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Adsorption of sodium lignosulfonates on hematite

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Abstract The adsorption of three sodium lignosulfonates on hematite was studied as a function of pH in the range from 4 to 10.5, and in the presence or absence of calcium ions (10^{-3} mol/L calcium choride). Intrinsic viscosity measurements demonstrated that the effective size of the macromolecules was not significantly affected under the experimental conditions. The adsorption results showed that electrostatic forces between the anionic polyelectrolytes and the hematite surface controlled the adsorption process although substantial non-electrostatic interactions were also clearly observed. The adsorption density inversely correlated with the anionicity of the tested lignosulfonates, especially with the content of sulfonic groups, with the least anionic polyelectrolyte producing the highest adsorption level. It was suggested that lateral repulsive electrostatic forces between the adsorbed macromolecules prevented dense adsorption of more anionic lignosulfonates. From this point of view, the effect of calcium on adsorption was attributed not only to its specific adsorption and surface charge reversal, but also to screening the anionic groups of lignosulfonates and minimizing the lateral repulsive interactions especially at high pH.

Keywords Lignosulfonates · Hematite · Intrinsic viscosity · Adsorption

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1 Introduction

Lignosulfonates are anionic polyelectrolytes obtained as a by-product of wood processing to extract cellulose. From the surface chemistry point of view, industrial applications of lignosulfonates can conveniently be divided into two broad classes: those that rely on selective adsorption of lignosulfonates on one, perhaps two components of an aqueous suspension of mixed solids, and those where the selectivity of lignosulfonate adsorption is of secondary importance. The use of lignosulfonates as, for example, selective depressants in the froth flotation of minerals would only be successful if the polyelectrolytes selectively interacted with the mineral to be depressed. However, some of the most common uses of lignosulfonates, such as rheology modifiers, dispersants, mud thinners, or binders, are based on total non-selective adsorption onto whatever substrates are present in suspension. Therefore, little effort has been made so far to develop lignosulfonate formulations that would offer selectivity in interactions with various components of mineral mixtures.

Interestingly, very few systematic studies actually deal with the adsorption of lignosulfonates on mineral surfaces, and especially with lignosulfonate adsorption in relation to the froth flotation process—the most important fine particle processing technology worldwide. Our recent contribution is perhaps one of the first on the subject (Ansari and Pawlik 2007a). Nevertheless, random samples of lignosulfonates were tested in several froth flotation applications, such as slime blinders in potash flotation (Arsentiev and Leja 1977), depressants of talc (Ma and Pawlik 2007), depressants of molybdenite in the flotation separation of molybdenite from talc (Hiscox et al. 1976; Kelebek et al. 2001), depressants of barite in the froth flotation of bastnaesite (Pradip and Fuerstenau 1991), or as depressants of carbonate minerals in phosphate flotation with fatty acid surfactants (Lu and Sun 1999). A level of selectivity can also potentially be achieved in the froth flotation of copper-molybdenum ores under certain physicochemical conditions (pH, concentration and type of ions) and only with certain types of lignosulfonates (Ansari and Pawlik 2007b). Some success was also reported in the flotation separation of plastics (Singh 1998; Le Guern et al. 2000, 2001). The vast majority of the published data were obtained with only one lignosulfonate. Wider applications of lignosulfonates in mineral processing are certainly hindered by the fact that there are perhaps dozens of different lignosulfonates which, depending on their origin (hardwood or softwood), vary in composition, molecular weights and weight distributions, and degrees of anionicity. Sulfonic, carboxylic, and phenolic functional groups are primarily responsible for the strongly anionic character of lignosulfonates. Although it is generally assumed that lignosulfonate molecules are spherical, there is still some debate regarding the exact structure and shape of the macromolecules (Vainio et al. 2008). Therefore, it should not be surprising that our understanding of the adsorption of lignosulfonates on mineral surfaces is generally very poor.

Although hematite is used in this study as a model oxide mineral, it is the most important component of oxide-based iron ores, it is often found in phosphate deposits, and hematite-like coatings may form on the surfaces of iron sulfide minerals (pyrite, pyrrhotite). There are also systematic studies on adsorption onto hematite of other complex anionic polyelectrolytes similar to lignosulfonates, such as humic acids (Vermeer et al. 1998; Vermeer and Koopal 1999), and the presented study demonstrates certain key features of lignosulfonate adsorption on the hematite surface which should also be applicable to other oxide systems.

2 Experimental

2.1 Materials

Three sodium lignosulfonates were received from Borregaard-Lignotech USA. The same lignosulfonates (in addition to three other) were tested in our earlier studies (Ansari and Pawlik 2007a, 2007b; Ma and Pawlik 2007). Selected properties of the samples, as provided by the manufacturer, are presented in Table 1. The D619 and 750 samples are softwood lignosulfonates, while the D648 is a hardwood lignosulfonate. All samples were dry powders and were used as-received.

Hematite was obtained from Alfa-Aesar. The sample was analyzed by x-ray diffraction, which confirmed that the fine powder was 100% pure hematite (α-Fe_2O_3). The total BET (Brunauer, Emmet, Teller) specific surface area of the sample was 8.8 m^2/g, as determined from nitrogen adsorption using a Quantachrome-1MP BET analyzer equipped with a 1-mm Hg pressure transducer. The volume-average particle size was found to be 2.7 µm (Malvern Mastersizer 2000). In addition, the porosity of the hematite powder was also determined with the Quantachrome unit. The density functional theory (DFT) method was then used to obtain the pore size distribution of the sample. Figure 1 shows the porosity of the sample, given as the cumulative specific surface area contained in pores smaller than a given pore diameter. A portion of these internal pore surface areas was not available for polyelectrolyte adsorption and as such were omitted in calculating the adsorption densities. More detail on estimating the molecular sizes of the lignosulfonates will be provided in the results section.

Table 1 Selected chemical properties of the tested lignosulfonate samples

Sample	Ca [%]	Na [%]	Total Sulfur [%]	Sulfonate Sulfur [%]	Carboxylic Groups [%]	Molecular Weight [kDa]
D-619	0.0	9.0	7.0	6.0	3.2	25
D-648	0.1	15.9	11.1	8.1	7.4	5
D-750	0.0	8.0	3.2	2.7	7.4	6

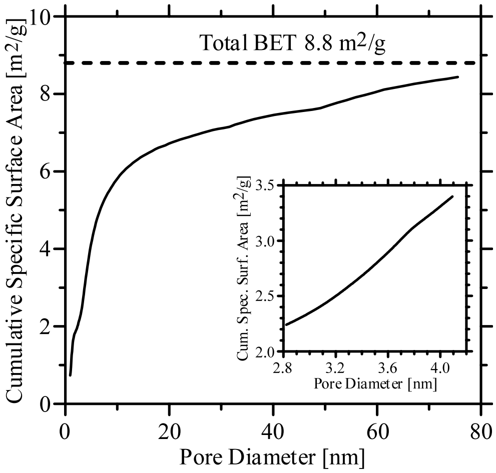

Fig. 1 Porosity of the hematite sample presented as the cumulative specific surface area contained in pores smaller than a given pore diameter. The insert shows only the range of pore sizes of the same dimensions as the calculated molecular sizes of the tested lignosulfonates

2.2 Determination of intrinsic viscosities of lignosulfonates

The intrinsic viscosity of a polymer is a measure of the size and conformation of the polymer in solution, and the magnitude of this parameter reflects the hydrodynamic resistance of individual polymer chains to flow. The intrinsic viscosity is also a function of the molecular weight of the polymer. High molecular weight polymers are characterized by high intrinsic viscosities. A polymer in a fully extended chain conformation will also exhibit a high intrinsic viscosity value. If the same chain, however, is forced to coil in solution (by changing pH, ionic strength, or temperature) the intrinsic viscosity of such a chain dramatically decreases. In other words, the intrinsic viscosity can be used to assess the effect of solution chemistry on the adsorbing polymer itself. Although many polymer adsorption studies recognize the importance of conformational changes of polymer chains in the adsorption process, very few works actually made an attempt to quantify the contribution of those phenomena, with the main focus being primarily on the surface chemistry and properties of the adsorbent.

In order to establish correlations between changes in the conformation of lignosulfonate macromolecules in solution and their adsorption on hematite, the behavior of the lignosulfonates in solution under different conditions was studied through intrinsic viscosity measurements. The kinematic viscosities of lignosulfonate solutions (typically five solutions) of different concentrations at 23 °C were measured with Cannon-Fenske capillaries using a PVS1 (Schott-Geräte, GmbH) photo-timing and processing system. The highest lignosulfonate concentration (about 150 g/L) was such that the relative viscosity at that concentration was on the order of 1.6–1.7. The intrinsic viscosity was then obtained by extrapolation using an equation proposed by Fedors in the following form (Fedors 1979):

$$\frac{1}{2(\eta_{rel}^{1/2}-1)}=\frac{1}{[\eta]c}-\frac{1}{[\eta]c_m} \tag{1}$$

where η_{rel} is the relative viscosity (the viscosity of the tested solution divided by the viscosity of the solvent), $[\eta]$ is the intrinsic viscosity, c is the lignosulfonate concentration, and c_m is the polymer concentration parameter with units of concentration. It can be seen that a plot of the dimensionless quantity $1/[2(\eta_{rel}^{1/2}-1)]$ as a function of $1/c$ should give a straight line with the slope equal to $1/[\eta]$. Hence, the intrinsic viscosity can readily be calculated from the slope.

The applicability of the Fedors equation to describe the viscosity results is actually an interesting experimental finding. Our viscosity data indicated that all the lignosulfonates showed a strong polyelectrolyte effect, i.e., plots of reduced viscosities as a function of lignosulfonate concentration were non-linear, and the usual extrapolation to zero concentration to obtain the intrinsic viscosity was not so straightforward. More importantly, the use of the Fedors equation allowed the intrinsic viscosities of the lignosulfonates to be measured under the same ionic strength and pH conditions as those of the adsorption tests without having to apply the iso-ionic dilution technique (Pals and Hermans 1948) in order to eliminate polyelectrolyte effects. It is also worth mentioning that the Fedors equation describes very well the behavior of polyacrylamide-based flocculants—a very different type of polymers (straight-chain, viscosity-average molecular weights on the order of 4–5 MDa)—of different degrees of anionicity in low ionic strength solutions including distilled water (Arinaitwe 2008). Examples of the Fedors representation of the raw viscosity data for determining intrinsic viscosities will be given in the results section.

Fredheim et al. (2003) used size exclusion chromatography and multi-angle laser light scattering to establish a Mark-Houwink-Sakurada (MHS) type of correlation between the weight-average molecular weights (M_w) and intrinsic viscosities ($[\eta]$) of several lignosulfonates produced by Borregaard Lignotech. The empirical equation had the following form (Fredheim et al. 2003):

$$[\eta]=0.12M_w^{0.36} \tag{2}$$

Since the intrinsic viscosity values provided by Fredheim et al. to derive (2) were obtained in a 0.1 mol/L NaCl solution, a number of intrinsic viscosity measurements (using the Fedors equation) were also performed in 0.1 mol/L NaCl in order to calculate the weight-average molecular weights of the tested lignosulfonates with the use of (2). It was found that the molecular weights of the lignosulfonates estimated from intrinsic viscosities were 10200 for the D619, 7600 for the D648, and 9000 for the D750. These values, although only qualitatively correlating with the data in Table 1, were subsequently used for calculating average molecular sizes of the tested lignosulfonates, as analyzed in the discussion section.

2.3 Zeta potential measurements

The zeta potential of hematite as a function of pH in 0.01 mol/L sodium chloride, and in the presence or absence of 0.001 mol/L calcium chloride, was measured through electroacoustics with the use of a Zeta Probe (Colloidal Dynamics, Warwick, RI, USA). A 10% (wt.) suspension of hematite—the same solids content as in subsequent adsorption experiments—was automatically titrated using 2 mol/L sodium hydroxide and hydrochloric acid solutions. A series of zeta potential measurements by potentiometric titration were also performed in the presence of the tested lignosulfonates. In this case, hematite was first conditioned at 20% solids in 0.01 mol/L NaCl (or in 0.01 mol/L NaCl + 0.001 mol/L $CaCl_2$) for 10 minutes. Afterward, the same volume of a 500 mg/L lignosulfonate solution in the background electrolyte was added to the hematite suspension to reach a solids content of 10%, and the entire mixture was mixed for a further 30 minutes. Thus, the final lignosulfonate concentration in these tests was 250 mg/L.

2.4 Adsorption measurements

For adsorption tests, 5 grams of hematite were first conditioned in a mechanical shaker for 10 minutes with 25 ml of a 0.01 mol/L sodium chloride solution with pre-adjusted pH, after which a lignosulfonate solution in the background electrolyte of known concentration and preset pH was added to the suspension, and the whole mixture was conditioned for a further 30 minutes in the shaker. Typically, several solutions of different lignosulfonate concentrations were tested at a given pH value. Afterward, the solids were separated from solution by centrifuging for 20 minutes at 10,000g, and the clear solution was assayed for the presence of lignosulfonates using a Cary-50 (Varian) UV-VIS spectrophotometer at a wavelength of 280 nm (Lin and Dence 1992). Blank corrections were taken for all samples by subjecting a suspension of hematite in a 0.01 mol/L sodium chloride solution (at a given pH, with or without 0.001 mol/L $CaCl_2$) to the shaking-centrifuging procedure, and measuring the absorbance of the resulting solution at 280 nm. The equilibrium concentration of lignosulfonate left in solution after adsorption was then read from a calibration curve prepared separately for each set of pH and ionic strength conditions, and the amount adsorbed was calculated from the difference between the initial (known) concentration and the equilibrium (measured) concentration. The BET surface area (corrected for the porosity of the sample) was then used to calculate the adsorption densities of lignosulfonates on the hematite surface.

3 Results and discussion

As for any polyelectrolyte, the molecular size and conformation of lignosulfonates in aqueous solutions are a function of pH and ionic strength. Since experiments with lignosulfonates described in this study were carried out over a range of pH values and in the presence or absence of calcium ions, it became necessary to first establish the effect of water chemistry on the behavior of lignosulfonates themselves, and then to assess the role of those conformational changes of the polyelectrolytes in the adsorption process. This objective was achieved through intrinsic viscosity measurements. As an example of data evaluation, Fig. 2 shows a set of the raw viscosity results for the D619 lignosulfonate plotted according to the Fedors equation, while Table 2 summarizes all the intrinsic viscosities of the tested lignosulfonates obtained through this extrapolation procedure.

For comparison with the above data, the intrinsic viscosities of the lignosulfonates measured in 0.1 mol/L NaCl (pH = 8–9) were 3.3, 3.0, and 3.2 mL/g for the D619, D648, and D750, respectively. The results obtained in 0.01 mol/L NaCl show that the intrinsic viscosities of the lignosulfonates increase with increasing pH. This result was actually expected, which is a typical response of anionic polyelectrolytes to pH changes, but it was the relative changes with pH and the effect of calcium that were of greater significance to this investigation.

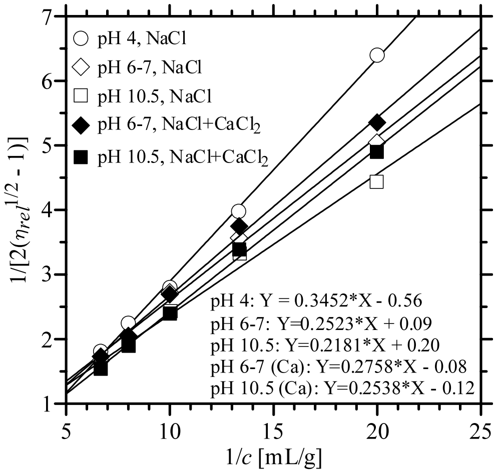

Fig. 2 An example of the graphical determination of the intrinsic viscosities of the D619 lignosulfonate with the use of the Fedors equation. Reciprocal slopes of the linear fits give the intrinsic viscosities (in mL/g) of the D619. Ionic strength: 10^{-2} mol/L NaCl with or without 10^{-3} mol/L $CaCl_2$

The intrinsic viscosities of the lignosulfonates from Table 2 were then used to calculate the equivalent Einstein radii of the macromolecules from the expression (Rezanowich and Goring 1960):

$$r_\eta = \left[\frac{30M_w[\eta]}{\pi N}\right]^{1/3} \tag{3}$$

where r_η is the radius of the equivalent Einstein sphere [cm], $[\eta]$ is the intrinsic viscosity [dL/g], M_w is the molecular weight (as calculated with (2)), and N is the Avogadro number. The resulting equivalent molecular diameters (calculated as $2r_\eta$) are summarized in Table 3.

Very similar values of the equivalent molecular sizes were also obtained using the diffusion coefficients of lignosulfonates reported by Kontturi and Kontturi (1987), and applying an equation described by the same authors in another contribution (Kontturi and Kontturi 1988).

Several trends should be noted in the data shown in Table 3. In the absence of calcium, increasing pH from 4 to 10.5 slightly increases the size of the macromolecules, but the relative change for a given lignosulfonate is rather small—about 20% for the D750, 17% for the D619, and only 7% for the D648. These changes are even less significant when one considers only the transition from pH 6.5–7 to pH 10.5. Such small changes are quite normal for polymers of compact spherical structures, but this overall trend is actually surprising since the D648 is most anionic and yet its relative expansion with increasing pH is the lowest among the tested reagents. As the degree of the dissociation of weakly acidic groups increases with pH, electrostatic repulsion between these negative charges on the macromolecule should stretch the chain into its most extended conformation characterized by a high intrinsic viscosity value. Along the same

Table 2 Intrinsic viscosities of lignosulfonates expressed in mL/g under different pH and ionic strength conditions

	in 10^{-2} mol/L NaCl			in 10^{-2} mol/L NaCl + 10^{-3} mol/L $CaCl_2$		
	pH 4	pH 6.5–7	pH 10.5	pH 4	pH 6.5–7	pH 10.5
D619	2.9	4.0	4.6	–	3.6	3.9
D648	2.6	3.1	3.2	–	3.1	2.7
D750	2.3	3.2	4.0	–	3.3	3.5

Table 3 Equivalent molecular diameters [nm] of lignosulfonates in solution under different experimental conditions

	in 10^{-2} mol/L NaCl			in 10^{-2} mol/L NaCl + 10^{-3} mol/L $CaCl_2$		
	pH 4	pH 6.5–7	pH 10.5	pH 4	pH 6.5–7	pH 10.5
D619	3.3	3.7	3.9	–	3.6	3.7
D648	2.9	3.1	3.1	–	3.1	3.0
D750	3.0	3.3	3.6	–	3.3	3.4

lines, the D750 and D619 are of comparable and low anionicity, but these polyelectrolytes exhibit the largest tendency to expand at higher pH. It appears that the high content of sulfonic groups in the D648 is sufficient to define the conformation of this reagent over a wide pH range, as if contributions from carboxylic groups were completely masked. It is also noteworthy that calcium has almost no effect on the expansion or contraction of a given lignosulfonate under the experimental conditions. All these observations allow an important conclusion to be drawn that the adsorption tests were carried out under the conditions of nearly constant molecular sizes. The intrinsic viscosity values also show that the small addition of divalent calcium does not result in binding of lignosulfonate macromolecules into larger complexes, which would be accompanied by a substantial increase in the intrinsic viscosity. It can therefore be reasonably assumed that variations in the adsorption behavior of a given lignosulfonate can primarily be attributed to differences in the type and magnitude of interactions between the lignosulfonate and the hematite surface, rather than due to changes in the size and conformation of the adsorbing polymer.

The effective molecular sizes in Table 3 were individually used for correcting the total specific surface area of hematite (8.8 m^2/g) for any internal pore surface areas that were not accessible to lignosulfonate adsorption. Depending on the lignosulfonate type and experimental conditions, the specific surface area correction was on the order of 25–40%. This fraction of the total area was contained within pores whose sizes (diameters) were smaller than the average lignosulfonate molecular sizes, and hence were not available for adsorption. The corrected, external, specific surface areas were then used for calculating the adsorption densities of the tested lignosulfonates. It should be noted that this surface area correction is based on the average equivalent molecular size of the tested lignosulfonates obtained from intrinsic viscosity data, and hence does not take into account the wide molecular weight (and size) distribution of the polyelectrolytes. Therefore, the obtained adsorption densities should still be treated with caution, although these values probably represent the best relative estimates of the true adsorption densities.

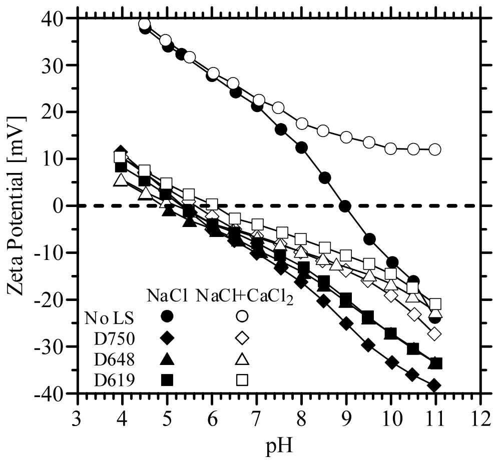

Fig. 3 The zeta potential of hematite in the presence and absence ("No LS") of lignosulfonates. Lignosulfonate concentration: 250 mg/L, ionic strength: 0.01 mol/L NaCl, or 0.01 mol/L NaCl + 0.001 mol/L $CaCl_2$

Figure 3 presents the results of zeta potential measurements in the presence and absence of lignosulfonates, and also with and without calcium in the system.

As can be seen from Fig. 3, the hematite sample has an isoelectric point (i.e.p.) just below pH 9. Although this i.e.p. value appears to be high for hematite, similar values were also reported in many other studies, as summarized by Kosmulski in a series of compilations of point of zero charge and isoeletric point data for oxides (Kosmulski 2009).

A lignosulfonate concentration of 250 mg/L in the adsorption tests would usually produce the highest adsorption points on any of the adsorption curves in Figs. 4 through 6. In some cases (pH 10.5), this level of lignosulfonate in so-

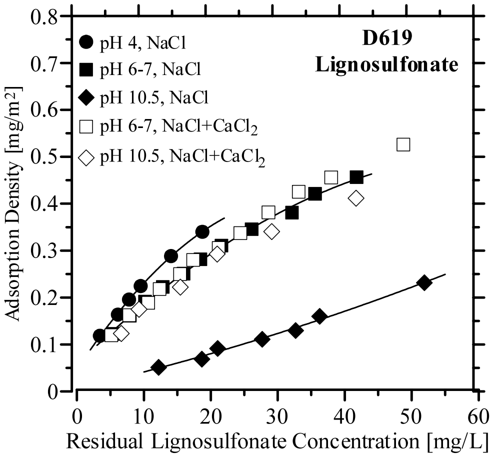

Fig. 4 Adsorption of the D619 lignosulfonate on hematite under different pH and ionic strength conditions. Ionic strength: 0.01 mol/L NaCl, or 0.01 mol/L NaCl + 0.001 mol/L $CaCl_2$

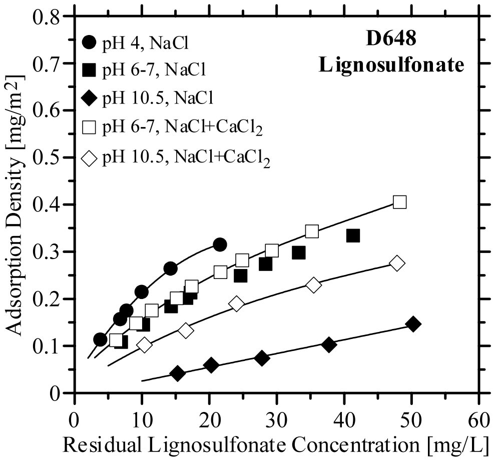

Fig. 5 Adsorption of the D648 lignosulfonate on hematite under different pH and ionic strength conditions. Ionic strength: 0.01 mol/L NaCl, or 0.01 mol/L NaCl + 0.001 mol/L $CaCl_2$

lution would actually be equivalent to adsorption and residual concentration values beyond the range shown in those figures. In other words, the zeta potential data in Fig. 3 reflect the conditions of very high lignosulfonate adsorption under a given set of pH and ionic strength conditions, in some cases even higher than the adsorption results shown in the subsequent sections.

In the absence of lignosulfonates, the addition of a small amount of calcium does not affect the zeta potential values below pH 8–8.5, but at pH above the i.e.p. the hematite surface becomes positively charged in the presence of 10^{-3} mol/L calcium chloride. This type of response shows that calcium starts specifically adsorbing on the hematite surface as the pH increases above the i.e.p., but it acts like an indifferent ion in the lower pH range.

All three lignosulfonates shift the position of the i.e.p. towards more acidic values, with the D648 producing the largest change from pH 9.5 to pH 4.9 which is consistent with the most anionic character of this lignosulfonate. Interestingly, both the D619 and D750 give i.e.p. values of 5.3 in the absence of calcium, and these two reagents are of similar anionicity judging from the amount of sodium in the samples and from the combined content of carboxylic and sulfonic groups. These rather dramatic changes in the zeta potential of hematite in the presence of lignosulfonates are a result of lignosulfonate adsorption within the compact (Stern) layer of the electrical double layer around the hematite particles. In the presence of calcium, the i.e.p. values slightly shift back towards more alkaline values: from 5.3 to 6.1 for the D619, from 5.3 to 5.7 for the D750, and from 4.9 to 5.2 for the D648. It is quite evident that the two curves for a given lignosulfonate in the presence and absence of calcium tend to overlap at lower pH values, but they differ much more substantially under alkaline conditions. These results indicate that the relative effect of calcium on lignosulfonate adsorption is much more significant under alkaline conditions. It should also be observed that even in the absence of calcium, the tested lignosulfonates make the zeta potential of hematite more negative at pH values higher than the pH of the i.e.p., when electrostatic repulsion between the anionic lignosulfonates and the negatively charged hematite surface should prevent lignosulfonate adsorption. This result immediately shows that lignosulfonate adsorption through specific non-electrostatic interactions substantially contributes to the overall adsorption process on the hematite surface.

Figures 4, 5 and 6 show the adsorption densities of lignosulfonates under different conditions for the D619, 648, and D750, respectively. In all three figures the same axis scales were used to highlight any similarities and/or differences between the various sets of results.

The adsorption densities of the lignosulfonates are low and quite similar at pH 10.5 in 0.01 mol/L NaCl. These adsorption densities indicate the magnitude of non-electrostatic interactions between lignosulfonates and the negatively charged hematite surface. Electrostatic repulsion is not capable of preventing adsorption of even the most anionic lignosulfonate. The nearly linear shape of the adsorption curves suggests that a low affinity type of adsorption of lignosulfonates takes place on the negatively charged hematite surface. It can still be noted that the most anionic reagent (D648) gives the lowest adsorption density at pH 10.5, while the other two lignosulfonates (D619 and D750) adsorb in slightly higher amounts.

At pH 4, when only the sulfonic groups of the lignosulfonates are still fully dissociated and the macromolecules become least charged under such acidic conditions, adsorption inversely correlates with the content of sulfonic groups. The D750 is characterized by the lowest amount of sulfonic groups (2.7%), and this reagent gives the highest adsorption density at pH 4 on the hematite surface. The D619 and D648

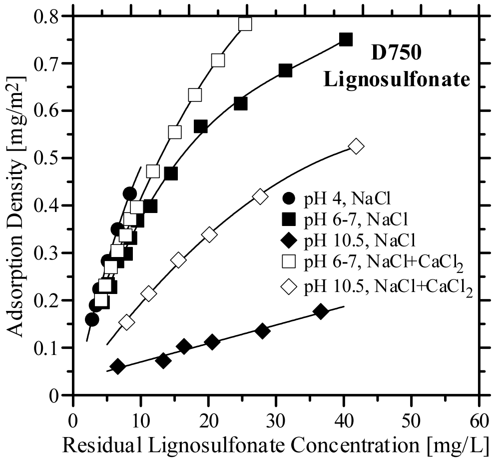

Fig. 6 Adsorption of the D750 lignosulfonate on hematite under different pH and ionic strength conditions. Ionic strength: 0.01 mol/L NaCl, or 0.01 mol/L NaCl + 0.001 mol/L $CaCl_2$

lignosulfonates, with the respective sulfonic group contents of 6.0% and 8.1%, give much lower adsorption densities.

Another important observation is that as the dissociation of the carboxylic groups of lignosulfonates increases with increasing pH and effectively makes the macromolecules even more anionic, the adsorption densities at pH 6–7 for a given lignosulfonate measurably decrease with respect to the adsorption levels found at pH 4. It is fair to assume that electrostatic attraction between hematite and lignosulfonates dominates the adsorption process at pH 6–7. At the same time, it is important to note that adsorption is higher under conditions when the surface is highly positively charged while the macromolecules are only weakly anionic (pH 4) which suggests that electrostatic attraction between the polymers and the surface is not the only adsorption mechanism operative at pH 4.

3.1 Role of calcium ions in lignosulfonate adsorption

It can be seen from Figs. 4 through 6 that the adsorption densities generally increase in the presence of Ca, with the relative changes in the amounts adsorbed being most pronounced at pH 10.5. Interestingly, the hematite surface is positively charged at pH 10.5 in the presence of Ca which should facilitate the adsorption of the anionic polyelectrolytes, and yet, as the degree of anionicity changes in the order D750 $\approx$ D619 $<$ D648, the amount of lignosulfonates adsorbed decreases in the same order. It is very significant to stress that the adsorption densities at any of the tested pH values, in the presence or absence of Ca, always follow the same trend: the D750 gives the highest adsorption levels, then the D619, and finally the D648.

It is noteworthy that calcium does not have an activating effect of the same magnitude on lignosulfonate adsorption at neutral pH 6–7 as it does at pH 10.5. The chemical affinity of calcium cations can be expected to be much higher towards the carboxylic groups of lignosulfonates than towards sulfonic groups. Calcium carboxylates are generally of much lower solubility in water compared to the solubility of calcium sulfonates, which is often utilized in selective precipitation and fractionation of lignosulfonates. Therefore, it could be expected that calcium should strongly interact with the lignosulfonates that contain a large amount of carboxylic groups, or with the D648 and D750 reagents among the studied polyelectrolytes, and for these reagents the impact of calcium on adsorption should be most pronounced. However, this potential interaction between calcium and carboxylic groups at pH 6–7 does not manifest itself in the experimental results: lignosulfonate adsorption is very weakly affected, the molecular sizes of the polyelectrolytes do not change, and there is no dramatic effect of Ca on the zeta potential of hematite (at pH 6–7) with or without lignosulfonates. It could also be hypothesized that if interactions of calcium cations with the carboxylic groups of lignosulfonates resulted in formation of permanent calcium-lignosulfonate bonds then any such binding or blocking of the anionic groups should decrease lignosulfonate adsorption on positively charged hematite at pH 6–7—assuming that carboxylic groups participate in the adsorption process on the oppositely charged surface. However, as the results indicate none of the polyelectrolytes exhibits a decrease in adsorption at pH 6–7 as a result of calcium addition, and the D750 actually shows a marked increase in adsorption in the presence of calcium.

Along the same lines, the degree of the dissociation of carboxylic groups should not significantly change with pH in the pH range from about 6.5 to 10.5 (assuming a pK_a value of 4.8 for carboxylic groups), and only about 0.7% of the total amount of calcium is converted into the calcium-hydroxyl complex ($(Ca(OH)^+)$) at pH 10.5. Therefore, it is reasonable to assume that the extent of chemical interactions between calcium and lignosulfonates at pH 10.5 is more or less the same as that at pH 6–7. Admittedly, the content of phenolic groups ($pK_a = 10.5$) in the tested samples is not known so their contribution to the anionicity of the reagents cannot be assessed. It may however be noted that increasing the pH from 6 to 10.5 does not markedly affect the effective sizes of the macromolecules, so at least the contribution of phenolic groups to polyelectrolyte expansion is not significant.

Overall, the results suggest that calcium does not directly affect the anionic macromolecules in any significant way, either by changing their molecular sizes or by binding functional groups through chemical interactions. It appears that the effect of calcium ions on lignosulfonate adsorption is primarily related to changes in the charging characteristics of the hematite-solution interface.

The apparent lack of strong interaction between calcium and lignosulfonates also brings out the question of how significant are the roles of the different functional groups of lignosulfonates in the mechanism of the adsorption process. If carboxylic groups do not strongly react with calcium in solution, then it also becomes hard to envisage any enhanced adsorption due to chemical interactions between the carboxylic groups of lignosulfonates and calcium adsorbed on the hematite surface at pH 10.5. From this point of view, interesting data have recently been reported by Wiśniewska et al. (2009) who observed desorption of calcium cations from a weakly negatively charged alumina surface upon adsorption of polyacrylic acid, which is not quite consistent with the often-presumed "anchoring" role of calcium ions on the adsorbent surface in adsorption of anionic polymers. Electrostatic interactions alone resulting from this surface charge reversal by calcium do not fully describe the results either. Using the magnitude of the zeta potential as a measure of the charging density of the hematite surface, it could be argued that the adsorption density at pH 10.5 in the presence of Ca should be lower than the adsorption density at pH 6–7 with Ca in the system. This line of reasoning seems to hold true for the D750 and D648 lignosulfonates, but not for the D619. In the case of the D619, the adsorption density at pH 10.5 in the presence of Ca is nearly as high as that at pH 6–7. Although this observation could be a coincidence, the D750 and 648 lignosulfonates have the same relatively high content of carboxylic groups, while the amount of these groups in the D619 is much lower.

It is intriguing to observe that all the presented adsorption results inversely correlate with the sulfonate group content in the tested reagents irrespective of whether carboxylic groups are ionized or not. The other lignosulfonate properties from Table 1 do not give such clear trends in the data. The absolute adsorption densities are the highest for the D750 lignosulfonate regardless of pH and ionic strength, followed by the D619, and the D648. Therefore, the presence and concentration of sulfonic groups seems to be of primary importance in defining the adsorption behaviour and anionicity of lignosulfonates. The results clearly show that it is the less anionic lignosulfonates D619 and D750 that generally give higher adsorption densities under all conditions, while the highly anionic character of the D648 seems to interfere with the adsorption of this reagent on the hematite surface even when the surface is positively charged. These observations strongly suggest that lateral electrostatic repulsion between the anionic macromolecules on the surface prevents dense adsorption on hematite. As lignosulfonate adsorption progresses, the hematite surface becomes more and more negatively charged thus bringing about stronger repulsion between the surface and approaching anionic macromolecules. The extent of this effect is not easy to quantify based on the experimental data since none of the adsorption curves reached saturation levels or adsorption plateaus under the experimental conditions. Simple geometrical calculations using the equivalent molecular sizes, specific surface areas, and a packing factor of 0.78 suggest that maximum adsorption densities at a monolayer coverage could be expected to be on the order of 1.5–1.9 mg/m^2 for the different reagents, which highlights how scarce is the adsorption of the D648 reagent in comparison to the D750.

If such lateral interactions between lignosulfonate molecules were primarily responsible for the observed adsorption levels, then the adsorption-enhancing role of calcium could be to diminish these repulsive forces by screening the anionic acidic groups. Indirect evidence of such a mechanism can actually be seen in the zeta potential data at pH 10.5. By comparing the zeta potential curves for the different lignosulfonates with or without calcium, it can be found that the addition of calcium makes the zeta potential values less negative—much more so at pH 10.5 than at pH 6–7. This result suggests that calcium partially neutralizes the negative charges originating from the anionic functional groups of lignosulfonates. As the preceding discussion implies, this interaction between calcium and the anionic groups is most likely of weak electrostatic nature, but it is sufficient to screen these groups and to minimize electrostatic repulsion between them. In essence, the effect of calcium is very similar to the effect of low pH on lignosulfonate adsorption. In both cases minimizing the influence of the anionicity of the macromolecules increases their adsorption on hematite.

4 Conclusions

Intrinsic viscosity measurements showed that the tested lignosulfonates did not substantially change their molecular sizes as a result of pH adjustments or calcium addition. Therefore, the effect of conformational changes of the macromolecules on adsorption was negligible under the experimental conditions.

The adsorption of lignosulfonates on hematite shows features that could be expected from anionic polyelectrolytes. The adsorption density of each lignosulfonate increased when the hematite surface became positively charged at pH values below the i.e.p. of the hematite sample. On the other hand, the amount of lignosulfonates adsorbed was lowered under alkaline conditions when the hematite surface was negatively charged. However, a comparison of the adsorption data obtained for lignosulfonates of different contents of anionic functional groups revealed that the less anionic reagents actually produced higher adsorption densities than the more anionic types under any of the tested pH and ionic strength conditions. This result was primarily attributed to lateral electrostatic repulsive interactions between the polyelectrolytes which prevented dense adsorption of the highly charged macromolecules. It was also found that the amount of lignosulfonates adsorbed decreased with the content of sulfonate groups in lignosulfonates, while other properties of the tested polymers did not clearly correlate with the adsorption results. This observation suggests that manipulating the content of sulfonic groups could be a way of controlling the adsorption behavior of lignosulfonates.

Calcium enhanced lignosulfonate adsorption only at pH values above the i.e.p. by specifically adsorbing on the hematite surface and reversing the surface charge from negative to positive. The adsorption data suggested that the role of calcium was not limited to creating favourable conditions for electrostatic attraction between lignosulfonates and the oxide surface. The screening of the anionic groups of the polyelectrolytes and hence reduction of lateral repulsive interactions was also a substantial contributing factor.

Overall, electrostatic attraction (or repulsion) was an important adsorption mechanism although substantial contributions from non-electrostatic interactions were also evident.

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