

# DETERMINATION OF ION-EXCHANGED CAPACITY OF CARBOXYMETHYLATED CELLULOSE FIBERS USING COLLOID AND CONDUCTOMETRIC TITRATIONS

Lars Wågberg, Lars Winter and Tom Lindström  
Swedish Forest Products Research Laboratory, Paper Technology Department  
Box 5604, S-114 86 Stockholm, Sweden

## ABSTRACT

The carboxyl group content of a series of carboxymethylated pulps has been determined by a colloid titration method, by conductometric titration and by means of  $^{14}\text{C}$ -labelling and the values obtained by the different methods have been compared.

It is shown that, under certain experimental conditions, the colloid titration method can be used to determine the carboxyl group content of cellulose fibers.

## INTRODUCTION

Today it is commonly accepted that the carboxyl group content of the pulp used in papermaking is important for paper strength, through fiber swelling, fines retention, sizing and adsorption of wet end additives such as cationic starches, wet strength resins etc. The development of techniques for the determination of the carboxyl group content of different pulps has therefore attracted attention and various methods have been developed (1).

Recently it has been shown that conductometric titration is also a suitable method for the determination of the carboxyl group content of cellulose fibers (2). Meanwhile, some workers have used colloid titration in combination with adsorption experiments (3) to determine the surface charge of different pulps (4, 6). No investigation has, however, yet been published concerning the stoichiometric relationship between the charges on the cellulose fibers and the quantity of the polymer adsorbed.

The purpose of this short presentation is to show that, under certain specified conditions, colloid titration following polymer adsorption can be used to determine the total carboxyl group content of carboxymethylated bleached pulps.

## EXPERIMENTAL

### Equipment

In order to detect the end point of the colloid titration an apparatus similar to the equipment described by Horn (7) was built. The conductometric titrations were performed using a Radiometer CDM 80 conductivity meter fitted with CDC 30 conductivity electrode. A microcomputer control system enabled automation of both types of titration.

To measure the amount of  $^{14}\text{C}$  in the radioactive carboxymethylated pulps they were burned in a Packard Tri-Carb Sample Oxidizer (Packard Instr. Co. Inc., Ill., USA). The radioactivity was measured in a Packard Tri-Carb 3255 Liquid Scintillation Spectrometer.

A microelectrophoresis instrument (Rank Bros., UK) equipped with a flat cell at  $25 \pm 0.2^\circ\text{C}$  was used to measure the z-potential.

### Materials

The pulp used in these model experiments was a dried Acetakraft<sup>R</sup> pulp from International Paper Co., Mobile, Ala., USA, with a native carboxyl group content of 3 meq/100g. It was carboxymethylated to different degrees of substitution (D.S.) with  $^{14}\text{C}$ -labelled monochloroacetic acid according to the procedure devised by Walecka (8).

Monochloroacetic acid, solvents and inorganic electrolytes were of analytical grade. The deionised water used had a conductivity of less than  $2 \mu\text{S}/\text{cm}$ .

Polymers used were 1,5-dimethyl-1,5 diazaundecamethylene polymethobromide (Polybrene) from Aldrich Chem. Co., USA and potassium polyvinyl sulphate (KPVS) from Wako Pure Chem. Ind. Ltd., Japan. The molecular weight of polybrene was determined by light scattering to be  $1.0 \times 10^4$ . Both polymers were used as received without further purification. Orthotoluidine Blue (OTB) was used as indicator.

## Methods

After carboxymethylation the pulps were thoroughly washed and refrigerated. Prior to the colloid and conductometric titrations the pulps were washed with 0.1 M HCL to remove any sorbed metal ions and to convert the cellulose carboxy groups to their H-form, and were then washed with deionised water. For the colloid titrations, the cellulose carboxyl groups were then converted to their Na-form through treatment with  $10^{-3}M$   $NaHCO_3$  and were washed with deionised water.

The adsorption experiments were all performed at a fiber concentration of 5 g/l in deionised water. To a series of at least five 100 ml samples different amounts of polybrene were added. The samples were stirred for 30 minutes in order to reach adsorption equilibrium. The suspensions were then filtered on a Buchner funnel, Munktell filter paper no. 3, and the clear filtrate collected. Using colloid titrations, with KPVS as polymeric anion and OTB as indicator, the concentration of polybrene in the clear filtrate was determined. In order to avoid disturbances from OTB during the titrations it was found necessary to keep the ratio of polybrene to OTB equivalents larger than 5.

The point at which the polybrene adsorption was shown by the colloid titration to be 90% was taken as indicative of the carboxyl group content. In preliminary adsorption experiments it was found that the z-potential of the suspension passed through zero when the polybrene adsorption was 90% (of added polymer), and also that the amount of polymer adsorbed at this level agreed very well with the carboxyl group content as determined by the other techniques. This detection level was then used throughout the experiments.

The carboxyl group content was evaluated from conductometric titrations by a method similar to that described in (2).

RESULTS

Correlation between colloid titrations, conductometric titrations and <sup>14</sup>C labelling.

In order to establish the relationship between the carboxyl group content monitored by the two titration methods and by the <sup>14</sup>C labelling technique, titrations were performed on the carboxymethylated bleached pulps with different D.S. values. The results are summarised in Table 1 and Fig. 1.

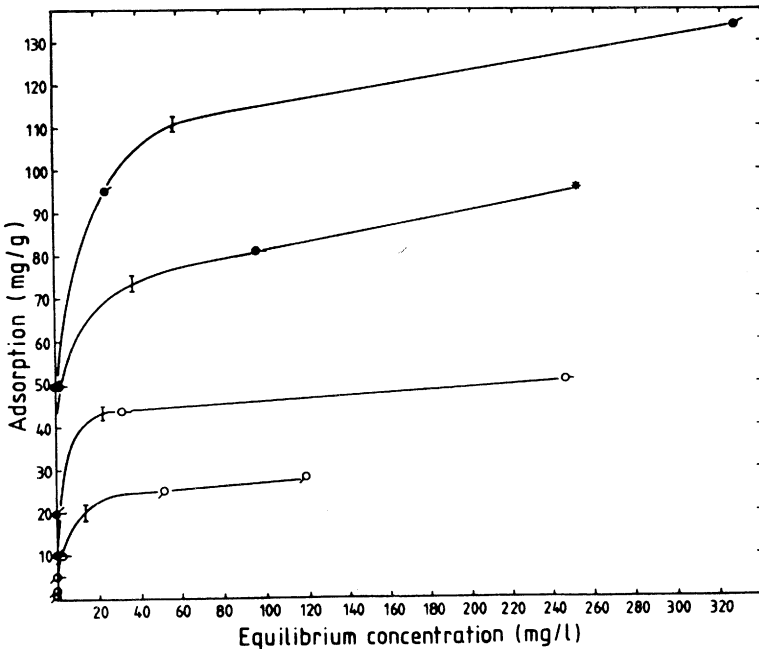


Fig 1—Adsorption of polybrene on carboxymethylated fibers with different D.S.values. In the figure, the letter I shows the position of the isoelectric point.

\* indicates that an extrapolation is made to an experimental point not contained in the figure.

D.S. levels:  $\circ$  = 0.013,  $\circ$ - = 0.029,  $\bullet$  = 0.052,  $\bullet$ - = 0.086

D.S.*	Colloid titr. (meq/100 g)	<sup>14</sup> C (meq/100 g)	Cond. titr. (meq/100 g)
0	0.80	0	3.0
0.013	12.5	8.1	13.8
0.029	21.7	17.8	24.9
0.052	36.1	31.1	38.9
0.086	56.6	51.0	58.7

\* As calculated from <sup>14</sup>C labelling.

Table 1 Charge on carboxymethylated fibers with different D.S. values determined by three different techniques. Colloid titration values were obtained by polybrene adsorption.

It can be seen in the table that there is a close agreement in the carboxyl group content obtained by the three different methods. The value obtained by the <sup>14</sup>C-labelling technique is somewhat lower than the value obtained by the titration techniques. This is to be expected since the native pulp contains some carboxyl groups (3 meq/100g). From Fig 1 it can also be seen that the 90% adsorption level, i.e. the isoelectric point, corresponds fairly well with the plateau-level in the adsorption isotherms.

## DISCUSSION

In Table 1 it is shown that, when polybrene is used as the cationic polyelectrolyte, the amount of cationic charges adsorbed at the isoelectric point corresponds rather well with the number of carboxyl groups on the fibres.

Furthermore the amount of adsorbed polymer at the isoelectric point i.e. the 90% adsorption level) is very close to the plateau level of the adsorption isotherm. These results clearly indicate that an ion-exchange between sodium ions and polybrene is the dominating adsorption mechanism for adsorption of the polybrene molecules. This is also in agreement with results from adsorption experiments with a polyamide-epichlorohydrin (PAE) wet strength resin (9) onto cellulose fibers, where it was shown that every two repeating units of PAE resin expelled one equivalent of calcium.

When considering the possibility of an ion-exchange between sodium ions and polybrene, several phenomena have to be considered. It is known (10, 11) that non-ionic polymers with a diameter larger than 50 Å are excluded from the smallest pores of the fiber structure. Since polybrene molecules have a length of about 450 Å in a fully extended state it might be suggested that these molecules cannot have full accessibility to the smallest cavities in the fibers. Even though the polybrene molecules have a relatively high charge density, some coiling of the molecules must be expected resulting in a radius of gyration smaller than 225 Å. Assuming a random coil the radius of gyration would be 26 Å. The true radius of gyration is thus somewhere between 26 Å and 225 Å. This suggests that the polybrene molecules may have accessibility to the smallest pores in the fibers. Other unpublished experiments in our laboratory have also shown that, when polymers with a high molecular weight ( $> 1.10^5$ ) are used, there is no 1:1 stoichiometry between the charges on the fibers and on the adsorbed polymer. This result indicates that the smallest pores in the fibers are not accessible to high molecular weight polymers.

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## Transcription of Discussion

### Determination of Ion-exchange Capacity of Carboxymethylated Cellulose Fibres using Colloid and Conductometric Titrations

by L. Wågberg, L. Winter and T. Lindström

**Nazir** You showed in your experimental procedure that you allowed the polymer to mix with fibre for a period of 30 minutes. In one of your graphs, you showed the difference between 30 minutes and 24 hours mixing time. Why did you select 30 minutes and why not, say, 5, 10, 15 or 20 minutes? Thirty minutes strikes me as a very long time.

**L. Wågberg** We looked at the adsorption after 5, 10, 15, 20 and 30 minutes. The system did not equilibrate until 20 minutes had elapsed and we chose 30 minutes to be on the safe side. For the non-treated sample, however, this time was evidently not enough for equilibrium concentration to be reached.

**C.B.Neal** Proctor and Gamble, Cincinnati, Ohio, U.S.A.

We have also used a colloid titration for determination of surface charge. One of the things we have done is to compare high and low molecular weight polymers. As the pulp is refined, the retention of the low molecular weight polymer remains constant, whereas retention of the high molecular weight polymer increases with increased refining. Our interpretation of this is that the high molecular weight polymer is confined to the surface and that the increase in retention reflects an increase in surface area via refining. A high molecular weight polymer, therefore, can be used to determine a relative surface charge very effectively.

**Wågberg** All I would like to say to this comment is that we are working with the same approach to the problems you mention.



Dr. T.M. Herrington Reading University, England

I would like to make two comments.

You emphasise the adsorption of polyelectrolyte as being dependent on charge effects. It is, however, generally accepted that hydrogen bonding is the dominant adsorption mechanism for polyacrylamide adsorption.

Secondly, for Kaolinite, a non-porous solid, we find that for two cationic polymers of identical cationic charge character, the polymer of lower molar mass has the greater adsorption gram for gram.

This is by way of a note of caution as to what is the relevant molar mass to be used to obtain definitive results.

**Wägberg** I would agree with your experience with Kaolinite. There have been recent articles in the "Journal of Colloid and Interface Science" stating that you have hydrogen bonding for a Kaolin/polyacrylamide system. We have studied the adsorption of non-ionic polyacrylamide on cellulose and we have seen no adsorption whatsoever. The polymer used in the experiments described here is of a very high charge density so we think that the adsorption mechanism is definitely an ion exchange mechanism.