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THE USE OF POTENTIOMETRIC TITRATION AND POLYELECTROLYTE TITRATION TO MEASURE THE SURFACE CHARGE OF CELLULOSE FIBRE

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ABSTRACT

The surface charge of cellulosic fibre was determined using two methods. The relative surface charge (PTC) of three bleached pulps was quantified using polyelectrolyte titration and compared with the absolute surface charge (So) measured by potentiometric titration. It was established that the polyelectrolyte titration method was a less tedious, but valid method of determining the surface charge of fibre, providing the titration method is standardised and the effect of variables such as suspension, pH, fibre concentration, ionic content and polyelectrolyte molar mass are eliminated. The method was used to construct a charge/pH isotherm of a bleached hardwood fibre similar to those constructed using potentiometric titration. Furthermore, the effect of refining of bleached hardwood and softwood krafts on the PTC was investigated.

INTRODUCTION

Interactions between the particulate and soluble fractions of papermaking suspensions are largely charge induced. Chemical deposition on to the solid surfaces influences process variables such as single pass retention and drainage of the furnish and determines sheet quality (that is to say the degree of sizing, wet and dry strengths and colour). The surface charge density of cellulose is reported to be a contributing factor in developing the tensile strength of low density paper structures [1]. Surface charge measurement techniques have therefore been developed to establish the charge characteristics of papermaking particulates and study their interaction with charged additives.

Considerable emphasis has been placed on the measurement of the zeta potential of suspended papermaking solids by electrokinetics as a means of predicting and controlling the manufacturing process. In the case of wood pulps it is not possible to define exactly where the zeta potential lies in relation to the surface of the fibre, as the latter is not ideally smooth but covered with fibrillar projections, thus making the assumption that the plane of shear at the surface coincides with the surface doubtful [2]. Over the years it has been customary to characterise pulps by their surface charge by determining zeta potential as a function of pH [3] although new methods have been developed, using potentiometric titration, to obtain isotherms of actual surface charge, derived from carboxylic acid groups on the fibre surface as a function of pH [4]. Previously, oxycellulose, with the cations removed was titrated with sodium hydroxide to yield a single end point. This gives the total carboxyl content and hence the total possible surface charge [5]. Dispersion of the cellulose in sodium chloride solution, followed by measurement of pH, yielded pK value and hence the degree of dissociation under those conditions. By using methylene blue, which has a high affinity for the carboxyl group, Davidson was able to construct an isotherm [6]. However, none of these methods were carried out at constant ionic strength, so that it was not possible to construct an isotherm solely for the dependence of charge on pH. The first attempt at generating a charge/pH isotherm for cellulose at constant ionic strength was made by Edelson [7]. In this work the method used was that developed by Herrington and Midmore [4].

The other method of surface charge determination used in this study was polyelectrolyte titration which is also referred to as "colloid titration" in the literature. Polyelectrolyte titration was initiated by Tarayama [8] and first used to determine surface charge of the papermaking suspension by Halabisky [9]. Since then a number of workers [for example, 10,11,13-16] have applied the technique to characterise cellulosic surfaces and measure the charge of the entire papermaking furnish which also includes mineral fillers. Attempts to measure and compare the results of applying different techniques to cellulosic fibre have been recent [10,11]. This work compares the outcome of using polyelectrolyte titration as a means of measuring surface charge of cellulose fibre with potentiometric titration. Three bleached pulps were used and samples from the same batch were subjected to both titrations. Polyelectrolyte titration was then used to construct a charge/pH isotherm of a bleached hardwood sulphate pulp. Furthermore, the technique was used to study the effect of refining on the polyelectrolyte titrated charge (PTC).

EXPERIMENTAL

Potentiometric Titration (Charge/pH Isotherms)

Analar chemicals were used throughout. The sodium hydroxide gave only a single end point when titrated against HCl confirming that it was free from carbonate. The water, supplied from a deionising plant was distilled and delivered through a Millipore milli-Q five cartridge water system (conductivity of 5×10^{-8}S cm^{-1}). Chemically pure nitrogen was used. All experiments were carried out under thermostatically controlled conditions at 25°C. The titroprocessor used for these experiments, was a Metrohm E636 linked to an E635 dosimat automatic burette. All pulps were supplied in the dry sheet form by Wiggins Teape R & D Ltd, Beaconsfield, UK.

Pulp Preparation

A blender was used to disperse 100 g of the fibre in 2 dm^3 of water for 90 seconds. The slurry was then filtered, using a sintered glass funnel, to produce a wet fibre pad. In order to remove any cations, the pad was redispersed in 4 dm^3

0.1 M HCl and left for approximately 16 hours. The suspension was again filtered and thoroughly washed using the conductivity water until the washings were free from chloride (as detected by using silver nitrate solution). Finally, the fibres were filtered over vacuum, until no more water could be extracted, and stored in a refrigerator at 5°C. The pulp content of the pad was about 22% dry solids.

Determination Of Charge

8 g of the wet fibre was dispersed in 450 g of the sodium chloride solution of chosen ionic strength giving a pH of about 4. Chemically pure nitrogen was passed through the solution for 40 minutes to remove residual carbon dioxide and was continued for the duration of the titration. A gas tight vessel was used to keep a positive gas pressure over the solution and a standard silver/silver chloride pH combination electrode was used to monitor pH. The titration of the stirred solution was carried out using 0.02 M sodium hydroxide solution leaving 4 minutes between the titration addition and the pH measurement. This time lag was necessary as equilibration of the system is slow due to the porous nature of the fibre. Using the same titrant, the titration was repeated in the absence of the pulp, using HCl to lower the pH, to the starting pH and allowing 1 minute between making the addition and taking the measurements.

Two correction were necessary to the data before processing it. These were due to the dilution effect of the water added with the pulp and the change in volume of the solution due to the addition of titrant. (The fibre was not fine enough to cause problems with the suspension effect.) The titre, equivalent to the initial drop in pH caused by the addition of pulp to the solution, was added to the difference in titre between the blank titration and the pulp titration. This gave the apparent surface charge of the pulp for any pH covered by the titration (equation (1)). Because of the large errors possible between pH measurement and volume addition at pH's below 3.5 and above 10.5, this continuous method is only suitable between these pH values. A single point method was used to obtain data below pH 3.5. 8 g of the wet pulp was dispersed in 130 cm^3 of sodium chloride solution of chosen acidicity. This was left stirred for 4 hours to equilibrate after which a sample of the supernatant was collected for determination of hydrogen ion concentration by potentiometric titration. This result, together with that of titrating a sample of the solution before the addition of the pulp, gave the charge at that pH of adsorption (equation (2)). The point of zero net surface charge is taken as the intersection of the isotherms for difference values of ionic strength.

$$So = - VcF/w \qquad (1)$$

$$So = [F(X_b t_b - X_p t_p)/xw \qquad (2)$$

S = Surface area
o = Charge
V = Titre difference
c = Titrant concentration
F = Faraday constant
w = Weight of dry pulp
X_b = Weight of solution before the addition of pulp
X_p = Weight of solution plus the weight of water added with pulp
t_b = Titre from analysis of X_b
t_p = Titre from analysis of X_p
x = Aliquot portion taken for analysis

Polyelectrolyte Titration

The Method

Cationic and anionic polyelectrolytes of high charge density and relatively low molar mass react nearly stoichiometrically to produce insoluble polyion complexes. In the presence of a dye indicator the reaction end point can be detected by a clear change in colour (Fig. 1). Trace quantities of soluble polymers of either charge can be measured this way. By treating anionic colloidal surface with polycations the surface charge density of solids can be determined.

The polyelectrolyte titration reagents used were the polyanion potassium polyvinyl sulphate (KPVS), supplied by Kodak, Rochester, N.Y., USA, the polycation 1.5-dimethyl-1, 5-diazaurdecamethylene polymethobromide hexadimethrine bromide (Polybrene) supplied by Aldrich Chemical Co, Milwaukee, USA, and the metachromatic dye toluidine blue. KPVS was standardised using a solution of hexadecyl deimethyl benzyl ammonium chloride and was found to have a charge density of

-0.377 C mg^{-1}. The charge density of Polybrene was +0.520 C mg^{-1} against KPVS.

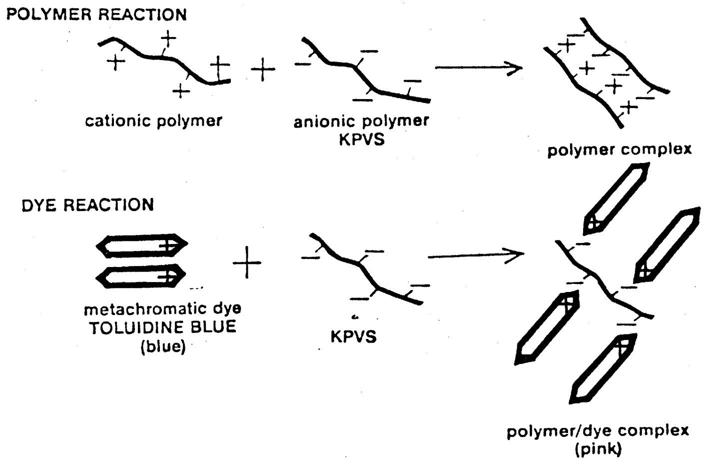

FIG. 1. Polyelectrolyte Titration Reactions

Determination Of Fibre Surface Charge

Deionised water was used throughout the work. The pH was adjusted using 1.0 M HCl and NaOH solutions. The fibre was prepared by disintegrating in a blender at a consistency of 50 g dm^{-3} in 100 cm^3 of water for 90 seconds. The resulting pulp was dewatered under vacuum by filtration and washed through to remove any extracted soluble organics. A sample weighing around 0.3 g oven dried fibre was taken from the wet pad and dispersed in 150 cm^3 0.1 g dm^{-3} solution of Polybrene. The pH of the fibre/polymer suspension was adjusted to 7.0 ± 0.1 before agitation for three hours to allow adsorption equilibrium. At the end of treatment the fibre was separated by centrifuging the suspension. Aliquots of the clear liquid were withdrawn and titrated against 0.1 g dm^{-3} KPVS solution, in the presence of toluidine blue, to determine the quantity of non-adsorbed Polybrene. The exact quantity of fibre treated was determined by filtering the centrifuged material and drying at 100°C to constant weight. The amount of polymer adsorbed per unit weight of fibre was calculated from the difference between polymer added and residual polymer detected. Adsorption was then expressed in terms of charge which was taken to be a measure of the charge density of the fibre surface.

Polycation adsorption over a range of suspension pH was estimated in a similar way. Blank titrations of the two polymers alone were carried out over the same pH range as the suspension to allow for any shifts in the reaction end point. Any slight shift was taken into account in the calculation of adsorbed charge.

Refining Pulps And Segregation Of Fines

A bleached eucalyptus pulp (Celbi) was pulped for 1.5 minutes in deionised water at 40.0 g dm^{-3} and then treated at four refining energies in a laboratory scale Escher Wyss conical refiner. A bleached softwood kraft pulp (Stora 32) was similarly disintegrated in a pilot plant hydrapulper and refined at seven refining energies at 24.0 g dm^{-3} in a Pilao JR-12 disc refiner. Fibre freeness was measured using the standard Tappi method for the determination of the Schopper Reigler value.

The fines content of the resulting pulps was determined using the Dynamic Drainage Jar (DDJ) following the standard procedure of fines separation. A known amount of the pulp was placed in the DDJ fitted with a 125 p (76 microns, 200 mesh) screen. Dispersant was added to the water used to flush the sample through, under constant stirring rate of 1000 rpm, until all fines were removed through the screen. The resulting long fibre was removed from the jar, filtered using a glass fibre disc and dried to constant mass at 105°C to determine the fines content.

Fines were similarly removed from the long fibre used for polymer titration but without the use of a dispersant. Although a copious volume of tap water was needed to flush the fines out, the final 2 litres of water used was deionised. The resulting long fibre was not dried but used for titration in the wet state.

All pulps and chemicals were used within two days of preparation and stored at 5°C when not used. The polyelectrolyte adsorption experiments were carried out using the method described above at an unadjusted pH of 6.5. PTC of the total pulp, containing long fibre and fines, and also the separated long fibres was determined over all the refining ranges. The disintegrated fibre alone was also used.

RESULTS AND DISCUSSION

Charge/pH Isotherms

Fig. 2 shows typical charge/pH isotherms of a bleached kraft pulp [12]. For the purpose of this study, only the surface charge (So) at a pH of 7.0 in 10^{-3} mol dm^{-3} NaCl for the three bleached pulps was required.

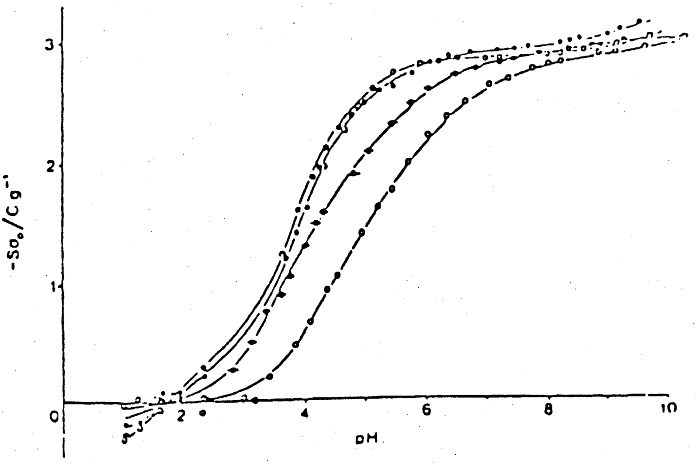

FIG. 2. Charge/pH Isotherm At 25°C For Bleached Kraft Pulp. [NACl]/mol dm^{-3} As Follows : ○ , 10^{-3}, ⊖, 10^{-2}, ●, 10^{-1}, ○ , 10^{0} [12]

The type of adsorption isotherm which results from the treatment of pulp with Polybrene is shown in Fig. 3. Adsorption for all pulps was measured well within the plateau region of the isotherm in the presence of excess polycation. The charge determined this way is referred to as the Polyelectrolyte Titrated Charge (PTC).

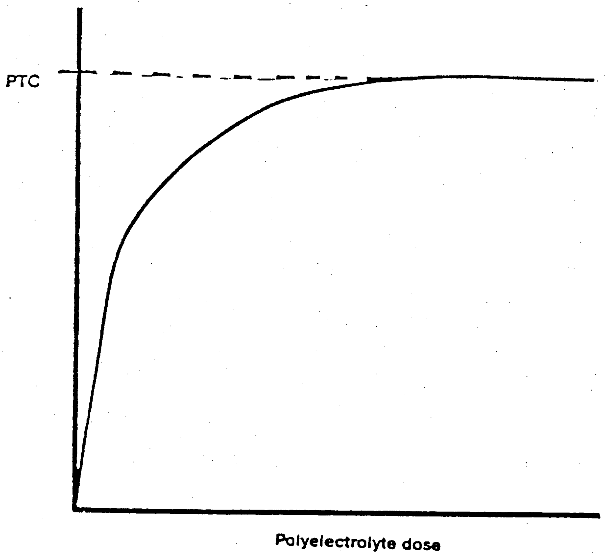

FIG. 3. Adsorption On Fibre As A Function Of Polybrene Dose

Table 1 shows the quantities of surface charge (So and PTC) of the three types of fibre as determined by the two titration techniques. The two sets of surface charges are not identical although the PTC of fibres (S) and (H) are similar in magnitude and within ± 0.31 C g^{-1} of So. Other workers [13] have shown closer agreements between charge/pH values and the PTC for carboxymethylated cellulose (CMC) fibre. Wagberg <u>et al</u> [10] (Table 2) compared the results of measuring the surface charge of CMC by C_{14}-labelling, conductometric titration and polyelectrolyte titration. It was concluded that, under certain conditions, polyelectrolyte titration could be used to determine the carboxyl group content of cellulose fibre.

Fibre	Surface Charge ($C\ g^{-1}$) So	PTC
Bleached Eucalyptus Kraft (A)	-4.15	-7.94
Bleached Softwood Kraft (H)	-2.30	-1.99
Bleached Softwood Kraft (S)	-3.37	-3.66

TABLE 1 Surface Charge Of Three Pulps Determined By Potentiometric Titration (So) And Polyelectrolyte Titration (PTC)

Degree Of Substitution	Colloid Titration (meq/100 g)	C_{14} (meq/100 g)	Cond. Titration (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

TABLE 2 Surface Charge Of Carboxymethylated Cellulose (CMC) Measured Using Different Techniques [10]

The assumption that the PTC is a measure of the total surface charge density has been questioned. Onabe [13] and co-workers carried out extensive adsorption studies using the polycation 1,1-dimethyl piperidinium-3, diallyl methylene chloride (poly-CMDAAC) and KPVS. Onabe [13] suggested that the apparent adsorption isotherms resulting from polyelectrolyte titration are composite isotherms made up of the individual isotherms of polyelectrolyte and water. The actual adsorption was calculated by making a correction for "non-solvent water". The higher accessibility of Polybrene than poly-DMDACC to the charged sites on the different structural levels in the porous cellulosic fibres has been demonstrated [11].

A previous study [14] concluded that the PTC is a function of polyelectrolyte adsorption and is therefore unlikely to be a measure of the absolute surface charge (So). The extent of polymer adsorption depends on the polymer molar mass, suspension pH and the presence of soluble electrolytes [15,16]. Furthermore, adsorption is shown to be affected by the consistency of the fibre treated and the concentration of the polymer. Higher adsorption occurs at low fibre consistency and high polymer concentration [15,16].

Under certain experimental conditions, however, polyelectrolyte titration has produced results which agree well with other methods of surface charge measure [10] (Table 3) and as shown here with potentiometric titration. The latter is a tedious and time consuming way of measuring surface charge requiring sophisticated titration apparatus. Polyelectrolyte titration, however, is a relatively uncomplicated exercise. When variables, such as the ionic content, the pH and the consistency of the suspension and the concentration of the polymer applied, are controlled polyelectrolyte titration proves to be a viable means of determining the surface charge of cellulosic fibre.

PTC/pH Isotherms Of Hardwood Fibre

The results measuring the surface charge of a bleached hardwood kraft pulp at different pHs by polyelectrolyte titration are shown in Table 3. The charge/pH isotherm (Fig. 4) shows an increase of surface charge density with increasing pH. The point of zero charge of the fibre is below pH 2.0.

pH	PTC ($C\ g^{-1}$)
2.0	1.24
4.0	6.20
6.0	7.01
8.0	9.60
10.5	12.22

TABLE 3 Surface Charge Of Bleached Hardwood Kraft Pulp (B) As A Function Of Suspension pH

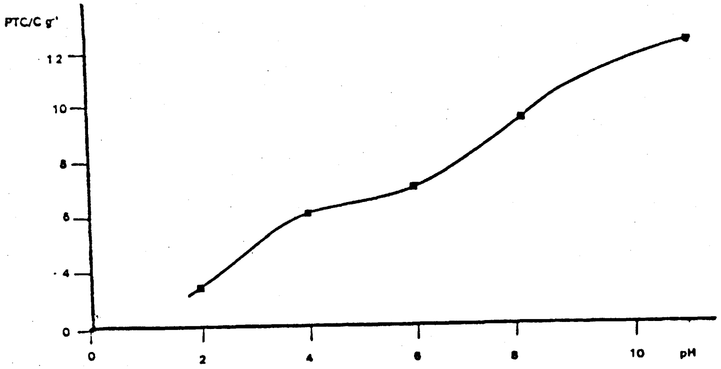

FIG. 4. Charge/pH Isotherm Of Bleached Hardwood Sulphate Pulp Isotherm Obtained By Polyelectrolyte Titration

Refining And PTC

Refining or beating of pulp is an essential process of paper manufacture and is carried out to a greater or lesser degree in all paper and board mills. Mechanical action of the refiner plates on the pulp fibrillates the fibres, reduces fibre length and generates fines. Fibrillation and shortening of fibres is beneficial to sheet formation and paper properties while fines can be lost from the sheet during formation and leave the system via the effluent carrying adsorbed chemical additives.

Both fibrillation and fines cause an increase in the total surface area of the pulp. If this also leads to the exposure of more adsorption sites on the fibre surface, then this should be reflected in the PTC parameter.

The results of the refining treatment and fines content of the two pulps and the PTC of the total pulps and long fibre are shown in Tables 4 and 5 for the hardwood and softwood respectively.

Refining Energy (kWht^{-1})	° Schopper Reigler	Fines (%)	PTC Total Stock (C g^{-1})	PTC Fibre Only (C g^{-1})	Calculated PTC Fines (C g^{-1})
0	19.0	13.5	7.29	6.98	9.29
50	29.0	16.2	5.93	8.30	-
100	37.0	20.3	6.92	7.98	2.73
150	51.5	22.7	6.87	8.52	1.28
200	65.0	25.1	7.16	7.45	6.31

TABLE 4 PTC Of Bleached Hardwood (Eucalyptus) As A Function Of Refining

Refining Energy (kWht^{-1})	° Schopper Reigler	Fines (%)	PTC Total Stock (C g^{-1})	PTC Fibre Only (C g^{-1})	Calculated PTC Fines (C g^{-1})
0	11.5	4.7	3.85	4.18	-
54	33.5	10.1	4.80	4.68	5.92
77	52.0	12.9	4.64	4.27	7.13
104	64.5	16.0	4.38	4.19	5.40
131	74.0	16.5	4.99	5.76	1.13
158	78.5	17.4	4.70	5.87	-
185	83.0	20.2	5.09	6.97	-
212	86.0	21.2	5.22	4.66	7.26

TABLE 5 PTC Of Bleached Softwood Kraft As A Function Of Refining

Results show that there are no significant correlations between the degree of refining of hardwood and PTC, i.e. polymer uptake at the plateau levels of adsorption. PTC of the fibre alone shows no increase with the expected increase in fibrillation. Similar results were obtained for softwood up to 65° Schopper Reigler but there is some indication of higher PTC values at greater readings. The calculated PTC of fines shows considerable variation for both pulps. The results are consistent with the earlier observations which show higher surface charge per unit weight for hardwood than for softwood.

The lack of a positive correlation of PTC with the degree of refining is unexpected and cannot easily be explained. The expected increase in surface area of fibre has not led to an increase of PTC and the gradual increase in the levels of fines with refining does not influence polymer uptake. The results suggest that within the normal practical range of refining, the cationic demand of the fibre remains constant inspite of fibrillation and an increase in the fines levels. Since PTC was calculated from the plateau adsorption values this does not imply that the rate of polymer uptake or the degree of adsorption below the plateau levels also remains unaffected by refining. Hence the implication of the independence of fibre surface charge from refining are unclear. It would suggest that chemical uptake, contrary to expectation, is not significantly affected by fibre fibrillation and fines. Only the addition of mineral filler fines would then result in higher chemical demands. If the fibre fines remain unsubstantive to chemicals either due to physical effects or the protection of charged surface sites, then their retention could be lowered. The separation of fines from the fibre by drainage through the wire may then expose their surface to the chemicals present in the whitewater and result in an increased uptake. If this is so then the charge demand of fines in the entire stock may be different from that in the whitewater.

CONCLUSION

Good agreement was obtained between the results of cellulose surface charge density measured using potentiometric titration and polyelectrolyte titration. The charge determined by potentiometric titration is assumed to be the absolute surface charge and that measured by polyelectrolyte titration as the polyelectrolyte titrated charge (PTC) which is a function of polymer adsorption. It is possible to construct charge/pH isotherms by polyelectrolyte titrate.

The application of PTC measurement technique to investigate the effect of refining on surface charge produced results contrary to expectation. Further investigations are needed to establish the interactions between fibrillated fibre, fibre fines and polelectrolytes.

ACKNOWLEDGEMENTS

The author would like to thank Dr T M Hardman and Mr J C Petzold of the Chemistry Department, Reading University, for supplying the results on the surface charge (So) of three fibres and Miss T L Safadi of Pira for her assistance.

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Transcription of Discussion

THE USE OF POTENTIOMETRIC TITRATION AND POLYELECTROLYTE TITRATION TO MEASURE THE SURFACE CHARGE OF CELLULOSE FIBRE

R. I. S. Gill

Erratum

On page 451. Reference [1] should read R.S. Amipulski

Dr. T. Lindstrom Modo, Sweden

I think you have obtained the result I would expect. Polybrene is a sufficiently low molecular weight polyelectrolyte to be able to penetrate the cell wall and have access to all the charges in the cell wall. Some hemicellulose could be lost during beating but I would not expect any substantial changes in the surface charge as determined by colloid titrations, with low molecular weight polyelectrolytes. On the other hand, if you had used a high molecular weight cationic polyelectrolyte it would only have access to the charges on the outer surface of the fibre. You increase the total surface in the system during refining then you open up more space for the high molecular weight polyelectrolyte to gain access to more carboxyl groups, in that case I would expect an increase. For very low charged cellulosic materials, it takes rather a long time to come to equilibrium. If you allow for this longer contact time, you will however in this case also obtain a 1:1 stoichiometry between fibre charges and the added cationic polyelectrolyte (polybrene). It is a matter kinetics.

Miss H.G.M. van de Steeg, Wageningen Agricultural University,The Netherlands

Can I make a comment on your finding that the consistency influences the amount of polymer absorbed - this can be explained by polymer absorption theory. The basis is that the polymer you are using is polydisperse, that is the polymers do not all have the same molecular weight. The polymers with the largest molecular weight adsorb preferentially and this causes the effect. I can elaborate on this afterwards.

Prof. F. Onabe, University of Tokyo, Japan

I would like to make a few comments based on our past experience in this area. In this kind of work one has to establish the relationship between actual surface charge and PTS value by titration. I think PTS value particularly reflects the amount of adsorption of polyelectrolytes on the surface of cellulose and parameters such as chain length of polymer as mentioned by Dr. Lindstrom which has a considerable effect on the amount of absorption. To establish the validity of this method it is necessary to measure the porosity and surface area data, etc. Do you still support the idea that a simple and reliable method of colloid titration measures the surface charge of fibres?

Dr. R.I.S. Gill

There is no simple method. But the reasonably straight forward polymer titration methods show some degree of consistency in determining surface charge. If we can use these for more realistic investigations e.g. the effect of charge on retention, sheet dewatering and sheet properties this will be useful. We are trying to establish the validity of these methods.

Dr. R.S. Ampulski, Procter & Gamble Co. USA

I wish to reiterate and confirm what Tom Lindstrom said about the molecular weight of the polymer you are using. I think you should be using a molecular weight of the order of 3 million and that alpha methyl glycochitosan should give this molecular weight discrimination for being able to determine the differences between surface and internal charge. In our work we have previously defined surface charge as that charge which is available to a high weight cationic polymer, specifically α-methylglycochitosan (~3,000,000 Daltons)(Your Ref.1)

The size of polymer one uses in the titration is solely dependent on the type of information one wants from the determination. For example, in a papermaking process where one is using high weight polymers (e.g. cationic starch) the quantity of available anionic bond sites could be determined by using a high weight cationic polymer in the titration. Low weight cationic polymers can be used to determine the total cationic demand of the fibre.

Prof. T. Lindstrom, Modo, Sweden

I would like to return to the effect of stock consistency on your experiment. I do not think that there is a simple explanation for your findings. I do not think that it is the effect of polydispersity because all these highly cationic polymers have a high affinity for adsorption onto the substrate. This means that the molecular weight has very little effect on the adsorption in the low molecular weight region. From unpublished work carried out at STFI we have the experience that consistency has no influence on polybrene adsorption. These results contradict your results. So maybe we should discuss the matter further to find out the differences.

Dr. L. Wagberg, SCA Teknik AB, Sweden

Dr. Odberg and I would both like clarification as to what we mean by surface charge and total charge. The outer surface of cellulose is a couple of M^2 per gramme and total surface can be as much as 200 M^2 per gramme. When I talk about the surface charge of fibres I am referring to the external surface charge which may be measured by a high molecular mass polymer.

People also tend to mix things up when trying to match the charges from geometric reasoning. How can a polymer charge separated by, for example, 7 Angstroms match charges on fibres separated by 50 Angstroms? Dr. Odberg and I have discussed this issue with the department of Physical Chemistry at the University in Lund, Sweden who have given us the suggestion that if you consider the Debye length in solution you might have a clue. As long as the Debye length in solution is larger than the distance between the charges on the polymer you simply have a huge multivalent charge on the polymer and you will then have an interaction between this multivalent charges and the multivalent charge on the fibre surface. This is then really why you can have an ion exchange between the polymer and the surface.

In the figure below the Debye length is plotted as a function of the salt concentration and in the diagram we have also included times for the separation of charges on the fibres at different charge densities. To the left at the 1/ line the cellulose surface appears as a multivalent charge while on the right it should be possible to detect the discrete charges on the fibres. The matching between the charges on the polymer and on the fibre surface should hence appear in solutions to the left of the 1/ line; whereas solutions to the right of this line should show deviations from a matching between the charges.

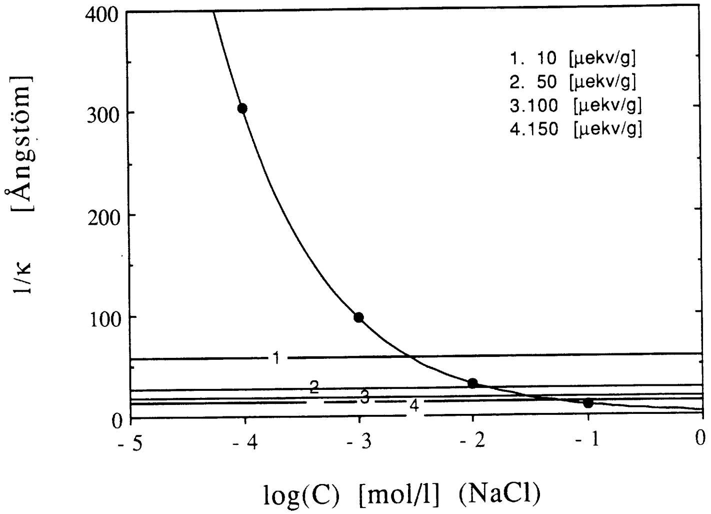


Figure The Debye length as a function of salt concentration in an NaCl solution. The horizontal lines correspond to the distance between charges on the fibre surfaces of different charge densities, assuming a specific surface area for the fibres of 200m^2/g.

R.L. Anderson, Scott Paper Co. USA

Were your fibres never dried or dry lap material?

Dr. R.I.S. Gill

They were dried.

R.L. Anderson

I think this may cause some difference. I have trouble understanding how you achieved these results. What we see with small highly charged debonded molecules is just the opposite.

As we refine and increase the amount of fines there is an increase in the absorption of debonded chemicals onto the fines and onto the surface compared to untreated materials. If this could be explained I would be grateful.

Dr. R.I.S. Gill

We would have expected a greater uptake of the polymer given the conditions with fibrillation in spite of what Tom (Lindstrom) is saying in that there is no change in surface charge. This is something I cannot personally explain.

Prof. J. Marton, SUNY, USA

I believe it is very important to always emphasise the accessibility of the surface to the materials in question, that is different, for instance, for low molecular weight surfactants or high molecular weight polymers. Increasing refining renders an increasing amount of carboxyl groups available for the cationic starch or other high molecular mass polymers. I believe that this concept of surface availability should be included in your thinking.

D.G.N. Stirling, Wiggins Teape R & D Ltd. UK

I think there is some confusion around the Hall about the concept of total charge and surface charge. Presumably we are interested in the effect of this charge in the papermaking system. Can you give us guidance as to whether we are interested in what appears to be the total charge, as measured by yourself, or whether in fact we are more interested in what could be described as a surface charge measured by a very much larger molecule. Should it be a real surface charge with a large molecule or should it be this pseudo total charge with a small molecule?

Dr. R.I.S. Gill

It is difficult to answer that sort of question at present. We are quite a long way away from looking at the surface charge of cellulose either one way or the other and comparing them with what may actually happen on the papermachine and how the stock may interact, how flocculation may occur and how different types of flocculation influence, drainage or sheet formation - and how these relate to surface charge density. A lot of work has been done on potentiometric titration of cellulose and looking at what has been called the absolute surface charge. There are also adsorption techniques which are used to measure the different sorts of surface charges. We are some way behind in establishing which technique is suitable and can be applied to papermaking conditions.

Dr. K.I. Ebeling, James River Corp. USA

I believe that it is generally known that if you refine fibres the pick up of cationic dye goes up and one gets a higher colour density even after allowing for the decreasing role of light reflectance - so some electrokinetic phenomena increases on the surface of the fibres as a function of refining.

Dr. I.I. Pikulik, Paprican, Canada

In your pre-prints you give a surface charge of bleached hardwood kraft pulp as the function of suspension pH. This change by a factor of about 10 from about pH 2 to pH 10.5. I was wondering if indeed there is a continuous change of surface charge through this range of pH or whether this is indeed an artefact of your method?

One of the earlier speakers mentioned that one of the species which contributes to the charge might be carboxylic acid. The pK_a of the carboxylic group is typically around 5 and so by the time we are at pH 3 only about 1% should be dissociated and at pH 7 most should be dissociated. What are the other substituents which cause a change in the charge density outside this range?

Dr. R.I. Gill

I can't really answer these questions at the moment, can we discuss it later?

Dr. L. Odberg, STFI, Sweden

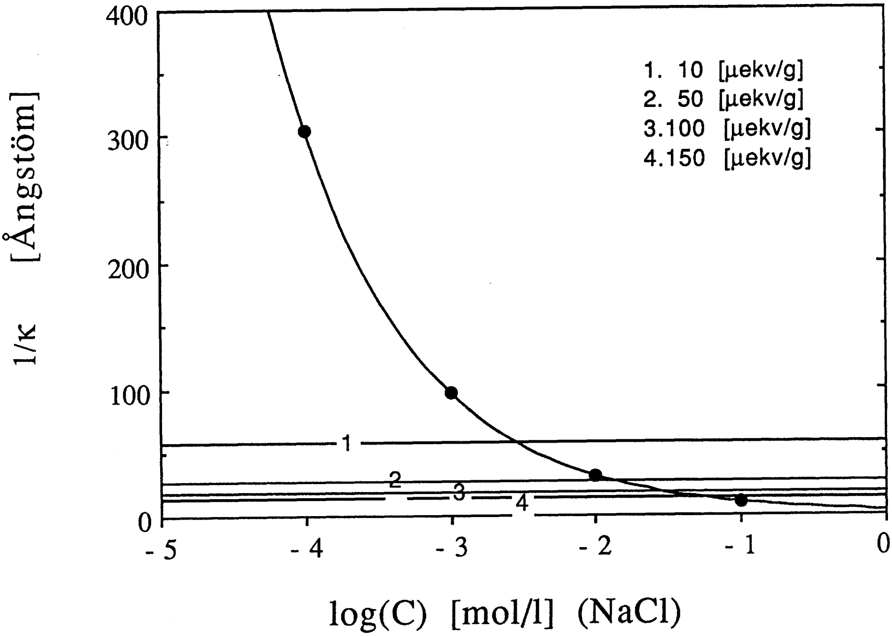
I would like to comment on that question. For polyelectrolytes it is not a simple case of the usual pH/pK relationship. In the case of polyelectrolytes with carboxyl groups there is dissociation between pH 3 and pH 9. This is totally consistent with the theory. When the polyelectrolyte is highly charged it accepts protons very easily and as the charge gets lower so does the tendency to take up protons. The relationship is approximately:

$$pH = pK_a + 2 \times \ln \{ \alpha /(1 - \alpha)\}$$

I would like to add another comment on the total charge. We have done many of these measurements at STFI. In some cases you obtain the total charge easily in the same way as you get charge from conductiometric titration. You may obtain with one pulp the result after an equilibration time of 30 minutes. However, with another pulp the equilibration time could be 24 hours to reach all charges. As Tom (Lindstrom) said it is a matter of kinetics ie. how long the polymers will take to penetrate.

Dr. R.I.S. Gill

We allowed a contact time of 3 hours with polybrene.


1/κ [Ångstöm]
400
300
200
100
0
- 5
- 4
- 3
- 2
- 1
0
log(C) [mol/l] (NaCl)
1. 10 [μekv/g]
2. 50 [μekv/g]
3.100 [μekv/g]
4.150 [μekv/g]
1
2
3
4