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Interactions between lignosulphonates and the components of the lead acid battery. Part 2. Interactions with the electrolyte and lead sulphate growth

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Abstract

Several lignin based expanders underwent various physical and chemical tests. The results were compared with life time measurements for batteries with the same expanders. The aim was to gain understanding of the interactions between the expanders and the other components in the lead acid battery, and also, if possible, to find a quick and reliable screening test for the life time of batteries. The low pH of the sulphuric acid electrolyte will give both hydrolysis of the lignins and condensation. Hydrolysis seems to be detrimental to the performance. The lignosulphonate expanders seem to promote a dissolution–precipitation mechanism for lead sulphate formation.

1. Background

Expanders in lead acid batteries influence the size and shape of the lead sulphate particles formed during discharge [1–7]. In previous work [8] we looked at the interactions between the lignosulphonate expander and the different solid phases present in a lead acid battery. In this work we will look at the interaction with the electrolyte, that is sulphuric acid, and the lead ions dissolved in the sulphuric acid.

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 is 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, 2, 9].

The construction and testing of batteries is a time and energy consuming process. Several simple tests to screen the expander have been suggested. In this work we investigate whether simple properties of the expander can be used to predict to expander performance, and thus speed up the development time for new expanders. Understanding of the mechanism responsible for the performance of the expanders is also needed.

2. Experimental

2.1. *Surface tension*

The surface tension was determined by a Cenco de Noüy tensiometer with a platinum ring. The solutions used were 0.01–5% lignin in a phosphate buffer at pH approximately 6, or in unbuffered sulphuric acid solutions. The temperature was 23 °C. The values given are the average of three measurements. The experimental uncertainty is less than 0.2%. The surface tension is a measure of the surface activity of the lignins.

2.2. *Precipitation pH*

The precipitation pH was determined by dissolving the lignosulphonates in water and adding sulphuric acid until a precipitate or cloudy solution formed. Solutions with lignin in 6% sulphuric acid were filtered and the molecular weight distribution determined for the soluble fraction in this acid.

2.3. *High temperature stability*

The high temperature stability was determined in two different ways. 2500 ppm of the lignosulphonates were dissolved in sulphuric acid at three different strengths, e.g. pH 1, pH 3 and pH 5. The solutions were kept at room temperature, at 65 °C, and at 105 °C. The molecular weight distributions were checked at different times.

The high temperature stability was also determined in a solution of 4.16 g lead oxide, 17.17 g sodium sulphate and 14.95 g 36% sulphuric acid diluted to 1.0 l. The pH of this solution was 1.88. About 1.0 g of each of the lignosulphonates were dissolved in 20 ml of this solution and heated to 65–70 °C for 5 days. The samples were filtered off, dried and weighed. The percentage insoluble material was calculated. This gives a measure of the survival of the lignins in a battery environment.

2.4. *Molecular weight distribution*

Molecular weights were determined on a Jordi Glucose DVB 10000 Å 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.

2.5. *Changes in the lignins*

In some cases, it was necessary to look in more detail at the changes in the expanders. Standard methods for characterising lignosulphonates were employed. Details of these methods have been given earlier [10]. Details of the composition of the expanders are given in Table 1.

2.6. *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.

2.7. *Chemicals used*

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

Lead oxide was from Alfa. The carbon black used was Cabot Elftex 460. Sodium sulphate, sodium dihydrogen phosphate, potassium chloride, sodium hydroxide, and acetic acid were all from E. Merck.

The lignosulphonates are commercially available (Vanisperse A) or experimental products from Borregaard LignoTech. Details of the expanders' compositions and performances are given elsewhere [10].

2.8. *Crystal growth*

22.32 g (0.1 mol) lead oxide in 90 ml water and 0.056 g lignosulphonate in 10 ml water were mixed and heated to 80 °C with stirring. 46 ml 34% sulphuric acid was added drop wise. The solution was left standing for 4 h. The crystals were dried at 105 °C overnight before particle size determination.

3. Results and discussion

3.1. *Precipitation pH*

Sulphuric acid makes up the bulk of the volume of lead acid batteries. The lignins contain several functional groups that can be ionised. The most important are phenolic hydroxyl, carboxylic acids and sulphonic acids. The pK_a values of these groups are ~10, ~4, and ~1.5, respectively. This means that the number of dissociated groups, and thus the solubility, will be strongly pH dependent for the lignosulphonates. If the pH is lowered the solubility decreases, at some pH the lignins will precipitate out of solution. In Figure 1 the precipitation pH for a number of lignins are given as a function of their organic sulphur content. About 1% organic sulphur is in the form of unknown groups, while the rest is from sulphonic acid groups. We see from Figure 1 that with a high sulphonic acid content the lignosulphonates are soluble over the pH range found in a lead acid battery. More details about these expanders can be found elsewhere [10].

The solubility was also determined directly in gram per litre at three different pH values. The results are

Table 1. The analytical data for the expanders used in this study

Expander	M_n kDa	M_w kDa	–OMe %	S %	COOH %	–CHO %	CO %	–OH %	$(OH)_2$ %
UP-414	6.37	78.0	10.5	5.5	6.66	0.0	0.7	2.02	0.19
Vanisperse A	5.01	15.6	12.3	2.5	11.20	0.0	2.4	1.61	0.33
UP-391	6.65	21.5	10.8	1.8	12.60	0.1	2.0	1.52	0.34
UP-392	5.72	23.6	10.7	1.6	13.52	0.6	0.2	1.56	0.34
UP-393	3.62	25.5	9.4	1.4	12.62	0.0	1.5	2.01	0.31
UP-413	6.84	81.0	10.0	4.9	8.96	0.0	0.2	1.76	0.21
UP-415	7.15	67.1	10.4	5.6	7.94	0.0	0.3	1.85	0.19
UP-416	2.08	24.8	11.2	1.1	11.79	0.2	0.9	0.78	0.28
UP-417	7.17	50.9	8.3	7.0	8.15	0.2	0.7	1.56	0.18
UP-418	10.9	73.0	10.9	6.0	4.50	0.0	0.2	2.10	0.18
M	4.61	29.7	12.5	2.5	8.61	0.0	1.5	2.70	0.28
D	4.14	23.3	10.8	3.4	8.37	0.0	1.0	2.4	0.26

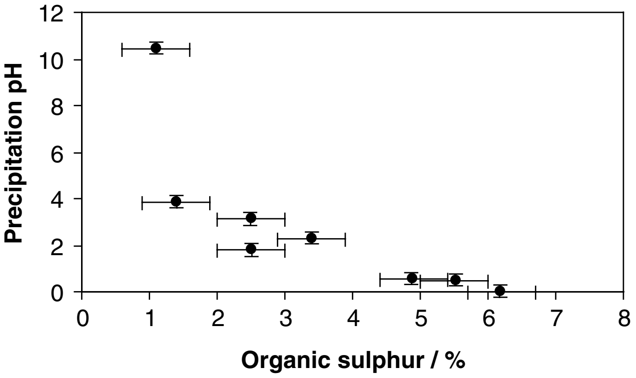

Fig. 1. The inverse relationship between organic sulphur content (mostly sulphonic acid groups) and the precipitation pH.

given in Table 2. With a high sulphonic acid content, the lignosulphonates are freely soluble in acid.

3.2. *Stability of the lignosulphonate*

The lignin molecule contains many ether bonds. These can be hydrolysed in strongly acidic solutions. It has been speculated that this hydrolysis will break down the lignosulphonate and thus limit the life time of the expander in the battery, and consequently the battery itself.

The life times are taken from cycle test described in the literature [10]. The end of life for the battery depends somewhat on which property is chosen. However, there are only small variations between the different properties; if one test fails, the other will fail soon after. We take the cycle life as the average cycle life found from the two tests.

There is a competition between the hydrolysis that lowers the molecular weight of the lignosulphonates and condensation reactions leading to increased molecular weights. We checked the stability of UP-414 at three different pH values (pH 1, pH 3 and pH 5), and at three different temperatures (ambient, 65, and 105 °C). At ambient temperature there were no changes even after several months of storage. For the elevated temperatures, the results are shown in Figure 2. For pH 3 and pH 5 there are only small decreases in the molecular weight initially and then the molecular weight stays constant. The decrease is faster and more pronounced for the samples stored at 105 °C than for those stored at 65 °C.

Table 2. Solubility of the expanders in sulphuric acid at three different pH levels

Sample	pH 3/g l^{-1}	pH 2/g l^{-1}	pH 1/g l^{-1}
UP-414	> 100	> 100	> 100
Vanisperse A	12	–	3.2
UP-393	1.8	–	1.3
UP-413	> 100	> 100	92
UP-416	1.8	–	1.3
UP-417	> 100	> 100	> 100

For UP-393, UP-416 and Vanisperse A the UV adsorption at 350 nm was used, for the others the UV adsorption at ~280 nm.

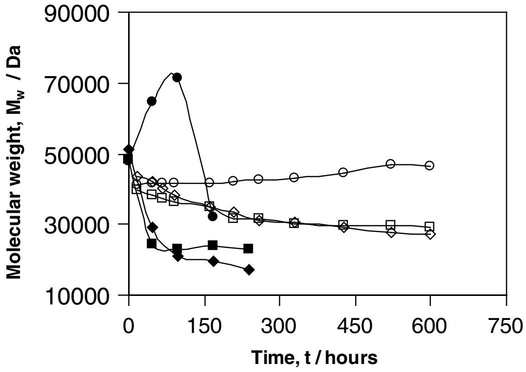

Fig. 2. The changes in weight average molecular weight over time when UP-414 is heated to 65 or 105 °C, at three different pH values. Sulphuric acid is used to adjust the pH. Circles, pH 1; squares, pH 3; and diamonds, pH 5. Filled symbols for 105 °C, open symbols for 65 °C.

For pH 1, the development appears more complex. At 105 °C the molecular weight first increases for 80 h, and then decreases. The increased molecular weight shows that the condensation reaction is the dominant one. When the condensation has proceeded far enough the lignosulphonate will form a gel. We are thus only measuring the molecular weight of the sol fraction, this will steadily decrease as more and more material is incorporated into the gel [11]. The solution becomes less coloured during the final stages of the experiment. After the experiment, a deposit was seen on the glass walls of the test tube, confirming that an insoluble product had formed.

The experiment at 65 °C did not proceed for long enough time to reach the gel stage; we thus only see the molecular weight increase.

The condensation reaction dominates over the hydrolysis for UP-414, but both may still take place, thus leading to major rearrangements of the lignin molecules. The hydrolysis should give increased amounts of phenolic hydroxyl groups. We could not detect any significant increase in the amount of phenolic hydroxyl at the end of the experiment. For the samples heated to 65 °C at pH there was a decrease from 2.1 to 1.77% phenolic hydroxyl. This is significant at the 90% level, but not at 95%. It thus seems that the hydrolysis is of minor importance, but on the other hand it is also clear that there are probably other changes in the molecular structure than just an increase in molecular weight.

Several expanders were tested at pH 1 and 105 °C, which was the only condition that had any noticeable impact on UP-414. The results are shown in Figure 3. Two of the expanders show a sharp drop in the molecular weight initially; they all have life times of less than 10 cycles when tested in batteries at 0.2% dosage [10]. Four of the expanders show a slow increase in molecular weight; they all have a life time of more than 10 cycles when tested at the same dosage. It seems that the break down of the expander is an important factor in limiting cycle life time of the batteries. However, this graph does not tell the full story. We

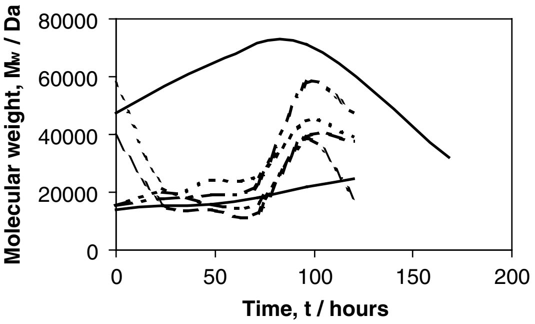

Fig. 3. The changes in weight average molecular weight for UP-414 and five other expanders that are soluble in acid. The pH is 1 and the temperature 105 °C. The expanders that show a fast initial decrease in molecular weight also have the shortest cycle life times. Full thick line, UP-414; full line, Vanisperse A; dotted line, UP-415, dashed line, UP-417; dash-dot, M; and dash-double dot, D.

see no hint of the dosage effect, e.g. the fact that the optimal dosage varies from expander to expander. With too much expander, we might get over-expansion of the negative paste and shedding of active material. This will severely limit the cycle life of the negative plate, even if the expander is still present and unadulterated. Too low dosages, on the other hand, might not give a sufficient surface coverage to exhibit the positive effects of the expander.

For the expanders that are only sparingly soluble at pH 1 there is very little change in the measured molecular weight over time. Of course for these expanders we are only measuring the molecular weight of the soluble fraction and this might not be relevant for the majority of the material. For sparingly soluble expanders the cycle life time cannot be screened by this simple test. We also note that, even for soluble expanders, we cannot find a quantitative relationship between the cycle life time and the stability in hot acid.

In lead acid batteries there are other components in addition to the sulphuric acid present. Thus some stability tests in the presence of lead oxide and sodium sulphate were also undertaken, to better simulate the environment in a real battery.

The result for stability in the presence of lead oxide and sodium sulphate is difficult to interpret. The total weight of lignin powder might be reduced both due to break down of the molecules or due to the solubility of the compounds. We have already shown that if we compare the stability as a function of sulphur content for a number of compounds we see that higher sulphur content gives a lowered stability [12]. This is most certainly because more sulphonic acid groups give a higher solubility. The compounds will be in solution, and not remain as powders. It is clear from Table 3, that the stability determined by this method corresponds well to the precipitation pH. As seen in pure sulphuric acid, some of the lignosulphonates will increase molecular weight upon prolonged contact with hot sulphuric acid, while others will break down. There is no correlation between the stability and material left in solution.

Table 3. Stability in the presence of lead oxide, sodium sulphate and sulphuric acid.

Sample	Material left/%	Precipitation pH	Cycle life time cycles (opt.dosage %) [10]
UP-414	59.3	0.5	15.0 (0.4)
Vanisperse A	80.8	3.1	14.2 (0.15)
UP-393	84.6	3.8	16.6 (0.2)
UP-413	58.0	0.5	11.4 (0.1)
UP-416	81.0	10.4	13.2 (0.4)
UP-417	49.8	0.0	10.4 (0.2)

3.3. *Surface tension*

Lignosulphonates are surface active compounds. Their surface activity will depend strongly on pH. This is because of the pH dependent solubility as discussed above (Section 3.1). We also determined the surface activity of a number of possible expanders.

The results are shown in Figures 4–6. Figure 4 shows the effect of pH and concentration on the surface activity of UP-414. The higher the concentration of the

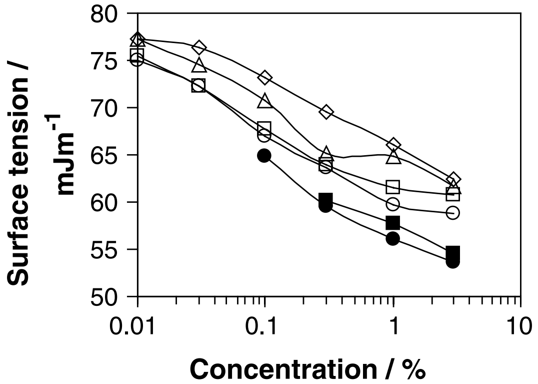

Fig. 4. The surface tension as a function of concentration and pH and acid concentration for UP-414. Diamond, pH 8.0, square, pH 6.4; triangle, pH 6.0; circle, pH 5.4; filled square, 3% H_2SO_4; and filled circle, 6% H_2SO_4.

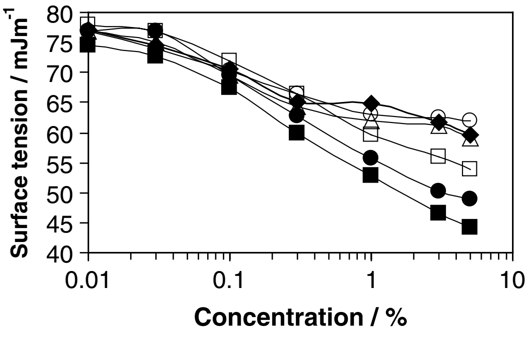

Fig. 5. The surface tension as a function of the concentration for six soluble expanders at pH 6.0. Filled diamonds, UP-414; filled squares, Vanisperse A; open triangle, UP-413; open circle, UP-415; open square, UP-417; and filled circle, UP-418.

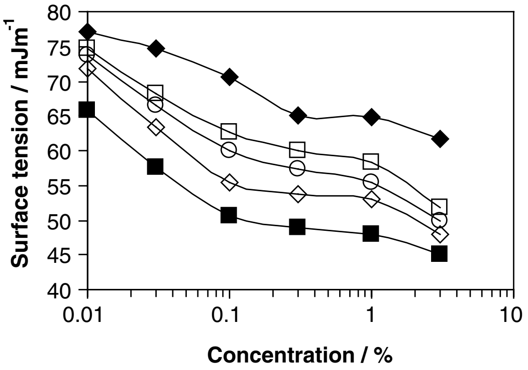

Fig. 6. The surface tension as a function of the concentration for UP-414 and four poorly soluble expanders at pH 6.4. Top to bottom; UP-414, UP-391, UP-392, UP-393, UP-416.

expander, the lower the surface tension. In these plots, there is no levelling off of the surface tension. E.g. the surface is probably not saturated even for 5% lignosulphonate solutions. It should also be noticed that lowering the pH increases the surface activity. This will of course mean that the surface activity of the expander will vary during the operation of the battery. For a discharged battery with weak acid, the surface activity is low, while for the fully charged battery the surface activity of the expander is also larger. Typical concentrations of expanders in a battery are 0.1–0.4% on negative paste weight, while the weight of the acid is 1.5 times the weight of the negative mass. Even if all expander leached into the acid, the concentration would only be 0.05–0.25%. This would only have a small effect on the surface tension in real batteries.

Figure 5 shows the surface tension of UP-414 together with several lignosulphonate based expanders in a buffer at pH 6.0. There is a much larger surface activity of Vanisperse A compared to UP-414. Vanisperse A also has a better initial performance. However, UP-417 which most closely matches Vanisperse A with respect to surface tension, has a rather poor initial performance.

Figure 6 shows the surface tension of UP-414 together with several kraft lignin based expanders in a buffer at pH 6.4. We notice the much larger surface activity of the kraft lignins compared to UP-414. The surface activity increases as the degree of sulphonation decreases. In this series of expanders the best initial performance is again found for those with the largest surface activity.

The influence of the surface energy on the critical radius for nucleation, above which nuclei will grow spontaneously, has been discussed [6]. The surface tension measures the air–water interface. This is not the same as the solid–water interface, but should give a reasonable indication of the effectiveness of the different lignins in lowering the interfacial tension. A lower interfacial tension will lower the critical radius, and should thus give more nuclei. The formation of many smaller crystals instead of a few large ones should be favoured. This is the opposite of what is generally observed with the addition of lignins [1–7]. Clearly other effects of the lignins must be more important [6]. Also the total amount of lignosulphonates present is too low to appreciably influence the surface tension.

3.4. *Crystal growth*

Figures 7 and 8 show the particle size distribution for lead sulphate grown from lead oxide at 80 °C in the presence of different lignins. The lead oxide has a fairly sharp peak with most of the particles just below 10 μm. When the reaction takes place without lignins present, we obtain a bimodal distribution for the lead sulphate. There is one peak which corresponds fairly well with the original lead oxide distribution, and there is another peak with much larger particles. With lignins present, the smaller part of the bimodal lead sulphate is removed. We grow much larger crystals. There is very little difference between the different lignins. The poor expander UP-417 seems to have its peak at slightly smaller particle sizes than the others. Similarly, the poor UP-418 seems to show the remnants of the bimodal distribution with a shoulder at smaller sizes.

The reaction of lead oxide to lead sulphate can be summarised as a two step reaction.

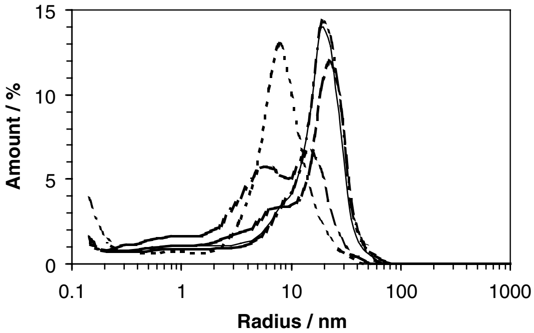

Fig. 7. The growth of lead sulphate crystals in the presence of different expanders. Dotted line, the initial particle size distribution of the PbO starting material. Full line, Vanisperse A; dashed line, UP-418; dash-dot, no lignosulphonate; and dash-double dot, UP-414.

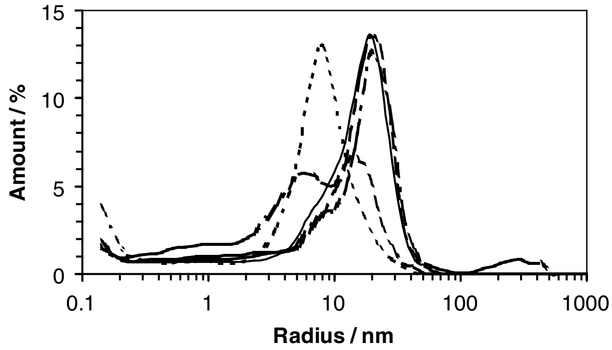

Fig. 8. The growth of lead sulphate crystals in the presence of different expanders., Dotted line, the initial particle size distribution of the PbO starting material. Full line, UP-417; dashed line, UP-415; dash-dot, UP-413; and dash-double dot, no lignosulphonate.

$$PbO + 2H^+ = Pb^{2+} + H_2O$$

$$Pb^{2+} + SO_4^{2-} = PbSO_4$$

This reaction can proceed more or less in one step, in which case the lead ion would not have time to migrate away from the solid PbO surface. The lead sulphate will then precipitate onto the surface and quickly passivate it, to stop further reaction.

Alternatively, the lead ions could have enough time to migrate some distance away from the surface before reaction with the sulphate ions. The lead sulphate will then form by a new crystallisation step from the – at least locally – supersaturated solution.

The lead sulphate grown without lignins present shows that many of the particles still have the same sizes as the original lead oxide. This we interpret as lead oxide being passivated by a lead sulphate layer on the surface. In the presence of lignins, crystals grow bigger and the original sizes can hardly be found. We interpret this as the lignins helping to complex the lead ions and keep them in solution. A similar effect of lignins has been described for the transformation from lead to lead sulphate by capacity vs potential studies [4, 7], cyclic voltametry [4–6, 13–16], potentiostatic transients [15–17], and electrochemical impedance [15, 16]. Strong interactions with the ionic intermediate and the expander have 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 [4]. It has been concluded that polar groups, mainly the sulphonate groups, can "trap" Pb^{2+} [16]. We have previously found a good correlation between the amount of lignosulphonate and lead in solution [8].

The results shown in Figures 7 and 8 appear to be in disagreement with the claim that the expander stabilises fine particles, and that the large ones become smaller in plain litharge negative plates [1]. In the negative paste, there is relatively little water (typically 150–170 g/kg of lead oxide) and limited stirring. In our system on the other hand, there is plenty of water (4480 g/kg of lead oxide) and good stirring. Any transport of lead ions away from the surface will thus be much more efficient in our experimental set up than in a real battery plate. The adsorption of the expander to the surface will also take longer in our system than in a real battery plate, as there will be a much longer distance to travel before the expander molecule reaches the surface, and a lower lignosulphonate concentration in the solution.

It should be noted that in the experiment described lead sulphate is formed from lead oxide. During the operation of real batteries lead sulphate is formed from metallic lead. This might cause differences. However, the promotion of the dissolution–precipitation mechanism should be valid in both cases.

The observation that lignin has to be in the plate and not in the electrolyte during formation [18] is, of course, not contradictory to any effect of dissolved lignosulphonates during battery operation.

We have not analysed the particles formed further and are thus not able to determine whether they are pure lead sulphate, or whether they are some mixed lead oxide/lead sulphate species. If our interpretation of the events is correct the larger crystals formed in the presence of lignin ought to be pure lead sulphate.

Willihnganz [2] concluded that the expanders do not attach themselves to lead 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.

3.5. *Interactions with carbon black*

In addition to the organic expander carbon black and barium sulphate are also added. It was noted early that Vanisperse A, which is a good expander for lead acid batteries, also is an excellent carbon black dispersing agent [19]. It was speculated that the effect of the expander was due to an efficient distribution of the carbon black in the paste. If this is the case, we would expect a positive correlation between the initial performance of the battery and its cycle life time. The initial structure formed is better and it will take longer for it to deteriorate below an acceptable level. In Figure 9 the viscosity vs dosage curves for interaction of Vanisperse A, UP-414 and UP-418 with carbon black are shown. The data show two features. What is the optimum dosage of the lignosulphonate, and the viscosity at this dosage? The lower the optimum dosage and the lower the viscosity the better the dispersing agent. There is no correlation between the carbon black dispersing efficiency and the effect in lead acid batteries. We have previously found an inverse correlation between the

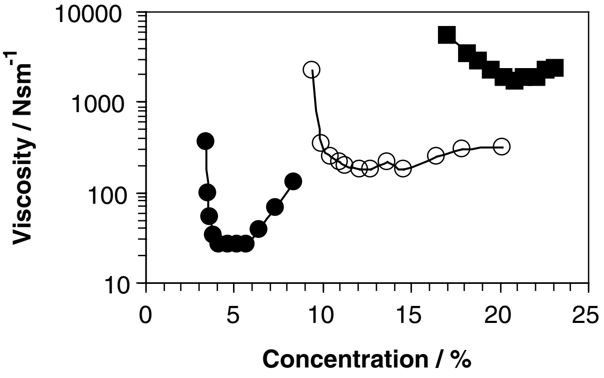

Fig. 9. Viscosity vs dosage curves for the dispersion of carbon black with different expanders. Filled circles for Vanisperse A, filled squares for UP-414, open circles for UP-418.

initial performance and cycle life time [12]. This also supports the finding that a good initial performance will not necessarily survive for a longer time.

The adsorption isotherms for Vanisperse A and UP-414 on carbon black have been published previously [8]. More of the high molecular weight UP-414 than of the low molecular weight Vanisperse A adsorbs to the carbon black.

3.6. *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 precipitates 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 between the ionic intermediate and the expander have 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 [4]. This was attributed to a complex formation. The formation of lignosulphonate–lead complexes has also been assumed previously to account for the growth of large lead sulphate crystals [16, 21].

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 saw no differences between UP-414 and Vanisperse A with respect to the formation of this precipitate.

As discussed previously [8] the expander performs several different tasks in the battery. It is thus not surprising that simple physical or chemical tests like those undertaken in this study will bear little relevance to what is going on in a real battery. Each of these tests focuses on only one or very few properties and cannot illuminate the full complexity of the problem.

We have previously looked at analytical data for the same expanders and failed to find simple correlations between battery performances and chemical structure [12].

4. Conclusions

The stability of different lignosulphonates in sulphuric acid varies. Some break down quickly, while others increase in molecular weight. Lignosulphonates that show a stable molecular weight when heated in sulphuric acid give long cycle life time when tested in batteries. However, this simple test fails for lignins that have too low a solubility in strong acids.

The lignosulphonates seem to promote a dissolution–precipitation mechanism for lead sulphate formation from lead oxide.

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