

REACTIONS OF METALS WITH CELLULOSE

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Reactions of cellulose with heavy metals in the form of their soluble complexes and sodium salts of *amphoteric* metals have been studied and it has been found that metals such as Cu, Pb, Cd, Sb, Sn, Fe and Cr get firmly attached to the cellulose chain by replacing the hydrogen atoms in the two secondary hydroxyls. For these reactions with cellulose, the metals in the form of their soluble complexes, must essentially be present in such a potential but masked form that their corresponding hydroxides are readily available when cellulose comes in contact with these solutions.

Introduction

Cellulose is a highly indispersible polymer and requires powerful swelling agents to bring about chemical reactivity in cellulose in aqueous medium. Concentrated solutions of caustic alkalis can be cited as familiar examples. In the swollen state, the secondary hydroxyls in cellulose acquire a marked reactivity but this cannot be used for reactions with heavy metals, as the latter gets precipitated in the form of their hydroxides. Dissolution of cellulose and hence its reaction in ammoniacal solutions of the metals¹ or in organic amines² have attracted considerable attention and offered wide scope for industrial utilization of these reactions.

Water-soluble polyhydroxy organic compounds such as glycerol and tartaric acid have the specific property of keeping the hydroxides of heavy metals in solution when alkali is added to the solutions of salts of these metals. The metal remains in "masked" form in the complex solution³ which reacts with cellulose when the latter is introduced into the former. The mechanism has been discussed in a previous paper.⁴

Recent work⁵ shows that cellulose can be completely dissolved in very high concentrations of reactants in the system " Fe^{+++} -NaOH-tartarate". The scope of the present paper is limited in the sense that it does not seek complete dispersion of cellulose as brought about in the above case, but the object has been to study a few heavy metals which would react with cellulose in the manner as described in the earlier paper.⁴

The cellulose-metal complexes react with anions (which give normal insoluble salts of these metals under ordinary conditions) and yield the corresponding insoluble salts on cellulose in situ. One obvious advantage is that under these conditions, in some cases, the insoluble salts of these metals are not precipitated in the water-soluble complexes of the metals as would be the case in the absence of the compound which exercises the "masking influence". For example, if soap solution is added to the system " Pb -NaOH-tartarate", no lead soap

is thrown out. Here the emphasis is on the high concentration of the masking agent. Similarly sodium plumbite having an excess of alkali has the power to prevent the precipitation of lead soap, but the sulphide and chromate are instantly thrown out.

Experimental

Chemicals.—The metals studied in the present investigation may be grouped as (A) Metals such as Cu, Cr, Cd, and Fe whose hydroxides are insoluble in excess of sodium hydroxide and require the presence of glycerol/tartarate to keep the hydroxides in solution and temporarily masked. (B) Metals such as Sb, Sn, and Pb, whose hydroxides are soluble in excess of sodium hydroxide and for which the use of tartarate can be dispensed with.

Aluminium and zinc do not react either under group A or B. The reactions of copper from group A have already been communicated. Of group B, Pb and Sb have been studied in detail and are discussed below.

The chemicals used in these experiments were either A.R. or Pure (Merck). Stock solution of lead nitrate and sodium hydroxide contained 10 percent and 20 percent of the chemicals, respectively. Lead nitrate solution has a tendency to develop a turbidity due to hydrolysis, which was prevented by adding a few drops of concentrated nitric acid.

Sodium plumbite was prepared by adding 75 ml. of 20 percent sodium hydroxide to 100 ml. of 10 percent lead nitrate warming the solution to remove the slight turbidity, diluting and making up the volume in a litre flask. Although less amount of alkali (65 ml.) would have sufficed for this purpose, an excess of alkali was purposely used which in this case exerts the masking influence. The resultant solution of sodium plumbite contained 6.385 g. Pb per litre.

Cellulose Material.—Commercially bleached do-sooti with the following constructional details was used in these experiments.

Wt. per sq. yd. 7 oz., ends/picks 34/34 both double; counts: warp/weft 14/14s (42.2 Tex). The material was further purified by desizing and scouring and dried in air. Pieces weighing 1.0 ± 0.05 g. of the air-dry material were introduced into 25 ml. of the sodium plumbite solution and the treatment continued for 5 minutes at 30°C., by constantly agitating the fabric and the solution with hand. At the end of the treatment, the pieces were taken out, rinsed in water till the washing showed no alkaline reaction towards litmus.

The determination of lead on the fabric was carried out by removing the metal with 25 ml. of 5 percent nitric acid, followed by washing. The combined extract and washings were neutralized with ammonia, acidified with acetic acid and lead precipitated as lead dichromate, which was titrated. Incidentally it was noticed that the fabric pieces acquired a purer white after the lead was removed. This may be due to mild oxidizing action of sodium plumbite on residual colouring matter. It was also observed that lead on the fabric could be quantitatively precipitated as dichromate in situ by boiling the treated piece in excess of acidified (acetic) potassium dichromate solution. Subsequently the dichromate was liberated from the fabric and the amount of lead so determined and that left in the solution at the end of the experiment combined together made the total amount of lead with which the experiment was initially commenced. In the subsequent experiments, lead was determined in this manner. Further the absorption of lead by cellulose being fairly high and quick, the duration of the experiments was restricted to 5 minutes only. Some of the variables studied are described below.

All the percentages of lead were calculated on the basis of oven-dry cellulose and except where stated to the contrary, the ratio of the solution to the air-dry weight of the fabric was kept at 25:1, the oven-dry weight of the pieces being very nearly 1 g.

(i) *Effect of Temperature on the Absorption of Lead.*—1 g. pieces of cellulose were treated in 25 ml. of sodium plumbite solution containing 6.385 g. Pb per litre for 5 minutes at 30, 50 and 70°C. The percentage of lead absorbed at these temperatures by cellulose was 8.32, 8.00 and 7.66, respectively which shows that absorption is slightly reduced as the temperature is raised. This is normally characteristic of cases which show rapid absorption, such as physico-chemical absorption of certain substantive dyes by cellulose, which also show less absorption at elevated temperature.

(ii) *Effect of Volume of the Solution of Sodium Plumbite.*—The experiments were carried out in

the same manner as above (i) except that the temperature was kept at 30°C. and the volume of the solution taken was varied. The percentage of lead on cellulose so determined was 8.32, 9.42, 10.31 and 10.30, respectively when 25, 50, 75 and 100 ml. of sodium plumbite solution were used. The increase in the absorption of lead is not pronounced when the volume is increased many times and much larger amounts of lead become available for reaction.

(iii) *Effect of Concentration of Sodium Plumbite.*—Keeping the ratio of lead nitrate and sodium hydroxide the same as before, the effective amount of sodium plumbite was varied in the solution meant for the treatment of cellulose. The following data was obtained:

Concentration of Pb in the solution, g./litre	Percentage of Pb absorbed by cellulose
1.596	4.22
3.192	6.30
6.385	8.32
12.770	12.70

It is apparent from the above that while the concentration of lead in sodium plumbite solution is increased four times, the corresponding increase in the absorption of lead by cellulose is only two-fold.

(iv) *Effect of Concentration of Alkali on the Absorption of Lead.*—For these experiments sodium plumbite solution contained larger amounts of sodium hydroxide than described in (i) to (iii) earlier. Sodium plumbite solutions prepared from 10 ml. of 10 percent lead nitrate solution and 7.5, 15 and 30 ml. of 20 percent NaOH and made upto 100 ml. gave the following absorption figures for lead for the respective concentrations of alkali: 8.33, 8.01, and 6.55 percent. This clearly shows that higher concentrations of alkali tend to exert the desorbing influence and therefore give lower yields. The ratio of the solution and cellulose was kept at 25:1 at 30°C.

Since the plumbite solution contains 6.385 g. of Pb per litre, 25 ml. will contain 0.1596 g. of Pb. Amount of lead absorbed by cellulose at this concentration is 8.33%. In other words, Pb absorbed by 1 g. piece of cellulose, as is the case, is 0.0833 g. which is 52.2 percent of the original amount of lead available for reaction and the balance 47.8 percent is left behind in the solution.

In another experiment carried out on cotton canvas of 18 oz. per sq. yd. where the volume of the solution used was only five times the air-dry weight of the fabric, the following data was obtained:

Air-dry weight of the scoured fabric	360 g.
Volume of the sodium plumbite solution taken	1800 ml.
Concentration of Pb in the original solution	6.256 g./l.
Concentration of Pb in the residual solution	1.781 g./l.

This gives an amount of 8.055 g. of Pb uniformly distributed on 360 g. of cellulose and the residual amount of Pb is nearly 28.5 percent of the original concentration, which is much lower as compared to the same figure for 25:1 ratio of the solution to cellulose. The residual solution can be replenished and used again to economise the chemicals.

Leaching by Water.—Lead and cellulose combine very firmly and the amount of Pb leached by water at 100°C. is fairly low. Pieces of cellulose treated with lead were refluxed in 200 ml. of water at the boil for two hours. The following figures were obtained: Control 10.51; Residual 9.30 percent of Pb; Loss 11.48 percent.

Absorption of Lead by Cellulose in the Presence of Tartarate.—As has been discussed earlier, 10 ml. of 10 percent lead nitrate solution required 6.5 ml. of 20 percent NaOH solution for complete precipitation and redissolution. By adjusting the quantities of alkali and sodium potassium tartarate, it was found that one ml. of 20 percent NaOH and 6 ml. of 20 percent tartarate solution were sufficient to keep all the Pb in solution, present originally in 10 ml. of 10 percent lead nitrate. Amounts of alkali and tartarate less than these will either give a turbid solution or if a clear solution is obtained, it will be liable to become turbid on standing or heating the solution. Table 1 gives the amount of lead absorbed in the presence of tartarate when the pieces were treated for 5 minutes at 30°C. and 25:1 liquor ratio.

TABLE 1.

S. No.	Value of X, ml.	Percentage of Pb absorbed
1.	1.0	1.56
2.	1.2	2.41
3.	1.5	3.34
4.	3.5	3.72
5.	4.5	4.65
6.	5.5	4.97
7.	6.5	5.18
8.	7.5	4.40

10% Pb (NO₃)₂; 10 ml. + 20% sodium potassium tartarate; + 6 ml. + 20% NaOH, X ml. made upto 100 ml.

Corresponding value for this reading without sodium potassium tartarate is 8.33 percent.

It will be seen from the Table 1 that although tartarate helps in keeping Pb in solution even with less amount of NaOH, nevertheless, it exerts more masking effect than NaOH alone and therefore, gives lower figures for the lead absorbed by cellulose. Further, effect of changing the amount of alkali in regions of lower concentration is more pronounced in this case than in (iv) where in very high concentrations, the amount of alkali was increased twice and four times, but did not produce such a shift in the absorption of lead.

Reaction of Antimony with Cellulose

For this study antimony potassium tartarate was selected as the chemical supplying antimony as antimony trichloride hydrolysed readily when its solution was prepared and required large amount of hydrochloric acid for clear solution, which is not desirable.

In most of the experiments, 5 percent stock solution of antimony potassium tartarate containing 1.858 percent Sb was used; in some cases, a 10 percent stock solution prepared by warming was also used. 75 ml. of 5 percent stock solution required 13.5 ml. of 20 percent NaOH for the precipitation and redissolution of antimony and the volume was made upto 100 ml. Other solutions were prepared by keeping the same ratio of chemicals as above. Although solutions so obtained remained stable at room temperature and even on boiling, a fresh solution was always prepared for carrying out the individual experiments. All the experiments were conducted at 30°C. for a period of 5 minutes only as raising the temperature and prolonging the reaction time did not produce any significant change in the absorption of antimony by cellulose.

The experiments were performed on commercially bleached dosooti which was further purified as in the case of a similar study with lead by using pieces weighing 1.0 g. ± 0.05 and 25 ml. of the reacting solution. Since the reaction time was limited to 5 minutes, constant agitation of the solution and fabric with hand was considered adequate. At the end of the experiment, cellulose was removed and washed free of chemicals. Antimony from the cellulose was removed with 20 ml. of 10 percent HCl, titrated against permanganate, and the percentage of Sb calculated on the basis

of moisture free cellulose. Some of the variables studied are discussed below:

(i) *Effect of Concentration of Antimony on the Absorption.*—Alkaline solutions containing various amounts of antimony but keeping the same ratio of chemicals as described earlier were prepared and the absorption studied for 5 minutes at 30°C. The absorption figures are given below:

Concentration of Sb in alkaline solution g./litre	% of Sb absorbed by cellulose
6.967	1.35
13.935	1.90
27.870	2.65

A more concentrated solution of antimony potassium tartarate required heating in order to give antimony contents higher than 27.870 g./l in the alkaline solution and was not considered necessary, yet it will be seen that while the concentration of Sb in the reacting solution is increased four times, the corresponding increase in the absorption is only two-fold.

(ii) *Effect of Alkali on the Absorption of Antimon.*—In this case the final alkaline solution contained 13.935 g./l of Sb but varying amounts of sodium hydroxide. Table 2 gives the results at 30°C. and 25:1 liquor ratio.

TABLE 2.

S. No.	Value of X, ml.	Amount of Sb g./100 g. of cellulose
1.	6.75	1.90
2.	13.50	1.69
3.	27.00	1.44
4.	54.00	1.28

10% antimony potassium tartarate; 37.5 ml. + 40% NaOH, X ml. made upto 100 ml.

In the case of reading at serial 4, the cellulose had become swollen greatly showing the causticizin geffect, yet the amount of Sb absorbed decreased gradually when the concentration of alkali was increased many times.

(iii) *Effect of Volume on the Absorption of Antimony.*—Using the same ratio of chemicals as in S. No. 1 of Table 2 and employing 25, 50 and 100 ml. of the solution for 1 g. of cellulose pieces, the absorption figures were 1.90, 2.00 and 2.36 percent, respectively.

(iv) *Absorption of Antimony in the Presence of Additional Amounts of Tartarate.*—In all these experiments, no allowance has been made for the role of tartarate which becomes available from antimony potassium tartarate. It was found that 37.5 ml. of 10 percent antimony potassium tartarate in the presence of 15 ml. of 20 percent sodium potassium tartarate required only 3.6 ml. of 20 percent NaOH as against 13.5 ml. of the alkali in the absence of additional tartarate. The effect of alkali and tartarate together is to further reduce the absorption of Sb as shown in Table 3.

TABLE 3.

S. No.	Value of X, ml.	Sb absorbed g./100 g. of cellulose
1.	3.6	0.63
2.	6.0	0.68
3.	7.5	0.69
4.	10.0	0.67
5.	13.5	0.62

10% antimony potassium tartarate + 20% sodium potassium tartarate; 15 ml. + 20% NaOH, X ml. made upto 100 ml.

The corresponding value without additional tartarate for this reading is 1.90 percent.

Leaching Action by Water on Absorbed Antimony.—One gram pieces treated with antimony were refluxed for one hour in 200 ml. of water at the boil and the residual amount of Sb determined. The values are given below:

Control 1.84%; Residual 1.40% of Sb;
Loss of Sb due to leaching 23.95%.

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