The melting point of sagittol is 77–78° (uncorr.); its average specific rotation in 95% alcohol is +26.15° at an average concentration of of 2.252 g. per 100 cc. Sagittol crystallizes as very fine needles, the optical properties of which have been determined.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES.

XXXI. THE BEHAVIOR OF CELLULOSE TOWARD SOLUTIONS OF ALUMINUM SALTS

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In view of the important role played by aluminum sulfate in the process of the rosin sizing of paper, many investigations have been carried out to ascertain the mechanism of the adsorption by the cellulose fiber. Schwalbe and Robsahm,[2] using sulfite pulps, claimed that cellulose decomposed aluminum sulfate up to 3% of its weight, but Schwalbe[3] in a re-investigation of the problem states that neither cotton nor pulp takes up appreciable amounts of aluminum hydroxide from aluminum sulfate solutions. Sutermeister[4] found that the amount adsorbed was never greater than 0.3% of the weight of the fiber and was independent of the concentration of the aluminum sulfate solution employed.

It was concluded by Tingle[5] that the observed withdrawal of aluminum hydroxide from solutions of aluminum sulfate in the presence of cellulose is due to the non-cellulosic constituents of the fiber. He could detect no adsorption by ordinary analytical methods where the cellulose was of a reasonable degree of purity, and concluded that within the limits imposed pure cellulose will adsorb no aluminum hydroxide from the solution.

In the case of aluminum acetate, and also in some cases with aluminum sulfate, Haller[6] found "negative adsorptions" by analysis of the residual solutions, but actually in every case, some fixation of aluminum hydroxide by the fiber had occurred. Durst[7] also found that "negative adsorption" took place with wood pulps from aluminum acetate solutions. The ash

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[1] Research Fellow, Pulp and Paper Research Institute, Montreal, Canada. The authors desire to express their thanks to the Canadian Pulp and Paper Association for financial assistance rendered in connection with this investigation.

[2] Schwalbe and Robsahm, *Wochenblatt*, **43**, 1454 (1912).

[3] Schwalbe, *Z. angew. Chem.*, **37**, 125 (1924).

[4] Sutermeister, *Pulp and Paper Mag. of Canada*, **11**, 803 (1922).

[5] Tingle, *J. Ind. Eng. Chem.*, **14**, 198 (1922).

[6] Haller, *Chem.-Ztg.*, **42**, 597 (1918).

[7] Durst, *ibid.*, **43**, 373 (1919).

content of the original pulp however, decreased, although aluminum was present in the ash after adsorption.

This so-called negative adsorption appears to be due partly to adsorption of water by the fiber[8] and partly to the entry into solution of the mineral constituents of the ash of the pulp.

Michaelis and Rona,[9] using the salts of basic and acid dyes with cellulose, first advanced the theory of "Exchange Adsorption" which has been applied to the case of aluminum sulfate and cellulose by Roschier[10] and by Kolthoff.[11]

According to the latter investigator, the ash is supposed to act as a type of calcium permutite, exchanging aluminum for calcium thus

$$3\text{Ca-permutite} + 2\text{Al}^{+++} \rightleftharpoons 2\text{Al-(permutite)}_3 + 3\text{Ca}^{++}$$

The purpose of this investigation was to determine (a) whether "ash-free cellulose" adsorbs aluminum compounds from solutions of aluminum salts; (b) the hydrolysis of the aluminum salts in solution and the effect of this factor on the adsorption; (c) the nature of the "Exchange Adsorption."

Preparation of Materials.—The aluminum sulfate, obtained from Merck and Co. gave an analysis Al_2O_3, 16.64%; SO_3, 39.00%. Solution in water left a small amount of insoluble residue amounting to 0.15%. The clear solution obtained on filtering gave a ratio of $Al_2O_3:SO_3 = 1:3.001$. The material was taken therefore as a representative sample of normal aluminum sulfate.

Owing to the difficulty of obtaining either pure aluminum acetate or chloride, these were prepared from the normal aluminum sulfate solution and the corresponding barium salt. Equivalent solutions were mixed and the precipitated barium sulfate was removed by centrifuging. The solution was then adjusted until no precipitate was obtained on the addition of either component.

Owing to their instability the aluminum acetate solutions were kept at 0° when not in use.

The celluloses used were

A. Cotton cellulose, α-content, 99.1%; ash, 0.05%.
B. "Brown" α pulp (i), α-content, 95.3%; ash, 0.14%.
C. Whatman Ashless Filter Paper, No. 42, α content, 99.8%; ash, 0.01%.
D. "Brown" α pulp (ii), α-content, 95.0%; ash, 0.08%.

The ash in each case contained calcium, iron and silica except C, which contained no iron.

The solutions employed for adsorption were shown to be free from calcium, iron and zinc.

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[8] Percival, Cuthbertson and Hibbert, THIS JOURNAL, **52**, 3257 (1930).

[9] Michaelis and Rona, *Biochem. Z.*, **97**, 57 (1919).

[10] Roschier, *Papierfabrikant*, **49**, 757 (1928).

[11] Kolthoff, *Pharm. Weekblad*, **58**, 233 (1921).

Experimental

The Adsorption from Aluminum Salt Solutions.—The adsorption was carried out at 25.0° in a glass vessel closed with a firmly fitting glass cap to prevent evaporation.

Three hundred and fifty cc. of each of the respective solutions was used for each experiment and 20 g. of air dry cellulose, or pulp, which was shaken up well with the solution and allowed to stand in the thermostat for about twelve hours.

At the end of this time the liquid was filtered off and the cellulose washed with 2000 cc. of distilled water three times in succession, making a total of six liters, the operation extending over one hour. The material was then dried for a few minutes at the pump, transferred to a beaker and 50 cc. of strong hydrochloric acid (*d*, 1.18) was added, the mixture then being allowed to stand at room temperature for two hours. The acid was filtered off and the cellulose thoroughly washed with 800 cc. of water, the filtrate and washings being collected and evaporated to 100 cc. Ammonium chloride was added to the latter and the mixture boiled. This was followed by the addition of ammonium hydroxide to precipitate aluminum hydroxide which was collected, ignited and weighed as Al_2O_3.

Analysis of the ash of the cotton or pulp after the adsorption and acid treatment failed to reveal the presence of alumina, indicating the efficiency of the process for removing adsorbed aluminum hydroxide.

Effect of Dilution and Hydrogen-Ion Concentration on the Adsorption from Aluminum Sulfate Solutions.—The hydrogen-ion concentration measurements were made using a Leeds and Northrup potentiometer in conjunction with a calomel half cell and a hydrogen electrode.

The effect of dilution (and the corresponding change of *P*H) on the adsorption was studied with respect to cotton cellulose "A."

The results are given in Table I; *v* represents dilution in liters per gram molecule and the adsorptions are expressed in grams of Al_2O_3 per 100 g. of cellulosic material. Throughout this paper they will be designated as *N*.

TABLE I

EXPERIMENTS WITH SURGICAL COTTON (SAMPLE A). EFFECT OF VARIATION IN CONCENTRATION OF ALUMINUM SULFATE SOLUTIONS

v	*P*H	*N*
4.86	2.84	0.050
16.91	3.09	.053
18.06	3.13	.060
50.20	3.24	.062
84.50	3.33	.080
340.20	3.54	.072

It is evident that the adsorption increases slightly with increasing dilution.

The influence of hydrogen-ion concentration was studied on celluloses C and D ("Brown" α pulp and Whatman's ashless filter paper).

The change in *P*H was accomplished by the appropriate addition of carbonate-free sodium hydroxide solution. The slight precipitate which formed in the preparation of the solutions for Expts. 3 and 4, Table II, was filtered off and the clear solution used in the adsorption experiments.

It is evident that a change in *P*H value brings about a marked alteration in the adsorption.

Since an analysis of each of the equilibrium solutions indicated the presence of calcium and iron in appreciable amounts, the question naturally arose as to whether the entire adsorption was due to this factor.

TABLE II

EXPERIMENTS ON THE EFFECT OF VARIATION IN HYDROGEN-ION CONCENTRATION OF ALUMINUM SULFATE SOLUTIONS

No.	*v*	*P*H	Brown α pulp (D)	Whatman's ashless filter paper
1	50.2	3.24	0.054	0.020
2	49.4	3.65	.060	.031
3	49.5	3.83	.082	.033
4	53.9	3.83	.081	.035

It was also of interest to determine whether all of the constituents originally present in the ash passed into solution during a single adsorption, or were progressively removed in decreasing amounts upon a repetition of the first treatment.

Successive Adsorption Experiments in Solutions of Aluminum Sulfate.—Successive adsorption experiments were carried out in the following manner. The actual experimental method was exactly the same as previously described for a single adsorption. After removal of the hydrochloric acid extract, the cellulose sample was washed repeatedly, using a total volume of four liters of water, then dried at the pump and the adsorption process repeated.

The results are given in Table III for an aluminum sulfate solution, *v*, 51.2; *P*H, 3.25.

TABLE III

RESULTS

Adsorption	No. 1	No. 2	No. 3	No. 4
% Adsorption per 100 g. *N* (B′)	0.070	0.023	0.018	0.010
% Adsorption per 100 g. *N* (C′)	.020	.011	.007	.005

With both cellulose products, calcium, and in the case of cellulose B, iron, was found in the solution after the first adsorption, but apparently very little in the subsequent treatments.

The treatment of the cellulose with hydrochloric acid solution (about 25% HCl after dilution with the water in the pulp) results in a small amount of degradation as shown below.

Alpha-cellulose determinations were made using a slight modification of the American Chemical Society method[12] on the pulp "B" after adsorption from aluminum sulfate solution and treatment with hydrochloric acid; this gave an indication of the extent to which this degradation had taken place.

[12] Moore, M.Sc. Thesis, McGill University, May, 1930.

The α-cellulose values after successive adsorptions and acid treatment are given in Table IV.

TABLE IV

α-CELLULOSE VALUES

Adsorptions	No. 0	No. 1	No. 2	No. 3	No. 4
Alpha-cellulose value	95.3	92.1	90.8	..	88.2

The "successive adsorption" method of attack was extended to aluminum acetate and chloride solutions, to find how the increased degree of hydrolysis and the specific nature of the anion would alter the amount of aluminum hydroxide taken up. The results are given in tables V and VI

TABLE V

EXPERIMENTS WITH ALUMINUM ACETATE SOLUTIONS

v, 49.7; P_H, 4.41

Adsorption	No. 1	No. 2	No. 3	No. 4
% Adsorption (N) Sample B	0.119	0.084	0.063	0.059
% Adsorption (N) Sample C	.051	.042	.039	.034

A trace of calcium was still found in the residual liquid after the third adsorption using Sample B.

TABLE VI

EXPERIMENTS WITH ALUMINUM CHLORIDE

v, 49.1; P_H, 2.97

Adsorption	No. 1	No. 2	No. 3	No. 4
% Adsorption (N) Sample B	0.065	0.047	0.029	0.024
% Adsorption (N) Sample C	.024	.018	.014	.014

Qualitatively, calcium appeared to be removed as slowly as in the case of aluminum acetate.

Discussion of Results

A consideration of Table I leads to the conclusion that a slight increase in adsorption of aluminum hydroxide takes place with dilution, involving a correspondingly smaller hydrogen-ion concentration. The same effect is apparent in Table II, where dilution is practically constant and hydrogen-ion concentration decreases in approximately the same way.

It would appear therefore that in addition to exchange adsorption, at least part of the latter is to be attributed to the removal of $Al(OH)_3$ from the solution, formed by hydrolysis of the aluminum sulfate.

Tables III, V and VI represent successive adsorption experiments from solutions of the sulfate, acetate and chloride, respectively.

It is to be noted that the difference between the first and second adsorption values in Table III is very marked as compared with corresponding values in Tables V and VI.

Since, as indicated above, a large part of the calcium and iron is removed after the first adsorption from aluminum sulfate solution, while the removal is much slower in the other two cases, it would appear logical to assume that adsorption is closely associated with the calcium and iron content of the ash.

Inasmuch as a slight amount of degradation arises from the action of the hydrochloric acid which is used to remove the aluminum hydroxide, the validity of the successive adsorptions might be considered as depending on the extent to which this degradation takes place.

However, Freundlich[13] has shown that the adsorption by a pure cellulose is much less than for a cellulose which has been subjected to drastic chemical treatment. Also Clibbens and Ridge,[14] in studying the rate of oxycellulose formation, show that the greater adsorption of methylene blue occurs at the point of maximum degradation.

From this evidence, therefore, one would anticipate an increased adsorption by the cellulose with an increasing number of treatments with hydrochloric acid.

If the decreasing values found for successive adsorptions cannot be attributed to a degradation of the fiber it would seem that the conclusion is permissible that the amounts of aluminum hydroxide taken up by the fiber depend on two factors (i) a "natural" and (ii) an "exchange" adsorption.

The "natural" adsorption is a variable quantity possibly depending on the specific nature of the fiber, the extent of hydrolysis of the solution, the hydrogen-ion concentration and the anion; under normal conditions it plays a minor role in comparison with that of the "exchange" adsorption.

According to Michaelis and Rona[9] and Kolthoff,[11] the "exchange" adsorption depends on the replaceable elements in the ash.

If it is comparable to the case of the permutite the "exchange" adsorption must be a fixed amount depending only on the ash constituents.

A consideration of Table III for aluminum sulfate shows that the first adsorption may be made up of a relatively high "exchange" value and a small "natural" adsorption. Since nearly all of the calcium and iron is removed in the first treatment, the successive values are much lower, and the fourth value is presumed to correspond to the "natural" adsorption of a cellulose free from replaceable ash constituents under those conditions. In the case of the other salts of aluminum the removal of these replaceable constituents is much slower (Tables V and VI), as evidenced by the gradual decrease of the values of N, which is further substantiated by the experimental fact that a definite amount of calcium was present even after the second treatment.

Assuming the "exchange" adsorption to be a property of the aluminum ion, and having the same value for each of the three different aluminum solutions used, the "exchange" value can be calculated in the case of the sulfate, and applied to the other salt solutions to calculate the "natural"

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[13] Freundlich, *Cellulosechemie*, 7, 57 (1926).

[14] Clibbens and Ridge, *Shirley Inst. Mem.*, VI, 1 (1927).

adsorptions. These values thus calculated are shown to agree with the value of N at the fourth adsorption (selected as the natural adsorption in the case of aluminum sulfate), and this is taken as the mean "natural" value.

The calculation is carried out in the following way. From Table III each of the first three adsorptions represents "exchange" combined with "natural" adsorption. Natural adsorption for cellulose B = 0.010 and this amount of aluminum hydroxide (expressed as Al_2O_3) is adsorbed in each case as well as the amount contributed by the exchange process.

Hence total "exchange" adsorption for cellulose B $= 0.070 + 0.023 + 0.018 - 3 \times 0.010 = 0.081$, and for cellulose C $= 0.020 + 0.011 + 0.007 - 3 \times 0.005 = 0.023$.

Taking these values as fixed, the mean "natural" adsorption from the results contained in Table V for aluminum acetate is calculated thus

Total adsorption $= 0.119 + 0.084 + 0.063 + 0.059 = 0.325$

Exchange adsorption from above $= 0.081$

Therefore mean natural adsorption $= \dfrac{0.325 - 0.081}{4} = 0.061$

A comparison of the observed (value at fourth adsorption) and calculated "natural" adsorptions, is given in Table VII.

TABLE VII

COMPARISON

Salt	v	P_H	% Adsorp., sample B Observed	% Adsorp., sample B Calculated	% Adsorp., sample C Observed	% Adsorp., sample C Calculated
$Al_2(SO_4)_3$	51.2	3.25	0.010	..	0.005	..
$Al(C_2H_3O_2)_3$	49.3	4.41	.059	0.061	.034	0.036
$AlCl_3$	49.1	2.97	.024	.021	.014	.012

The values agree very closely and it would seem therefore that "exchange" adsorption ceases after four adsorptions.

The "natural" adsorptions from solutions of aluminum acetate and chloride are much greater than from the sulfate solutions. This is to be anticipated since the hydrolysis is more marked in the former solutions.

Denham[15] and Pelling[16] by electrometric methods determined the extent and mechanism of the hydrolysis of aqueous aluminum sulfate and chloride solutions, and showed that the chloride suffered greater hydrolysis than the sulfate under identical conditions, and that a single water molecule was most probably concerned in effecting the hydrolysis, *e. g.*, $AlCl_3 + H_2O \rightleftharpoons Al(OH)Cl_2 + HCl$.

In order to complete the comparison, the hydrolysis of aluminum acetate was studied using a similar technique. The results are given in Table VIII.

Comparison with the results of Denham[15] and Pelling[16] shows that of the three salts the acetate undergoes most hydrolysis. Furthermore, the

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[15] Denham, *J. Chem. Soc.*, **99**, 41 (1908).

[16] Pelling, *J. Chem. Met. Min. Soc. South Africa*, **26**, 88 (1925).

hydrolysis constant K corresponds most closely with the same mechanism as assumed for the other two aluminum salts

$$Al(C_2H_3O_2)_3 + H_2O \rightleftharpoons AlOH(C_2H_3O_2)_2 + C_2H_4O_2$$

TABLE VIII

HYDROLYSIS OF ALUMINUM ACETATE AT 25°

v	$C_H \times 10^4$	$100\ x$	$K \times 10^4$
7.64	0.589	3.77	1.94
15.28	.513	4.75	1.55
31.56	.447	5.99	1.21
49.70	.389	6.64	0.95
63.12	.389	7.43	.95
126.20	.347	9.41	.78
252.5	.347	13.45	.83

$100\ x$ = percentage hydrolysis.
$K = X^2/(1-x)v$, for the first stage hydrolysis.

Ostwald's dilution law was used to calculate the value of C_H and the ionization constant for acetic acid was taken to be 1.8×10^{-5} at 25°.

It is evident therefore, that since the three salts undergo the same type of hydrolysis, the natural adsorption is connected, for the most part, with the extent to which the equilibrium

$$AlX_3 + H_2O \rightleftharpoons Al(OH)X_2 + HX$$

is shifted to the right, concomitant with the change in hydrogen-ion concentration.

Whether aluminum hydroxide is taken up directly from the solution by the fiber as suggested by Bancroft[17] or whether the basic aluminum salts known to be present are first adsorbed and then decomposed by adsorbed water, is not clear,

The fact remains however that except in strongly hydrolyzed solutions, such as aluminum acetate, by far the major part of the adsorption is due to the exchange process between iron and calcium (presumably as silicate) and the aluminum salts.

The conclusions to be drawn are that with solutions of these three salts of aluminum, the adsorption by cellulose may be represented by a small "natural" adsorption on which an "exchange" adsorption is superimposed, the mechanism of the latter being comparable to the permutite theory as advanced by Kolthoff.

Summary

1. The adsorption from aluminum salt solutions by different celluloses has been studied and by successive adsorption experiments it has been shown that small but definite amounts of $Al(OH)_3$ are adsorbed by ash-free cellulose, *i. e.*, a cellulose free from constituents capable of "exchange."

2. The adsorption has been found to be made up of two effects, the

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[17] Bancroft, *J. Phys. Chem.*, **26**, 501 (1922).

"natural" adsorption and the "exchange" adsorption. The "natural" adsorption depends on the dilution and P_H value of the solution. The "exchange" adsorption seems to depend on the mineral content of the original ash, principally on the amounts of calcium and iron present.

3. The mechanism of the hydrolysis of aluminum acetate is shown to be the same as for the chloride and sulfate solutions, while the adsorption increases with increasing hydrolysis, being highest for the acetate.

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RING ENLARGEMENT WITH DIAZOMETHANE IN THE HYDROAROMATIC SERIES[1]

BY ERICH MOSETTIG AND ALFRED BURGER

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The present investigation was begun in a search for a preparative way to amino-alcohols of the type V, since compounds of this class may be expected to have interesting pharmacological properties. The oxide III appears to be the most convenient starting point for the synthesis of such substances; by simple addition of primary and secondary amines, with opening of the ethylene oxide ring, the oxide must be converted to amino-alcohols of the desired type. A method for the preparation of this hitherto unknown oxide lies in the action of diazomethane on cyclohexanone; the expected oxide represents, however, but one phase of the reaction.

The action of diazomethane on the carbonyl group in the aliphatic, aromatic, and heterocyclic series has been the subject of numerous recent investigations. Arndt and his co-workers[2] were the first to show that the reaction discovered by H. Meyer[3] and Schlotterbeck,[4] in which aldehydes are converted to the corresponding ketones by the action of diazomethane

$$\mathrm{RCHO} \xrightarrow{\mathrm{CH_2N_2}} \mathrm{RCOCH_3}$$

is not of general application. In some cases the reaction leads to the isomeric ethylene oxide derivative, while the ketone and a homolog are formed in small amounts as by-products. The mechanism postulated

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[1] This work was supported by funds from the Committee on Drug Addiction of the National Research Council.

[2] Arndt and Partale, *Ber.*, **60**, 446 (1927); Arndt, *Z. angew. Chem.*, **40**, 1099 (1927); Arndt and Eistert, *Ber.*, **61**, 1118 (1928); *cf.* Arndt, Eistert, and Amende, *ibid.*, **61**, 1952 (1928); Arndt, Eistert, and Ender, *ibid.*, **62**, 44 (1929).

[3] H. Meyer, *Monatsh.*, **26**, 1300 (1905); *Ber.*, **40**, 847 (1907).

[4] Schlotterbeck, *ibid.*, **40**, 479 (1907); **42**, 2559 (1909).