the CMC-like break), and the surfactant-like behavior (aspect of plot).

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