

Interactions between lignosulphonates and the components of the lead-acid battery

Part 1. Adsorption isotherms

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Abstract

The expander performs at least five different tasks in the battery. It is a fluidiser for the negative paste. It controls the formation stage of the battery. It controls the shape and size of the lead sulphate crystals formed upon discharge, and thus prevents the sintering of the active mass. It controls the rate of the lead to lead sulphate oxidation during discharge. Finally, it affects the charge acceptance.

To gain more understanding of these different effects the interaction between lead, lead(II) oxide, lead(IV) oxide, lead sulphate, barium sulphate and carbon black and the experimental lignosulphonate (LS) expander UP-414 has been investigated. We also compared with Vanisperse A and several other lignosulphonates, to elucidate the mechanisms operating. In most cases, we have studied concentration ranges that are both higher and lower than those normally encountered in batteries.

There is no adsorption of lignosulphonates to pure lead surfaces. Adsorption to lead sulphate is a slow process. In the presence of lead ions lignosulphonates will also adsorb to lead. The adsorption to lead(II) oxide is a fast process, and a strong adsorption occurs. In all these cases, it is preferably the high molecular weight fraction that interacts with the solid surfaces. Lead ions leaching from the surface complexes with lignosulphonates to give a more hydrophobic species. This allows the normally negatively charged lignosulphonate to adsorb to the negatively charged substrates.

The lignosulphonates have an ability to complex lead ions and keep them solvated. This confirms previous observations of the lignosulphonates ability to promote the dissolution–precipitation mechanism for lead sulphate formation on the expense of the solid-state reaction.

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1. Background

Expanders are used in lead-acid batteries to improve the performance of the battery [1,2]. Typically, a few tenths of a percent is added together with carbon black and barium sulphate. In this work we will refer to the organic part as the expander, although sometimes the lignosulphonate (LS), carbon black and barium sulphate taken together is called the expander.

The expander greatly improves the performance of starter, lightning and ignition (SLI) batteries. The cold cranking ability is greatly improved, and the life time of the battery several times longer than without the expander. Many natural and synthetic organic compounds have been used

for this purpose [1]. Lignosulphonates have proven to be very well suited as expanders [1–3].

The main function of the lignosulphonates seems to be the regulation of the crystal growth of lead particles [1,4–7]. During formation of the battery the lignosulphonates influence the ratio of tri basic and tetra basic lead sulphate, which consequently determines the amount of energetic structures and skeleton structures in the active mass [8].

The expanders also influence the size and shape of the lead sulphate particles formed during discharge [1,2,4,9–12].

For many years the positive plates have been the limiting element in lead-acid batteries. The drive to improve the negative plate, and hence also the negative expander, has thus been limited. Recent new designs have improved the positive plates greatly [13], and there is now also a strong interest in improving the negative plate performance. At the

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same time new technologies like the valve regulated lead-acid battery (VRLA) might put other requirements on the negative plates and expanders.

Emerging new uses for batteries like electrical vehicles (EV), or hybrid electrical vehicles (HEV), remote area power supplies (RAPS), and stand-by power for telecommunications also use very different charging and discharging cycles from the SLI batteries. There has thus also been an interest in tailor making negative expanders for different applications. Particularly an increased cycle life time of the battery has been of interest.

Better charge acceptance is also of great interest, both in connection with fast charging for EV applications, and to increase the trough-put in battery manufacturing.

One of the main obstacles for improving the expanders have been a good and detailed understanding of how they actually function in the battery. There have been several attempts to relate specific functional groups in the expander to the electrical performance of the complete battery (see [14,15] and references cited therein). So far, this problem seems to be too difficult to handle. This is probably due to the inherent uncertainties in both the analytical measurements for the expanders and the electrical measurements of the batteries [16]. The lignosulphonate expanders also have a large polydispersity, and the different molecular weight fractions will have somewhat different compositions. In addition to the many functional groups present in the expanders, there are also several compounds present in the battery. The amount of each is continuously changing during charge and discharge. The expander will interact with each of these compounds in different manners. In this work, we will look at the adsorption isotherms for the interactions between the lignosulphonates and the solid substrates. There are some isotherms for the interactions between lignosulphonates and lead or lead sulphate already described in [17], however this work is now fairly old, and neither the lignosulphonate nor the substrates are fully characterised. Although most of the work described here is performed with UP-414 where relevant we will also include other expanders in the discussion.

2. Experimental

2.1. Adsorption isotherms

Adsorption to lead, lead(II) oxide, lead sulphate, lead(IV) oxide, barium sulphate, and carbon black were investigated. 10 ml of the lignosulphonate solution (200, 2500 or 5000 ppm) was added to known amount of the substrates. The samples were shaken for the desired time on a Labinco Rock'n'Roller. The solid substrates were filtered off through a 0.22 μm Millipore filter. The liquid phase was diluted with NaOH solution to give a pH >12 and a known dilution. The total amount of lignin was determined using UV

spectroscopy and comparing with references of known concentrations. For most of the samples, the adsorption band at 280–282 nm was used. The UV-spectra of lignins show pH dependent extinction coefficients, it is thus necessary to compare all samples at sufficiently high pH. The adsorbed amount is calculated as the difference between the total amount added and the amount left in solution. The adsorption per gram of substrate is then calculated from the known amount of substrate used. During the filtration process, we might loose a little lignosulphonate particularly at low pH. The maximum amount lost is $\sim 2\%$ of the lignosulphonate in solution.

For the carbon black substrate, an extra filtration step after the pH adjustment was needed as some of the solid material passed through the 0.22 μm filter. After two filtrations the solutions showed no turbidity, and gave good adsorption isotherms.

For many of the samples, we also determined the molecular weight distribution after the adsorption, this gives additional important information about which fraction of the lignosulphonates that adsorb to the substrate.

2.2. Molecular weight distribution

Molecular weights were determined on a Jordi Glucose DVB 10,000 \AA column. The mobile phase consisted of 10% DMSO in water buffered to pH 10.5 with a sodium hydrogen phosphate buffer and 0.1% SDS added. A spectra system AS3500 sampler, P4000 pump, and UV2000 detector were used. The software allows the calculation of the different molecular weight averages (M_n , M_w , M_z and M_{z+1}) as well as polydispersity. The molecular weights are given relative to two in-house standards with M_w of 68,000 and 8300 Da, respectively. The relative values of the different lignosulphonate fractions are accurate to ± 2000 Da, while the absolute values depend on the accuracy of the standards. For the purpose of this study, the absolute molecular weights are of less importance.

2.3. Particle size distribution

The particle size distributions of the substrates were determined on a Microtrack X100 particle size analyser. Water was used as the fluid carrier. Each result is the average of three measurements. The suspensions were dispersed by ultrasound for 60 s before measurements.

2.4. Zeta-potentials

Zeta-potentials of the substrates were determined in buffer solutions of acetic acid and potassium dihydrogen phosphate ($\sim 1 \times 10^{-3}$ M of each), 0.1 M sodium chloride was added to give the same ionic strength in all solutions. Final pH adjustments were done with addition of sulphuric acid or sodium hydroxide. 22.0 ± 0.5 mg of the substrates were added to 50 ml buffer solutions and dispersed by

Table 1
The properties of the substrates used in this study

| Substrate | Surface (m ² /g) | Diameter (μm) | | | Isoelectric point | Zeta- potential, pH 7 |
|-------------------|--------------------------------|----------------------|----------------------|----------------------|----------------------|-----------------------------|
| | | <i>r_n</i> | <i>r_a</i> | <i>r_w</i> | | |
| Pb | 0.0794 | 0.359 | 3.346 | 10.19 | <1 | −30.2 |
| PbO | 0.266 | 0.154 | 1.184 | 7.274 | <1 | −31.6 |
| PbSO ₄ | 0.304 | 0.338 | 1.591 | 20.75 | <1 | −16.4 |
| PbO ₂ | 0.198 | 0.162 | 1.615 | 7.481 | <1 | −35.2 |
| BaSO ₄ | 0.474 | 0.553 | 1.508 | 3.127 | | |

ultrasound. The potentials were measured on a Malvern Zetasizer 4. Three replicate suspensions were made of each solution. Each suspension was injected three times and three measurements were performed on each injection. Each measurement again being the average of three raw data points.

2.5. UV-spectra

UV-spectra were recorded at a Perkin-Elmer Lambda 2S UV-Vis spectrophotometer.

2.6. Chemicals used

Sulphuric acid was a technical grade supplied by Borregaard Basis Chemicals. All other chemicals were of analytical grade.

Lead (batch no. 354781/1 40797, and lead sulphate (batch no. 383245/1 30499) were from Fluka. Lead oxide (batch no. B08 G33) was from Alfa. Barium sulphate (no. 19970707) was delivered by Kebo Lab. The carbon black used was Cabot Elftex 460. Lead(IV) oxide (no. K25659/07 920), sodium sulphate, sodium dihydrogen phosphate, potassium chloride, sodium hydroxide, and acetic acid were all from E. Merck. Ammonium hydroxide (25% solution) was from J.T. Baker.

For each of the substrates, only samples from one batch were used to avoid the problems with any batch to batch variations in the particle size distribution.

2.7. Characterisation of the substrates

Table 1 summarises the properties of the substrates.

The zeta-potentials are negative over the whole pH range studied. They are less negative at low pH. The lead sulphate shows much less variation than the other substrates. The curves of zeta-potential versus pH lead and lead oxide behave very similar. This is probably due to a thin oxide layer passivating the lead particles. We will call the lead particles with the oxide layer for native lead, while lead particles washed twice with ammonium acetate solution and twice with deionised water to remove any lead(II) salts will be called pure lead.

3. Results

3.1. Adsorption to lead

Lead is an important part of the negative plate. The collecting skeletal structure will be present both in the charged and discharged state. In the charged state, we will also have the energetic structure with a greatly increased lead surface. We thus investigated the interactions between lead and the lignosulphonates in some detail.

Some lead was washed twice with ammonium acetate solution at pH 6 to remove all lead(II) salts and then twice with ten times the volume of deionised water. This pure lead particles were investigated without drying to avoid any re-oxidation. Even after 168 h a maximum of 0.5% of the lignosulphonate was removed when 1.50 g lead was in contact with 20 ml of a 2500 ppm lignosulphonate solution. This is of the same order as that lost during the filtration.

Insufficient washing of the pure lead gave very fast adsorption of the lignosulphonate to the lead. This is probably due to the lead acetate being present and providing a ready source of lead ions.

Lead (1.50 g) and 0.10 g lead acetate in acetic acid was mixed with 20 ml 2500 ppm lignosulphonate solution. The solution was clear in 1.5 h. However, this time the lead particles are uncovered by any lignin, instead there is, after settling, a layer of lead–lignosulphonate on top of the settled lead particles.

The results that are described in the remainder of this work are with native lead particles covered with a thin oxide layer. As we will show this oxide layer will dissolve and have a strong influence on the adsorption mechanism. We believe that it is more relevant for the battery applications to compare with this oxide-covered surface than with the cleaned pure lead surface. In batteries, there will always be enough lead ions present to influence the adsorption.

3.1.1. Time effects

The adsorption of lignosulphonates to pure lead does not take place. The adsorption to native lead is a slow process. Fig. 1 shows how the high molecular weight fraction is removed first. We see that the removal is a slow process. On the other hand, as the ionic strength of the solution increases the adsorption process is much faster. As can be seen in Fig. 2, the addition of sodium sulphate increases the adsorption considerably.

UP-414 has a fairly high molecular weight ($M_n = 6700$ Da, $M_w = 51,000$ Da). We find that highest molecular weight fractions are removed first, while the lower weight fractions stay in solution. Vanisperse A has a much lower molecular weight ($M_n = 5700$ Da, $M_w = 14,000$ Da), in fact almost all the species in Vanisperse A are smaller than those that adsorb when UP-414 is in contact with lead. Nevertheless, we find that Vanisperse A adsorbs to about the same degree as UP-414 as determined by UV spectroscopy.

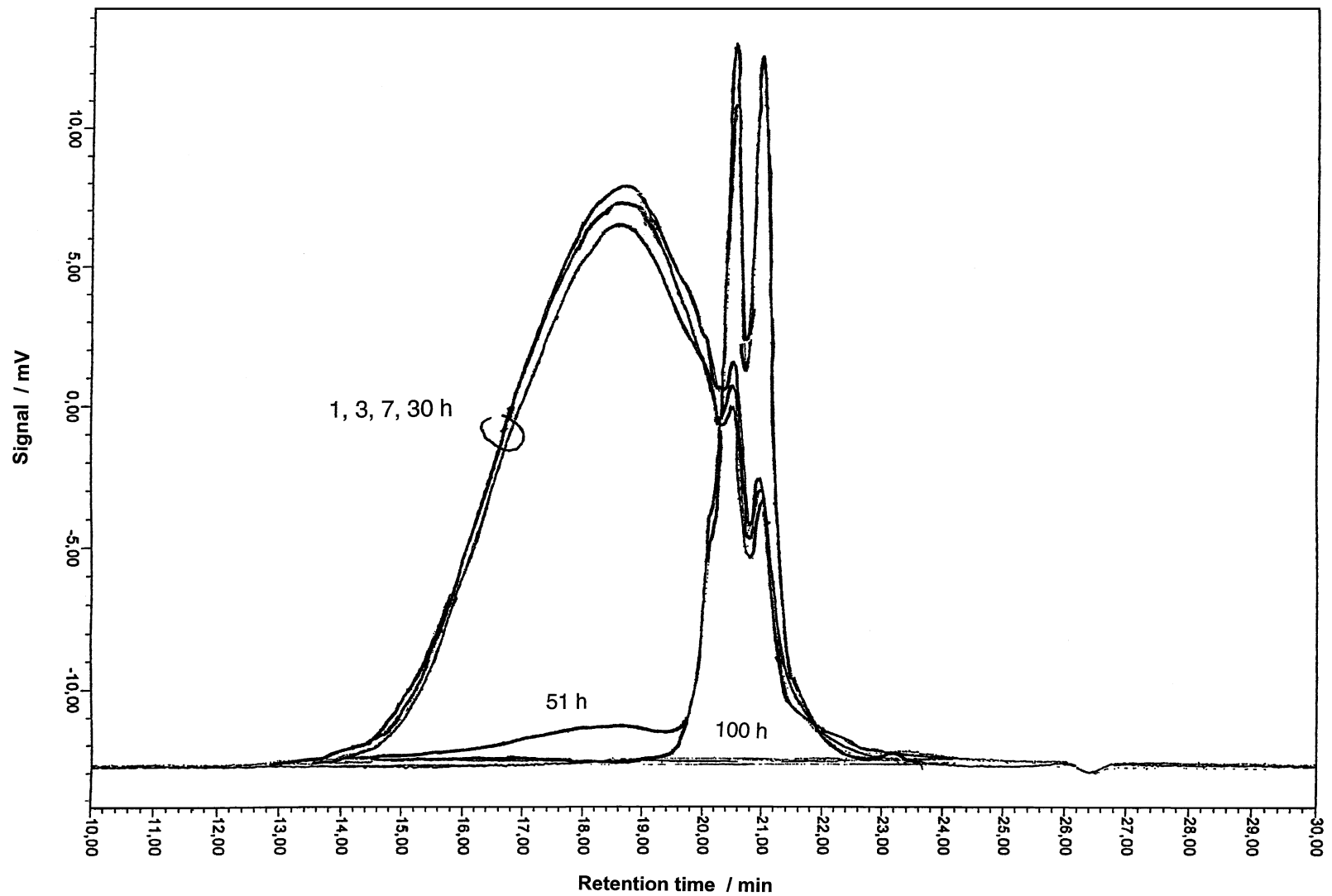


Fig. 1. A chromatogram showing the molecular weight distribution of the fraction remaining in solution for adsorption of UP-414 onto lead.

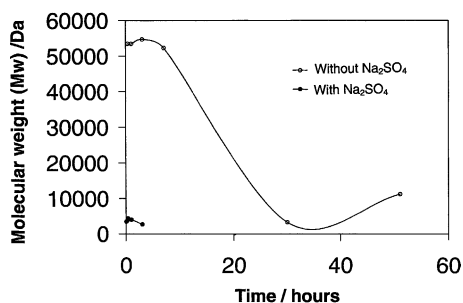


Fig. 2. The weight average molecular weight of the fraction remaining in solution for UP-414 in the presence and absence of sodium sulphate. In the presence of sodium sulphate the adsorption is fast, while in its absence the adsorption is slow.

For Vanisperse A it is also the highest molecular weight fractions that adsorb first.

The adsorption to native lead can be speeded up considerably by adding a drop or two of acetic acid (we did this in the form of acetic anhydride). Acetic acid will dissolve any lead salts present. It probably dissolves a thin lead oxide coating on the surface of the lead particles and releases lead ions into the solution much faster than with the ordinary dissolution of lead oxide.

3.1.2. pH effects

Fig. 3 shows the amount of lignosulphonate left in the solution for adsorption to native lead substrates at three different pH values. We see that at lower pH there is more material left in the solution. The adsorption to lead is less efficient at low pH. Interestingly the sulphuric acid is weakest when the battery is discharged. This is when the lignosulphonate interact strongest with the lead substrate. As the battery is charged, the sulphuric acid concentration increases and the interaction between lead and lignosulphonates becomes weaker. Fig. 4 shows clearly that the transition between the complete adsorption and the partial adsorption is pH dependent.

We would expect the dissolution of the lead oxide layer to be fastest at low pH. Thus, more lead should be released into the solution. On the other hand, a higher acid concentration also means more sulphate ions. The equilibrium concentration of lead ions should thus be lower. These

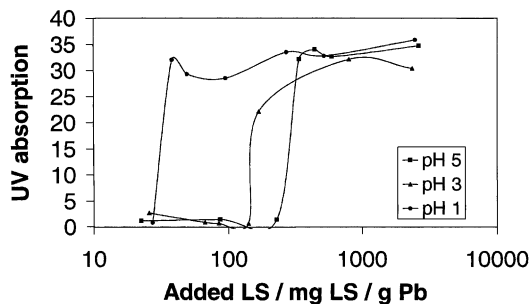


Fig. 3. The adsorption of UP-414 onto lead particles for three different pH levels.

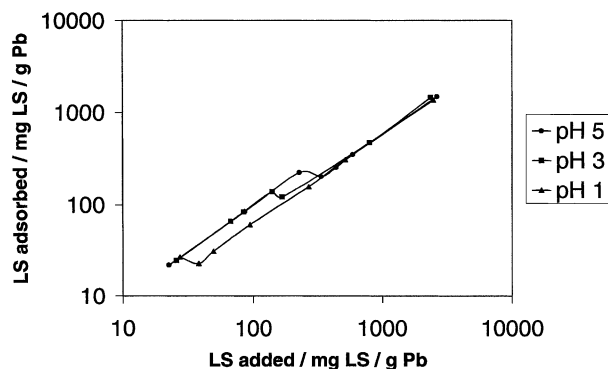


Fig. 4. The pH dependent transition from the full to partial adsorption of the lignosulphonates.

two mechanisms will act in opposite directions. As we will see in Section 3.1.3 adding sulphate without changing the pH will promote the adsorption. Lower adsorption at low pH must thus mean less interactions between the lead ions and the lignosulphonate. This is due to the protonation of lignosulphonates at low pH. At low pH the phenolic hydroxyl and carboxylic acid groups are protonated, and thus less available for reaction with lead ions. The sulphonic acid groups will also be partially protonated at low pH. As will be shown elsewhere [18] it is the reaction with the sulphonic acid group that renders the lead–lignosulphonates insoluble.

It has previously [17] been found that the adsorption of lignosulphonates to lead was essentially the same in 1.09 and 1.30 s.g. sulphuric acid. These sulphuric acid concentrations are so high that the pH is well below 1 in both cases.

3.1.3. Salt effects

When the pH is lowered by adding more sulphuric acid, the ionic strength of the solution is increased as well. To try to separate the pH effect from the effect of the ionic strength, some experiments with added sodium sulphate were performed. Lead sulphate is sparingly soluble. Adding sodium sulphate should thus push the equilibrium to give less lead ions in the solution. The reaction between lead ions and the lignosulphonates should thus be suppressed to some extent. Adding sodium sulphate ought to suppress the formation of the lead–lignosulphonate complex. It has also been shown that the sulphate ion adsorbs to lead surfaces [19]. This could displace some of the lignosulphonates and give a lower adsorption.

Fig. 5 shows the adsorption of UP-414 to lead in the presence of sodium sulphate at different concentrations. As can be clearly seen the removal of the lignosulphonates is fast and efficient. Extending the equilibrium time to 1 or 3 h will not lead to more adsorption than for 20 min equilibrium time. Lowering the pH will not force more material out of the solution, either. On the other hand, we should note that the 0.2 M sulphate is a higher concentration than we can expect in sulphuric acid. The pK_{a2} of sulphuric acid is 1.92. This means that there will not be more than 0.015 M

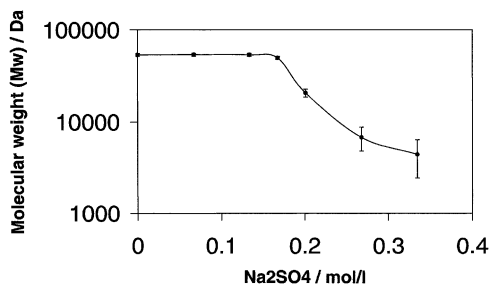


Fig. 5. The weight average molecular weight of the fraction remaining in solution for UP-414 in the presence of varying concentrations of sodium sulphate. For the highest sodium sulphate concentration the time and pH has also been varied.

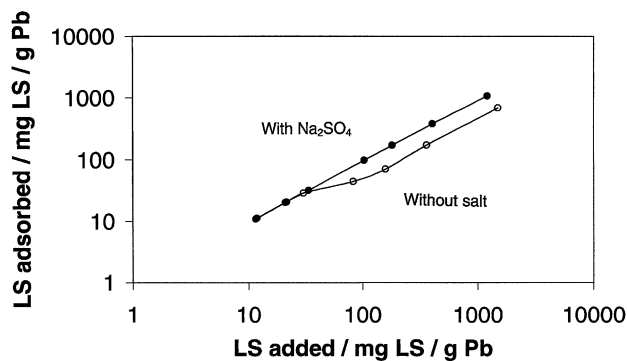


Fig. 6. The adsorption of UP-414 to lead particles in the presence and absence of sodium sulphate.

sulphate even at the lowest pH, due to the $\text{SO}_4^{2-} + \text{H}^+ = \text{HSO}_4^-$ equilibrium.

Fig. 6 compares the adsorption with and without added sodium sulphate. We see that with added salts nearly all the lignosulphonate is adsorbed irrespective of the amount added. This behaviour is in marked contrast to the one we find with lowered pH. At the lowest pH, e.g. highest ionic strength, the least amount of lignosulphonates are adsorbed. We can thus see clearly that a high ionic strength favours the precipitation of the lignosulphonates through a salting out mechanism. Na_2SO_4 is a very efficient salt for salting out. The lignosulphonates are probably already made more hydrophobic by interaction with the lead ions.

There is a strong influence of the amount of sodium sulphate added. The more sodium sulphate we add the less lignosulphonate remains in the solution. The molecular weight of the remaining lignosulphonate is also lower. This is shown in Fig. 5. We also see that there are only small changes if we increase the time for the highest addition rates of sodium sulphate.

We find that the lignosulphonates readily adsorb to the native lead particles. The adsorption is strong and a thick layer might form. In fact, it seems more like precipitation on a solid surface than like ordinary adsorption. However, in practical use in lead-acid batteries there is rarely more lignosulphonate present than that required to give a monolayer coverage.

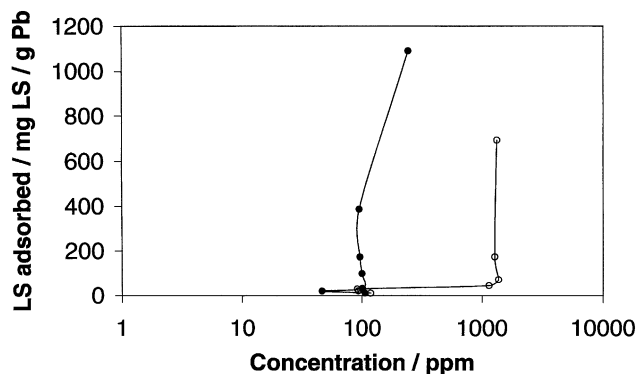


Fig. 7. Adsorption isotherms for UP-414 on to lead particles. The amount of lead has been varied while the concentration of UP-414 is 200 ppm (filled circles) or 2500 ppm (open circles).

3.1.4. Isotherms

Fig. 7 shows a plot of the adsorbed amount (in mg LS/g Pb) as a function of the concentration left in solution. This should be a true isotherm, but it is clearly not. We have worked with two different stock solutions, and varied the amount of lead. The two stock solutions were 200 ppm (filled circles) and 2500 ppm (open circles), respectively. Similar isotherms have been observed previously [17], and was taken as a sign of multilayer adsorption. A multilayer adsorption has also been concluded from capacitance measurements on the electrodes [12].

We see for both initial concentrations that the amount left in solution is very close to half the original concentration. In Fig. 8, the data are replotted, and two more series of experiments are added (one for each concentration of the lignosulphonate solution). What we find is two different behaviours. At low addition rates (less than 30–60 mg LS/g Pb) the amount adsorbed is the same as the amount added. At higher additions half the material is adsorbed, while the other half stays in solution. The amounts normally used in batteries is 0.1–0.5%, this is equivalent to 1–5 mg LS/g Pb, e.g. in batteries we would expect all the lignosulphonates to be adsorbed to the lead surfaces.

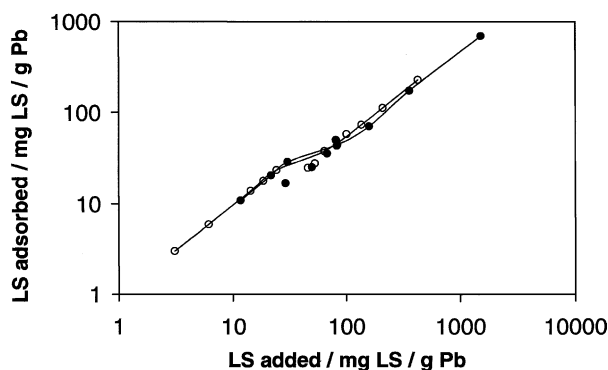


Fig. 8. Adsorption of UP-414 on to lead particles. The amount of lead has been varied while the concentration of UP-414 is 200 ppm (filled circles) or 2500 ppm (open circles).

From the specific surface areas of the lead ($0.0794 \text{ m}^2/\text{g}$) and the estimated foot-print of the lignosulphonate monomer (0.96 nm^2) we can calculate that 0.025 mg LS/g Pb should be enough to cover the surface. The amount found in Fig. 8 is three orders of magnitude larger. This could mean that the lead surface is pitted in some ways. It is also claimed that the lead easily corrodes [17], and thus any estimate of the surface is uncertain. In our case, it seems obvious that the lead surface is covered by a thin oxide layer that is easily corroded.

The adsorption of lignosulphonate to lead seems to be a two-stage process. Lead ions leached into the solution, either from the dissolution of the thin oxide layer or, very slowly, from corrosion of the lead particles, will complex with the lignosulphonates in solution to give a more hydrophobic LS–Pb complex which will adsorb onto the surface. First the lignosulphonate adsorbed to the “naked” lead surface gives a monolayer coverage. Here, it is direct interaction between LS–Pb complex and the surface. Then the LS–Pb complex will precipitate on top of this monolayer. There seems to be no upper limit to this precipitation, the highest value in our experiments is about 1.2 g of lignosulphonate to 1.0 g of

lead. It is clearly no longer a direct interaction with the surface.

The oxide covered lead particles are negatively charged at all relevant pH values, so is the lignosulphonate. We would thus expect an electrostatic repulsion between them. Nevertheless, we find that the lignosulphonates adsorb strongly to the lead surface. We believe that the dissolved lead ions react with the lignosulphonate in solution. This gives an electrically neutral and much more hydrophobic lignosulphonate that precipitates onto the surfaces of the lead particles. The same effect of cations interacting with lignosulphonate to give a more surface active species has been observed for Al^{3+} and Fe^{3+} with oil droplets as the surface [24–26], and is also quite general for all trivalent cations [27]. It has also been observed for Ca^{2+} , Fe^{3+} and Al^{3+} ions interacting with lignosulphonates in cement [28]. The effect is also well known for Ca^{2+} ions [21], and Mg^{2+} ions [29] interacting with polycarboxylates.

Any desorption process could not be observed when the electrodes were followed by capacitance measurements [12]. Washing with water did not remove the lignosulphonate from the lead surface, either [17]. On the other hand, at high cathodic potentials, desorption of the expander has

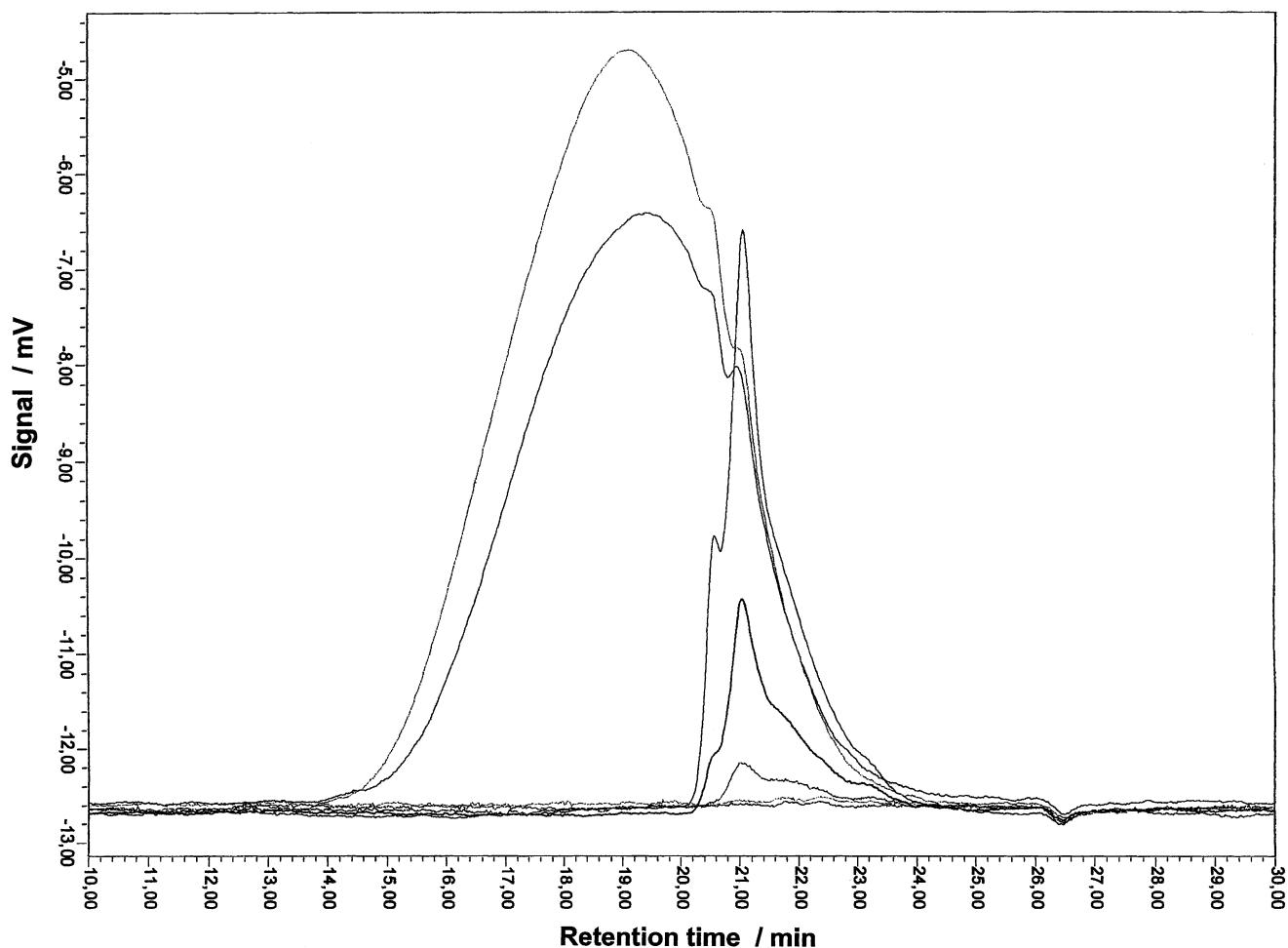


Fig. 9. Chromatograms of the remaining Vanisperse A when different amounts have been in contact with lead. From top to bottom: reference, 2433, 958, 363, 251, 103, and 25 mg LS/g Pb.

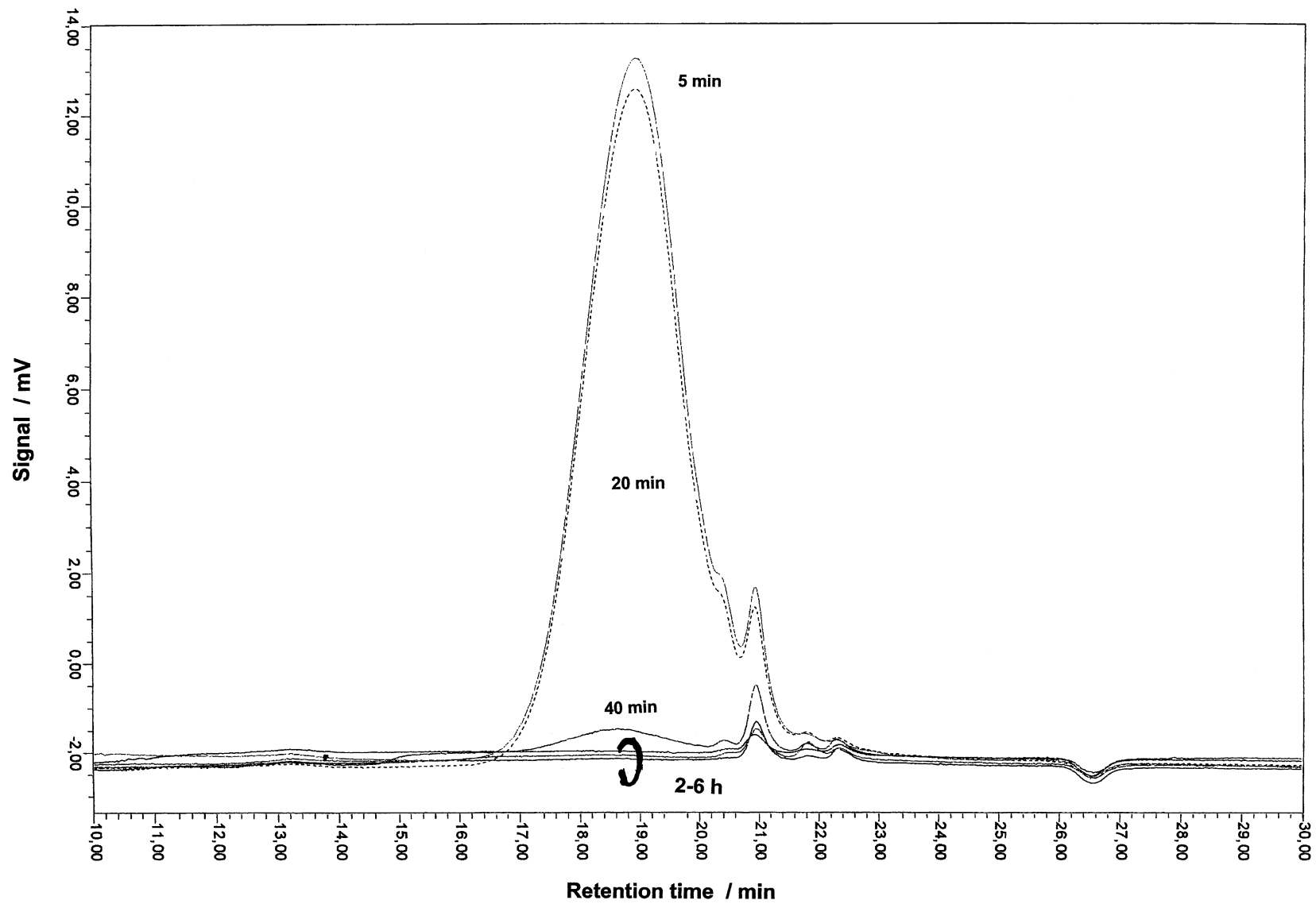


Fig. 10. Chromatograms of the remaining Vanisperse A when 2 mg LS/g PbO have been in contact with lead oxide for different times.

been noted [12]. We do not see any desorption, even when washing the lead particles with a sodium hydroxide solution. That we do not observe any desorption does not necessarily mean that the adsorption is irreversible. It could be due to the insoluble lead–lignosulphonate complex, which would effectively remove any lignosulphonate from the solution.

In addition to UP-414 5000 ppm of each of the following expanders were adsorbed onto 2.0 g of native lead. UP-391, UP-392, UP-393, UP-413, UP-415, UP-416, UP-417, UP-418 and Vanisperse A. We left the expanders in contact with the substrates for 17 h. UP-416, UP-393, and UP-392 were almost completely adsorbed, leaving only the lowest molecular weight fraction left in solution. These are also the expanders having the highest surface activity [14,15,18]. However, Vanisperse A, which has a similar surface activity does only adsorb slightly. UP-416, UP-393, and UP-392 are the three least soluble of the expanders, this is probably more important. The three expanders that adsorb fastest also have the lowest amount of organically bound sulphur. They will thus be the three which are saturated with lead ions fastest. This can also contribute to the speed of adsorption for these three compounds.

In Fig. 9, the resulting chromatograms of the Vanisperse A left in solution when different amounts (expressed as mg LS/g Pb) were in contact with lead. 10 ml solution and approximately 2 g of lead were used in all cases.

3.2. Adsorption to lead(II) oxide

The battery paste is made of leady oxide. This is mostly lead oxide with some unoxidised lead. The leady oxide is mixed with the organic expander, carbon black and barium sulphate, and sulphuric acid is added to give the required consistency. During this process the sulphate reacts with the leady oxide to give tri basic ($3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O} = \text{BS3}$) and tetra basic lead sulphate ($4\text{PbO}\cdot\text{PbSO}_4 = \text{BS4}$) [8]. The relative amounts of the two compounds depend on the temperature during the reaction. Higher temperature favours BS4, while lignin expanders suppress the formation of BS4. For a good battery the correct balance between the two compounds must be reached. The interaction between PbO and the lignosulphonate is thus important in the manufacturing of the battery. The interaction between lignosulphonate and PbO is thus of great interest.

3.2.1. Time effects

The adsorption of the UP-414 to lead(II) oxide was too fast to study in detail with the present set up. In 5 min all the material that could adsorb had already adsorbed to the surface. Shorter times are difficult to study with the present set up. The transfer and mixing of the powder and liquid takes a little time, while the filtration step takes approximately 2 min. The uncertainty in the timing thus becomes too great to draw meaningful conclusions. The much faster adsorption to lead oxide than to lead is probably due to the lead ions being more readily available.

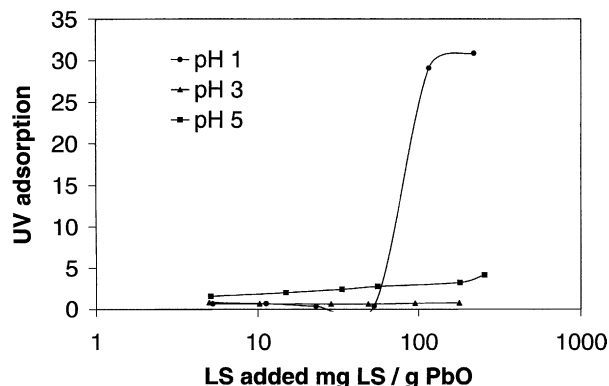


Fig. 11. The adsorption of UP-414 onto lead oxide particles at three different pH levels.

For Vanisperse A, the adsorption was slower. The results are shown in Fig. 10. Two milligrams LS per gram of PbO was used. This is close to the concentration normally employed in lead-acid battery production (0.2–0.4%).

3.2.2. pH effects

Fig. 11 shows the amount of lignosulphonate left in solution for the adsorption to lead oxide substrates at three different pH values. We see that at low pH there is some material left in solution. The adsorption is less efficient at pH 1 than at the higher pH levels.

3.2.3. Salt effects

The lignosulphonate can be fractionated by adding a neutral salt. We used 1.5 M potassium chloride. This gives a soluble fraction with a low molecular weight ($M_n = 3600$ Da, $M_w = 29,000$ Da), and a precipitate with a high molecular weight ($M_n = 11,300$ Da, $M_w = 59,000$ Da). Potassium will not give any insoluble salts with lignosulphonates so we can be sure that this is a pure salting out effect. We also avoid adding any additional sulphate, which we have already shown has a major effect on the adsorption (see Section 3.1.3). In Fig. 12, the adsorption of the solute and precipitate are compared. We see that the least soluble high molecular weight fraction is also most strongly adsorbed.

The precipitated fraction is obtained a solid sample and should contain little chloride. For the soluble sample the

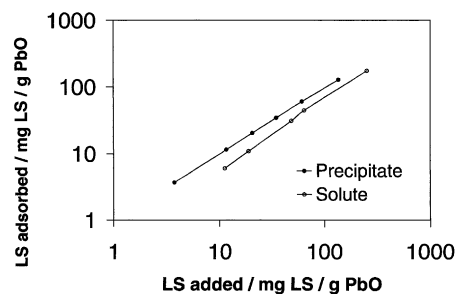


Fig. 12. The adsorption of the soluble part of UP-414, and of the precipitate when UP-414 has been fractionated by salting out with KCl.

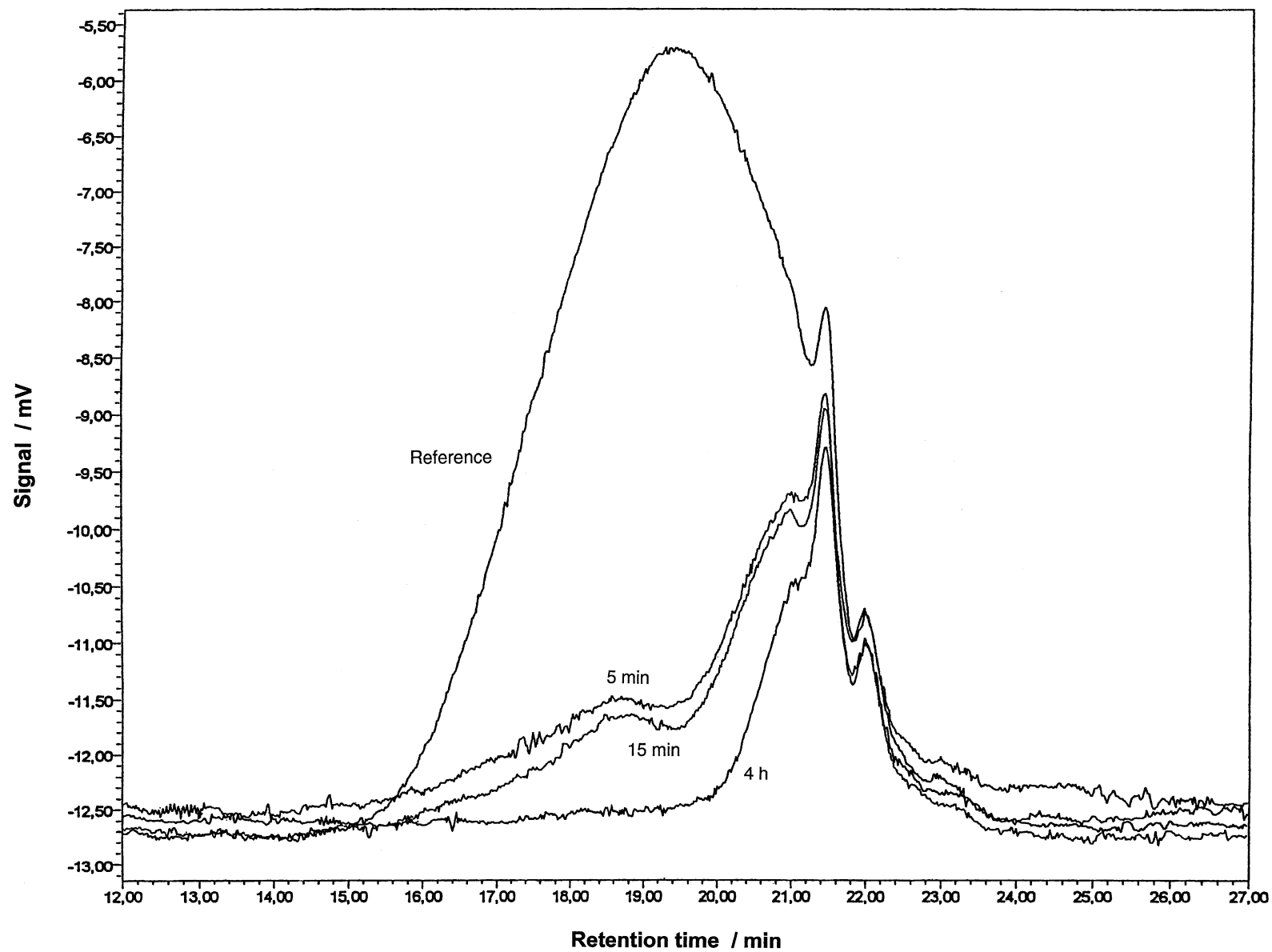


Fig. 13. Adsorption of UP-414 on to lead sulphate particles. The initial concentration of UP-414 was 200 ppm. The figure shows the molecular weight distribution of the fraction left in solution after different times.

chloride will still be present during the adsorption study. Lead chloride is two orders of magnitude more soluble than lead oxide, but with the relatively high chloride content, and low solubility of both lead salts it is possible that the substrate in this case will have a lead chloride coating. However, the preferential adsorption of the high molecular weight substrate can also be seen by looking at the chromatograms of the fractions left in solution. This is shown for Vanisperse A in Fig. 11.

3.2.4. Adsorption isotherms

The adsorption of lignosulphonate to lead oxide is similar to that on lead. We get a large amount of material onto the surface, while about half the material stays in solution. The adsorption to lead oxide is much faster than to lead. This could be due to the much greater availability of lead ions from lead oxide than from lead. Particularly at low pH we would expect some of the lead oxide to dissolve.

In addition to UP-414 5000 ppm of each of the following expanders were adsorbed onto 2.0 g of native lead. UP-391, UP-392, UP-393, UP-413, UP-415, UP-416, UP-417, UP-418 and Vanisperse A. We left the expanders in contact with the substrates for 17 h. Despite their varying surface activity they all left only traces of a low molecular weight material (less than 2000 Da) in solution. More than 95% of the lignosulphonate adsorbed for all these expanders. If the interaction of lead ions with the lignosulphonate to create a more hydrophobic entity is the first step in the adsorption process, there should of course be no direct correlation between the surface activity of the unmodified lignosulphonate and the adsorption.

3.3. Adsorption to lead sulphate

Lead sulphate forms during the discharge of the batteries. It is well known that lignosulphonates have a major influence on the size and shape of the lead sulphate particles formed [1,2,4,9–12]. Despite this, there is only one attempt to study the adsorption isotherms for lignosulphonates on lead sulphate particles [2].

3.3.1. Time effects

Fig. 13 shows the adsorption of different molecular weight fractions of UP-414. The process is slower than for lead(II) oxide, but still fairly fast. Most of the material (>60%) is removed within the first 5 min. The highest molecular weight fractions are removed first.

3.3.2. pH effects

The effect of pH is shown in Fig. 14. For pH 3 and 5 the adsorptions are nearly identical. For pH 1 the adsorption is less efficient at low concentrations, e.g. there is more lignosulphonate left in the solution. A striking—and surprising—feature of these curves is the levelling off of the UV adsorption. At low concentrations the UV adsorption increases with increased lignosulphonate concentration as

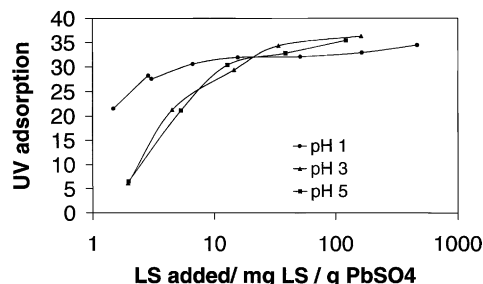


Fig. 14. The adsorption of UP-414 onto lead sulphate particles at three different pH levels.

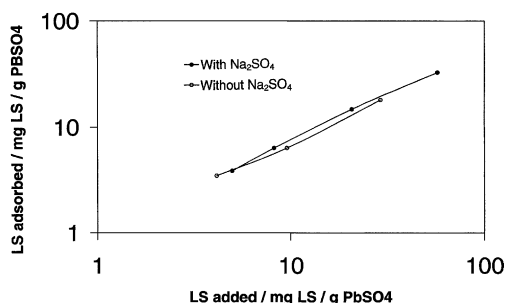


Fig. 15. The adsorption of UP-414 to lead sulphate particles in the presence and absence of sodium sulphate.

expected. Above a certain concentration, the UV adsorption will not increase when we add more lignosulphonate. In other words, all the additional lignosulphonate adsorbs to the surface.

3.3.3. Salt effects

As Fig. 15 shows there are hardly any differences between the adsorption in the presence of sodium sulphate and without sodium sulphate. In both cases roughly two-thirds of the UP-414 adsorbs to the lead sulphate particles.

3.3.4. Adsorption isotherms

The adsorption isotherms for lead, lead(II) oxide, lead sulphate and lead(IV) oxide are compared in Fig. 16. We see that UP-414 has a lower affinity for lead sulphate than for the lead and lead(II) oxide substrates. The difference between

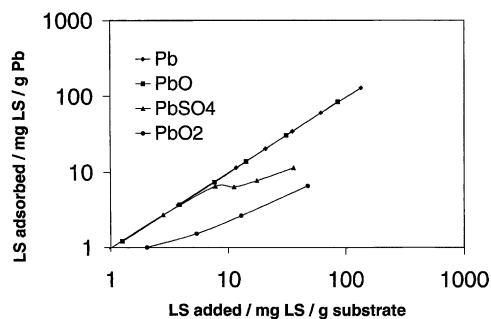


Fig. 16. A comparison of the adsorption of UP-414 onto four different substrates.

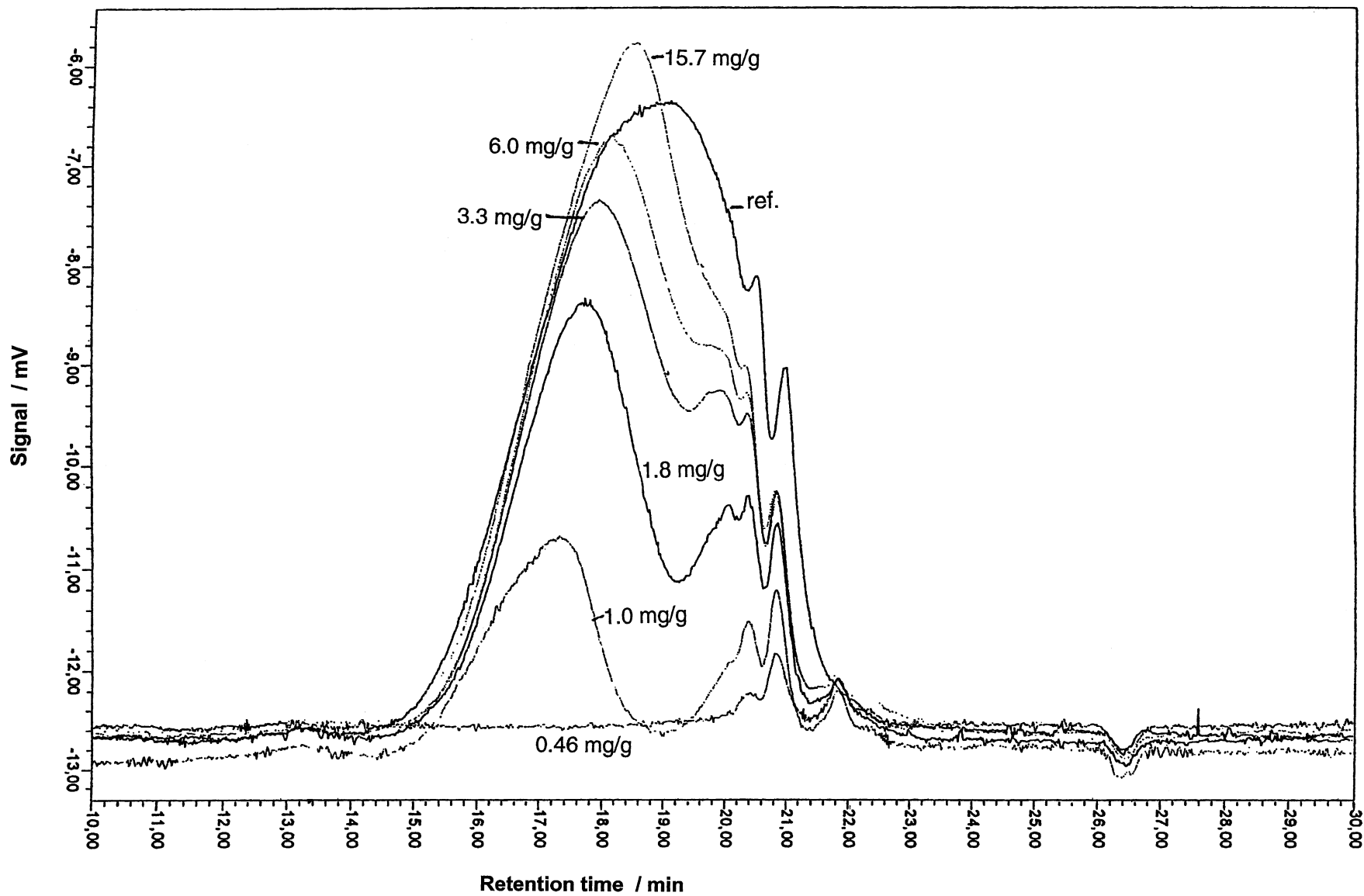


Fig. 17. The molecular weight distribution of the fractions remaining in solution for adsorption of UP-414 on to lead dioxide.

lead and lead sulphate has been observed before [17]. However, that work is done at 1.1 s.g. sulphuric acid, and as we have shown the expander affinity to the substrates is lower at low pH. Willihnganz [2] concluded that the expanders do not attach themselves to lead sulphate or barium sulphate. However, his experiments were rather crude. He added lead acetate to sulphuric acid and looked at the rate of settling of the lead sulphate formed with and without lignosulphonates in the acid. The high density of lead sulphate together with the low viscosity of the solvent will give a fast settling in all cases. It will thus probably be difficult to detect minor changes in the particle size distribution. We performed similar experiments and could not find any differences in particle size distribution for the different expanders. In all cases, the crystals formed were very small with average diameters of 1.4–1.7 μm .

3.4. Adsorption to lead(IV) oxide

The positive plates are made without expanders. However, as most of the expanders are, at least to some degree, soluble in the electrolyte, there is a chance that the expanders will migrate and attach themselves to the positive electrodes. At the positive electrode, the lignosulphonates will be subjected to oxygen and thus more likely to break down. We thus decided to check the affinity toward the major positive electrode component lead(IV) oxide as well.

3.4.1. Time effects

In Fig. 17, the adsorption of UP-414 to lead dioxide is shown. Here, the low molecular weight material is preferentially adsorbed, while the higher molecular weight material stays in solution. The low molecular weight material, as we have shown earlier, only weakly interacts with the negative plate materials. Adsorption onto the positive plate might accelerate the break down of the low molecular weight part of the expander.

3.4.2. Adsorption isotherms

The adsorption isotherms for lead, lead(II) oxide, lead sulphate and lead(IV) oxide are compared in Fig. 14. We see that UP-414 has a much lower affinity for lead(IV) oxide than for any of the other substrates.

3.5. Interactions with carbon black

In addition to the organic expander carbon black and barium sulphate are also added. In Fig. 18, the adsorption isotherms for UP-414 and Vanisperse A to carbon black are shown. We see that the saturation level for UP-414 is higher than for Vanisperse A.

3.6. Interactions with barium sulphate

Barium sulphate is very sparingly soluble. It has the same crystal lattice and dimensions as lead sulphate, and is added

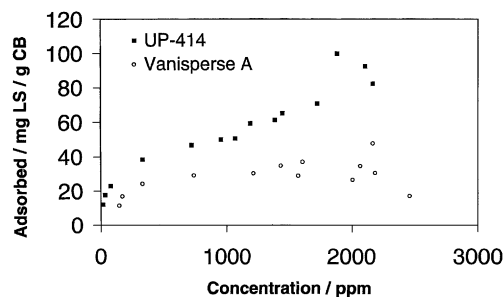


Fig. 18. Adsorption isotherms for UP-414 and Vanisperse A on carbon black.

to the negative active mass to provide seeds for the growth of lead sulphate. Interactions between barium sulphate and lignosulphonates are very similar to the interactions between lead sulphate and lignosulphonates. Figs. 19 and 20 show how large fractions of the different molecular weights that are adsorbed, as a function of time. We see that for the low molecular weight fractions the removal is very quick. There are hardly any changes over time. On the other hand, the removal here is not very efficient. It is clearly much low molecular weight material left in the solution. The UV-spectra of this material is very different from that of the lignosulphonates. We have not been able to identify this

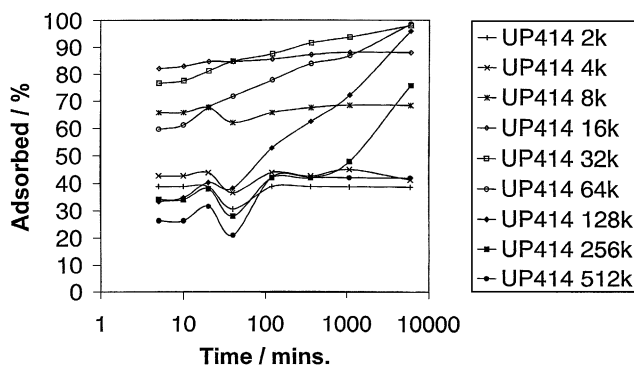


Fig. 19. The adsorption of the different molecular weight fractions of UP-414 onto barium sulphate.

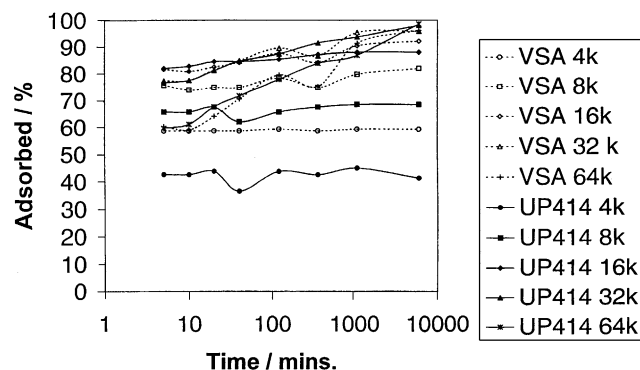


Fig. 20. A comparison of the adsorption of the lower molecular weight fractions of UP-414 with the same fractions of Vanisperse A. The substrate is barium sulphate.

material, but there are traces of unsulphonated monomers. For the intermediate molecular weights fractions, the adsorption is also fast, but much more complete. We find an increased adsorption with increased molecular weight. We also find that the equilibrium is approached slower with higher molecular weight. However, we should not conclude that the adsorption is a slow process, despite the fact that the high molecular weight fractions adsorb slowly. More than half the amount of lignin (as determined by UV) has already adsorbed during the first 5 min. Despite major differences in chemical composition, Vanisperse A and UP-414 of the same molecular weight adsorbs at the same rate, as shown in Fig. 20.

There are chemical and structural similarities between barium sulphate and lead sulphate, for these reasons it is not surprising that the adsorption to the two different substrates proceeds in quite similar manner. However, the solubility of barium sulphate is much lower than the solubility of lead sulphate (1.1×10^{-5} and 1.4×10^{-4} mol/l, respectively), we would thus expect much less barium ions in solution at equilibrium. If our suggested mechanism with the cations rendering the lignosulphonate more hydrophobic is correct, we would expect the this process to be more difficult and slower with barium sulphate than with lead sulphate. This is also what we observe.

Willihnganz [2] concluded that the expanders do not attach themselves to barium sulphate. His experiments might have been too crude to detect the small adsorption.

3.7. Lead ions

Lead ions will react with lignosulphonates to form insoluble lead–lignosulphonate salts [20]. It is thus not surprising that the lead ions leaching out into the solutions will give an insoluble lignosulphonate complex that will precipitate onto the surfaces.

After standing for several weeks some of the solutions that had been filtered from the lead substrates showed a precipitate. If the lignin solution had only been in contact with the substrate for a short time the precipitate had a metallic luster and formed dendritic structures, most of them attached to the glass surface, but some free in the solution. If the lignin solution had been in contact with the substrates for longer times, the precipitates were white and consisted of more rounded particles not attached to the glass. For the solutions which had been in contact with the substrates for more than 2 h no precipitate was ever discovered upon standing. Strong interactions with the ionic intermediate and the expander has been observed with a retention time of the lead ions in solution of 15–30 min with expander as opposed to only a few minutes without [9]. This was attributed to a complex formation. The formation of lead–lignosulphonate complexes has also been assumed previously to account for the growth of large lead sulphate crystals [6]. This has also recently been observed [23].

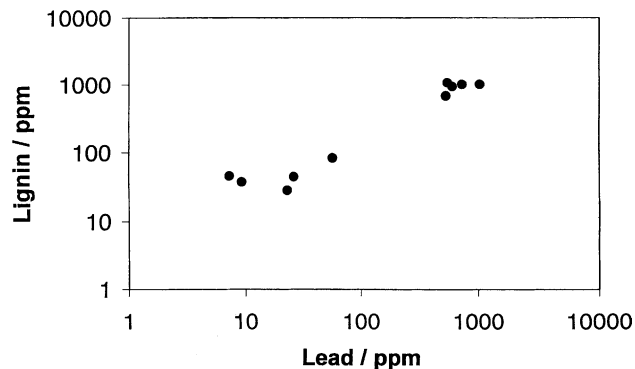


Fig. 21. The relationship between the amount of UP-414 and lead in solutions. For UP-414 that have been in contact with native lead particles.

We prepared an ammonium acetate solution (pH 6). The precipitates were soluble in this solution. The same was lead oxide and lead sulphate, while metallic lead was insoluble. We conclude that the precipitate is lead sulphate that has been complexed with the lignosulphonate, and slowly precipitates from the solution. We cannot see any differences between UP-414 and Vanisperse A with respect to the formation of this precipitate.

We tried to separate the effect of hydrophobic modification followed by adsorption, and precipitation of the insoluble salt by a method recently described [21]. The substrate (lead oxide) was suspended in water kept inside a dialysis membrane. The lignosulphonate solution was kept at the outside. The small lead ions can penetrate the membrane and mix with the lignosulphonate solution to form a precipitate in the outer compartment. The lignosulphonate cannot cross the membrane. No adsorption of a lead–lignosulphonate complex on the lead oxide substrate can thus take place. The solution was stirred for 72 h, without any significant changes in the lignosulphonate concentration. Thus, the lignosulphonate did clearly no just precipitate.

Fig. 21 shows the correlation between the amount of lead and lignosulphonate in solution. The molecular mass of the lignin monomer (~ 200 Da) is nearly equal to the atomic mass of lead (207.2 Da). Fig. 21 implies a nearly one-to-one correspondence between the amount of lead and the amount of lignin monomers. A trapping of Pb^{2+} ions to prevent the formation of $PbSO_4$ has also recently been suggested based different electrochemical techniques [23].

Upon standing some lead salts usually precipitated from the solution. It is clear that the lead–lignosulphonate complex is not stable. As the complexes are unstable, we did not attempt to look at differences between the different lignosulphonates in their complexing abilities.

4. Discussion

It has been concluded before that the expanders probably affects several aspects of the operation of a lead-acid battery [12], this is reinforced by our observations.

Lead ions will enter the solution, either via a dissociation of the salts for lead sulphate and lead oxide, or from the corrosion of the substrates for pure lead. For the native lead, we also have a thin oxide coating that will go into solution. In batteries there will of course always be lead ions available. The lead ions will complex with the lignosulphonate in solution. We can see clearly that some of the solutions contain much more lead than expected from the solubility product of lead sulphate. The neutral lead–lignosulphonate complex will be more hydrophobic than the original lignosulphonate and adsorb onto the surfaces, even if the surfaces themselves are negatively charged. About half the lignosulphonates with the lower molecular weights will form lead–lignosulphonate complexes that stays in solution, while the other half will adsorb onto the lead or lead oxide substrates. We should call this an adsorption and not a precipitation. If this was a precipitation of insoluble lead–lignosulphonates, the nature of the substrates should not matter. What we, and earlier workers in the field [17], find is that there is a large difference between the behaviour on native lead and lead sulphate. If the difference between lead and lead sulphate was due to differences in the availability of lead ions we would expect the precipitation on lead sulphate to proceed faster. The higher solubility of lead sulphate than lead oxide (1.4×10^{-4} and 7.6×10^{-5} M, respectively) should make more lead ions available. When extra sulphate is added to the system, we would expect less lead ions in the solution as the equilibrium is pushed towards the lead sulphate. Instead, we find that extra sulphate favours the adsorption. At lower pH, oxide will off course react as follows: $\text{PbO} + 2\text{H}^+ = \text{Pb}^{2+} + \text{H}_2\text{O}$, and release lead ions.

Our model compound studies [18] indicates that it is the sulphonic acid groups of the lignosulphonate that interacts with the lead ions. If the pH is lowered the sulphonic acid groups are protonated and less available for reaction with lead ions. Even if protonation of the phenolic hydroxyl, carboxylic acid and sulphonic acid groups should render the lignosulphonate more hydrophobic, we actually find more of the lignosulphonate in solution at the lowest pH.

Complexation with lead appears to be more efficient than the protonation when it comes to give a species that will adsorb to the surface. This could be an entropy effect. Protonation leaves the same number of species in solution and have little effect on the entropy (less electrostatic repulsion could actually mean a higher conformational entropy). The divalent lead ions could bridge two species and thus lower the entropy (two bridged oligomers will probably also restrict each others conformational freedom).

Neutral salt will help precipitate the lead–lignosulphonate complex onto the surfaces present. At all pH investigated the surfaces are negatively charged, so are the lignosulphonates. Added salts will screen the electrostatic repulsion and bring the lignosulphonates closer to the surfaces. The barrier they will have to overcome is smaller and adsorption is facilitated.

It also seems like a thin coverage of lignosulphonates on the surface of the particles will promote the adsorption of more of the hydrophobically modified lignosulphonate. This is most clearly seen for the controlled pH experiments with the lead sulphate substrate.

Batteries are dynamic systems. During the formation, discharging and charging the amount of the different lead compounds will vary, as well as their crystal shapes and sizes. At the same time the pH and ionic strength of the electrolyte vary, too. If the processes are too fast to reach equilibrium, there will be concentration gradient as well. During fast charge or discharge the temperature of the lead-acid battery will also increase. It is thus not obvious how our results, which are obtained for static systems, and mostly at times long enough to ensure equilibrium, relate to the battery performance.

However, there are some interesting observations that probably are relevant for the function of the organic expander in the batteries. Only half of the expander adsorbs to lead oxide, the other half remains in solution. The leady oxide paste contains mostly lead oxide. After formation, the paste in the negative plate is turned into lead. As not all the lignosulphonate is adsorbed onto the lead oxide, there will be more material left to cover the surface of the lead. This reservoir of lignosulphonates in the battery is probably important for the operation during cycling. It has earlier been concluded that only the part of the expander adsorbed on the leady oxide was effective during the formation [7]. The expander adsorbs strongly onto the lead oxide. We would expect this to block sulphuric acid and make the reaction to form basic lead sulphate more difficult if the reaction proceeds through a solid-state mechanism. It is found that the rate of formation of all the basic lead sulphates ($\text{PbO} \cdot \text{PbSO}_4$, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, and $4\text{PbO} \cdot \text{PbSO}_4$) is suppressed in the presence of lignosulphonate expanders [24]. The formation of $4\text{PbO} \cdot \text{PbSO}_4$ so strongly that this compound will be completely absent. The formation of all these basic lead sulphates proceeds first through a PbSO_4 intermediate. Excess PbO will react with water to give an alkaline solution. PbSO_4 will then be converted into different basic lead sulphates depending on the pH and sulphate concentration [22]. For $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ the rate of nucleation is faster, while the crystal growth is slower in the presence of an expander. For $\text{PbO} \cdot \text{PbSO}_4$ both the rate of formation and dissolution is lower in the presence of the lignosulphonate expander. We have no data on the relative affinities of the expanders to the different intermediate species and the basic lead sulphates.

Higher molecular weight material has a greater affinity for the lead surfaces, and will adsorb first. The collecting skeleton structure is formed first, this will thus preferentially be covered by the high molecular weight fraction. The energetic structures forms later during the formation. This will be covered by the lower molecular weight fraction. It is well known from colloid and surface chemistry that smaller polymers will desorb more easily than larger polymers. We

can only speculate as to what effect the different molecular weights will have on the cyclability of the energetic structure and the permanence of the collecting structure. We also note that for the lead sulphate it is the low to medium weight fractions that adsorb first and most easily. These are the same fractions that we can assume cover the energetic lead structures.

In a discharged battery the acid will be weak, and there will be little lead, and much lead sulphate present. In weak acid, the lignosulphonate has a strong affinity for the lead surface, which is only present in small amounts. During charging, more lead is produced while the strength of the acid increases. Thus, as there is more lead surface available for the lignosulphonate to adsorb onto, the affinity for the lead surface decreases.

5. Conclusions

A lead–lignosulphonate complex is formed in the battery acid. This complex has a greater affinity for the solid surfaces than unmodified lignosulphonate. This complex will adsorb strongly to lead oxide, weakly to lead sulphate. With a pure lead particle there are not enough lead ions present to give any adsorption. We also find that a soluble fraction of lignosulphonates will complex lead ions in the solution. This will promote the dissolution–precipitation mechanism for the lead to lead sulphate transformations.

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