Preferred citation: T.M. Herrington. The surface potential of cellulose. In **Papermaking Raw Materials**, *Trans. of the VIIIth Fund. Res. Symp. Oxford, 1985*, (V. Punton, ed.), pp 165–181, FRC, Manchester, 2018. DOI: 10.15376/frc.1985.1.165.

THE SURFACE POTENTIAL OF CELLULOSE

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ABSTRACT

Charge/pH isotherms were determined for various cellulose fibres: cotton linters, bleached sulphate and unbleached sulphate pulp. The charge was determined as a function of pH in 1.0, 10^{-1}, 10^{-2} and 10^{-3} mol dm^{-3} NaCl. The effect of various cations on the charge was also investigated. The surface areas of the fibres were determined by BET nitrogen adsorption; the pulps were initially in a 'never-dried' state and for the BET work they were specially prepared using solvent-exchange techniques whereby all the water was replaced by dry pentane. The surface areas of the fibres were also obtained using the method of negative adsorption: corrections for low surface potential were applied using Gouy-Chapman theory and the charge/pH isotherms. Surface areas obtained by these two entirely different methods are compared. Once drying the 'never-dried' pulps halved the surface areas.

Zeta potentials for cotton linters and bleached sulphate pulp were calculated from measurements of the streaming potential. These measurements were made at the same electrolyte and pH conditions as the charge/pH isotherms and the zeta potentials compared with the surface potentials calculated from Gouy-Chapman theory. It was found that the zeta potential is not a good relative measure of the surface charge and cannot be used for qualitative comparison between such similar materials as bleached sulphate pulp and cotton linters.

INTRODUCTION

The flocculation of cellulose fibres during the papermaking operation is a complex process with many variables. The flocculation depends on the charge on the surface of the fibres and customarily the zeta potential is taken as a measure of this. The zeta potential is the potential at the plane of shear and has been determined by many workers either from measurement of the streaming potential across a plug of cellulose fibres or else by microelectrophoresis techniques which require the very small particles of fines in the supernatant of a cellulose slurry. This study was undertaken to determine the charge at the surface of cellulose fibres and to compare the potential at the surface of the fibres with that at the plane of shear.

Four different types of cellulose fibres were used in this work :-

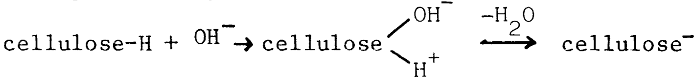
Cotton linters, dried sheets redispersed
Bleached Scots Pine Sulphate, never-dried
Unbleached Scots Pine Sulphate, never-dried
Unbleached Black Spruce Sulphite, never-dried

The Scots Pine and Black Spruce pulps were supplied by Pira and PPRIC respectively.

Previous workers investigating the surface charge of cellulose have treated the system as a polyacid and investigated the ion-exchange reaction between acidic protons and metal cations.

$$\text{cellulose-H} + M^+ \longrightarrow \text{cellulose-}M^+ + H^+$$

This reaction in aqueous solution is equivalent to the adsorption of hydroxide ions



$$\text{cellulose-H} + OH^- \rightarrow \text{cellulose}\begin{matrix} OH^- \\ H^+ \end{matrix} \xrightarrow{-H_2O} \text{cellulose}^-$$

The acidity of cellulose has generally been attributed to occasional carboxy groups within the cellulose structure, probably at the C6 position.

The charged cellulose fibres create an ionic double layer in aqueous solution. The Gouy-Chapman theory related the surface charge σ_o to the surface potential ψ_o. If adsorbed ions are present i.e. a Stern layer, than the electrical double layer equations start to apply at the Stern surface, a distance from the interface. The relation between surface charge and potential is given by

$$\sigma_o = (8n_i k\ T \varepsilon)^{\frac{1}{2}} \sinh (z_i e\psi_o/2\ k\ T) \qquad (1)$$

where n_i is the number of ions i per unit volume of the bulk solution. The zeta potential, as it is the potential at the surface of shear, would be expected to be of smaller magnitude than the surface potential ψ_o. It has often been approximated to ψ_δ, the potential of the diffuse double layer, implying that the slipping plane coincides with the layer of adsorbed ions. The surface charge density on cellulose, $S\sigma_o$, was obtained by titration methods. The specific surface charge σ_o was calculated for these data using a value for the surface area, S, obtained by BET nitrogen adsorption or by the method of negative adsorption. Using the Gouy-Chapman theory and assuming $\sigma_o = \sigma_\delta$, ψ_δ can be calculated. Cellulose fibres were used for the titration experiments so that to compare ψ_δ with the zeta potential of the fibres, the streaming potential method was used.

CHARGE/PH ISOTHERMS

The change in surface charge of cellulose fibres with pH is given by the amount of hydroxyl or hydrogen ions required to give that change in pH. As the surface charge on cellulose fibres is very small the effect on the titration medium must be allowed for by doing a blank titration with no fibre present. Since pH measures hydrogen ion activity, the ionic strength of the cellulose slurry and the blank must be the same. In the presence of a large excess of indifferent electrolyte any experimentally observed adsorption of H^+ or OH^- ions can be considered to have occurred only at the solid/liquid interface and not in the solution side of the double layer (1). The surface excess $\Gamma_i = n_i/S$, where n_i is the number of moles of ion i adsorbed per gram of cellulose and S is the specific surface area in m^2/g.

The basic technique consists of the potentiometric titration of a fibre suspension, in aqueous solution of constant ionic strength, with hydrogen or hydroxyl ions using a glass plus a silver/silver chloride electrode for pH determination. A sample of electrolyte solution of the same volume and concentration as the fibre suspension is then titrated with the same acid or alkali. Let n_{OH^-} be the extra number of moles of hydroxyl ions required to raise the fibre suspension from pH I to pH J, then n_{OH^-} is the number of moles of hydroxyl ions adsorbed on the surface and

$$\Delta_I^J \Gamma_{OH^-} = n_{OH^-}/S \tag{2}$$

Similarly if m_{H^+} extra moles of hydrogen ions are required to raise the fibre suspension from pHI to pHK, then

$$\Delta_I^K \Gamma_{H^+} = m_{H^+}/S \tag{3}$$

The surface charge is defined as

$$\sigma_o = F(_{H^+} - \Gamma_{OH^-}) \tag{4}$$

As only changes in surface excess can be determined it is necessary to find the pH at which the charge on the cellulose particles is zero. Although the cellulose fibres were purified by soaking in dilute hydrochloric acid, followed by washing, some of the cellulose could be in the form of its sodium salt, for example, and would have a charge on addition to water before any acid or alkali is added, i.e. the point of zero charge (pzc) is not the same as the zero point of titration. In the absence of specific adsorption, the charge on the cellulose surface at the pzc will be unchanged by varying the concentration of electrolyte. Thus the charge/pH isotherms are determined in various concentrations of electrolyte and where the isotherms intersect is arbitrarily assigned zero charge.

Charge /pH isotherms were obtained for cotton linters, bleached sulphate and unbleached sulphate pulp. The isotherms were constructed at 25°C over the pH range 1.3-10.3 and sodium chloride was used as the indifferent electrolyte. Four concentrations of indifferent electrolyte were employed, namely 1.0, 0.1, 0.01 and 0.001 mol dm^{-3}. The isotherms are given in Figs. 1-3. The charge is recorded as $-S\sigma_0$ in Cg^{-1} as this is what was actually measured.

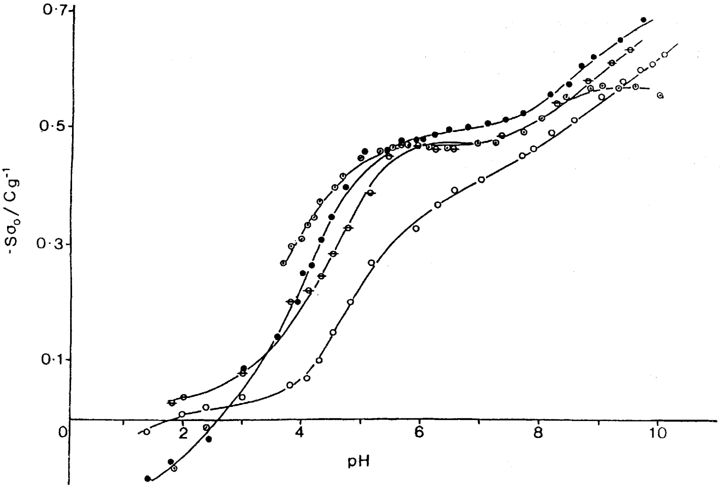


Fig 1—Charge/pH isotherm at 25° for cotton linters.
|NaC1| /mol dm^{-3} as follows: 0, 10^{-3}; ⊖, 10^{-2}; ● 10^{-1}; ⊙, 10^{0}.

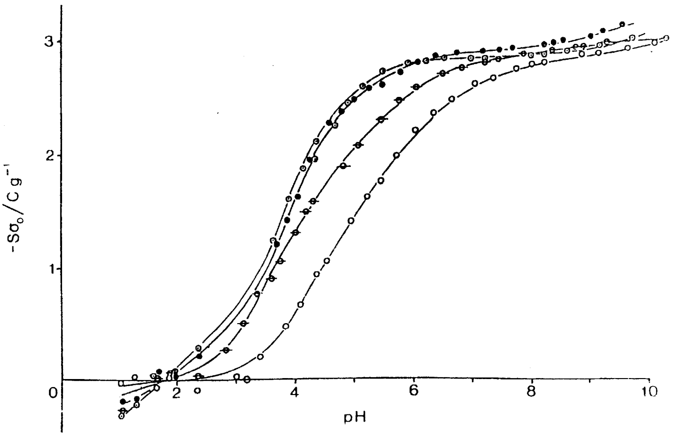


Fig 2—Charge/pH isotherm at 25°C for bleached sulphate pulp. |NaC1| /mol dm^{-3} as follows: O, 10^{-3}, ⊖, 10^{-2}; ●, 10^{-1}, ⊙, 10°.

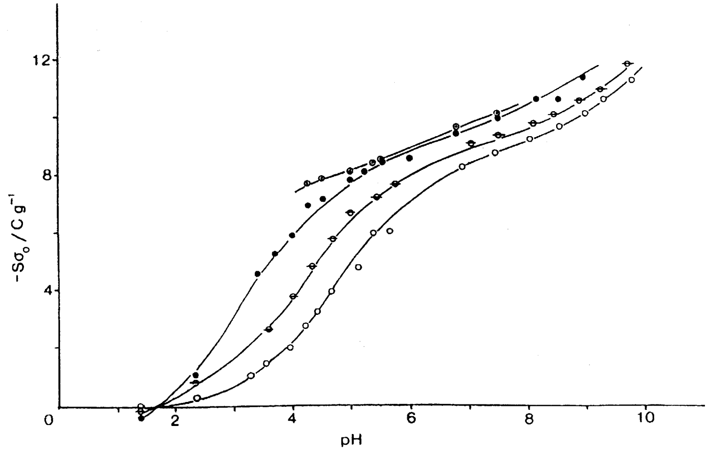


Fig 3—Charge/pH isotherm at 25°C for unbleached sulphate pulp. |NaC1|/mol dm^{-3} as follows: 0, 10^{-3}; ⊖, 10^{-2}; ●, 10^{-1}; ⊙, 10°.

Cotton Linters

For cotton linters the form of the charge/pH isotherm in the pH range 2.5-7.0 is characteristic of a monofunctional polyacid. The charge increases as expected with increasing pH as the degree of dissociation of the acid increases, and the plateau represents neutralization. The $-S\sigma_0$ values are low and the precise location of the pzc is not clear, although a value of between pH 1.5 to 2.5 can be estimated from the isotherms. The 0.1 and 1.0 mol dm^{-3} isotherms appear to have a slightly higher pzc than the lower concentrations of electrolyte, and this is probably explained by specific adsorption of chloride ion. The increase in charge after pH 7 may be explained in two ways. It may be that the swelling of the fibre, which occurs in alkali solution, opens up new acid groups with which the alkali reacts. Alternatively there may be a second weak acid group on the cellulose surface. The behaviour of the 1.0mol dm^{-3} NaCl isotherm is anomalous. Below pH 5 it lies in the expected order, above the 0.1 mol dm^{-3} isotherm. However, above pH 5 it drops to where it is almost coincident with the 0.01 mol dm^{-3} isotherm and at pH 8.5 it levels to a plateau. This behaviour seems to suggest that both swelling and a second weak acid group may be involved. The swelling of the fibre is suppressed by the high electrolyte concentration, which explains the drop in charge of the 1 mol dm^{-3} isotherm, the effective number of acid groups having been reduced. This would also explain the plateau region above pH 8.5, if the fibre in the lower concentrations of NaCl continued to swell and therefore react, after this group had been neutralized. Thus the 1 mol dm^{-3} isotherm may be considered to be the system in which any complicating effects of swelling are removed.

Bleached Sulphate Pulp

Like the isotherms for cotton linters, the bleached sulphate isotherms are characteristic of a monofunctional polyacid. However, in this case it is clear that a much higher charge density is involved. This is confirmed by the fact that the neutralization point is achieved at a much higher pH. The location of the pzc is clearer because of the higher charge density and it is estimated to be at a pH 1.75 ± 0.25. There is also clear evidence of charge reversal below pH 1.5. A mechanism for this reversal may be the protonation of the large numbers of oxygen atoms within the cellulose structure. As with the cotton linters, there is a degree of reaction above pH8 after neutralization has occurred; however, it is less market because of the overall high charge density. Again, it is interesting to observe that the 1 mol dm $^{-3}$ isotherm drops below the 0.1 mol dm $^{-3}$ isotherm and becomes coincident with that for 0.01 mol dm $^{-3}$ NaCl. This again is good evidence of the high electrolyte concentration suppressing swelling and thereby reducing the surface charge. The higher crossover point of pH 6.1, compared with pH 5.0 for cotton linters, also indicated a higher charge density, electrical effects dominating swelling effects until a high pH.

Unbleached Sulphate Pulp

From Fig.3 it is clear that the charge per gram at pH 7 is four times greater than for bleached sulphate pulp and some 25 times greater than that of cotton linters. There is no tendency to form a horizontal plateau with increasing pH, but on the other hand the charge does not show the rapid increase without limit of a silica sol (2). The behaviour suggests that several acid groups are contributing to the surface charge. Unbleached sulphate pulp contains a considerable quantity of lignin so that phenolic and other acid groups may contribute to the surface charge as well as carboxy groups.

SURFACE AREA

From the charge/pH isotherms it is apparent that for a given value of the pH, $-S\sigma_0$ increases in the order cotton linters < bleached sulphate pulp < unbleached sulphate pulp. In order to convert the surface charge for C g $^{-1}$ to C m $^{-2}$, the specific surface area, S, is required. The accepted surface area for cellulose fibres obtained by B.E.T. nitrogen abosrption is < 10 m^2/g. Stone and Scallan (3) obtained high values for the B.E.T. surface area of different types of pulp (100-300 m^2/g) using a method of solvent exchange. Schofield (4) determined the surfacearea of jute fibres by the negative adsorption of chloride ions. He obtained values of between 130 and 200 m^2/g for different sources of jute. It was decided to use both methods for the determination of the surface area of the cellulose fibres. One of the main advantages of the negative adsorption technique is that it eliminates all estimations of molecular sizes which are needed in the techniques of gas and dye adsorption; also the fact that the measurements are carried out in aqueous electrolyte solution makes this technique very suitable for the evaluation of surface area for charge/pH isotherms i.e. a 'wet' surface area is determined in contrast to the 'dry' surface area determined by gas adsorption.

In this work the 'never-dried' cellulose was dried in such a way as to avoid pore closure before N_2 adsorption. The water on the fibre was replaced successively by dry methanol and by dry pentane, so that on drying the fibres in the B.E.T. apparatus, the pores did not collapse. The method of negative adsorption depends on the equations of Gouy-Chapman theory. At the interface between a charged particle and the surrounding solution the co-ions, bearing the same charge as the interface are expelled from the interface i.e. negatively adsorbed; thus if cellulose fibres are placed in a solution of sodium chloride an increase in the concentration of the chloride ion in the bulk solution is observed. It can be shown that, if the surface potential is large, then a plot of the excluded volume, ΔV, against $1/B\sqrt{n_i}$, where B is the constant and n_i is the sodium chloride concentration, has slope S. Corrections were applied for low surface potential using the charge-pH isotherms (5). The fibres were oxidised to increase the charge and surface areas obtained for oxidised and non-oxidised fibres were in good agreement. The surface areas of the different pulps obtained by negative and nitrogen adsorption are given in Table 1.

Pulp	$S/m^2\ g^{-1}$	
	by negative adsorption	by nitrogen adsorption
Cotton Linters	48 ± 5	130
Bleached sulphate	126 ± 10	190
Unbleached sulphate	207 ± 9	265,240
Unbleached sulphate once dried	112 ± 6	120
Unbleached sulphite	210 ± 10	-
Unbleached sulphite once dried	122 ± 5	-

Table 1 Surface areas of different pulps obtained by negative and nitrogen adsorption

The negative adsorption values are all lower than those from nitrogen adsorption, which is as expected for the internal surface of a porous material; exactly the same effect has been found for silica gel (2). It can be seen that drying the fibres once halves the surface area; both methods show the same trend.

In Table 2 values of σ_0 in 10^{-3} mol dm^{-3} NaCl and pH 7 are compared using the surface areas obtained by both methods. The surface charge density, σ_0, increases in the order cotton linters < bleached sulphate pulp < unbleached sulphate pulp as would be expected from the nature of the fibres.

Pulp	$-S\sigma_o$	Nitrogen Adsorption		Negative Adsorption	
		S	$-\sigma_o$	S	$-\sigma_o$
	$C\ g^{-1}$	$m^2\ g^{-1}$	$10^{-3}\ C\ m^{-2}$	$m^2\ g^{-1}$	$10^{-3}\ C\ m^{-2}$
Cotton linters	0.41	130	3.2	48	8.5
Bleached sulphate	2.60	190	13.7	126	20.6
Unbleached sulphate	8.35	265	31.5	207	40.3

Table 2. Comparison of σ_o in 10^{-3} mol dm^{-3} NaCl and pH 7 using surface areas determined both by nitrogen and negative adsorption.

CALCULATION OF POTENTIAL FROM THE CHARGE/PH ISOTHERMS

If it is assumed that the surface charge determined by titration σ_o, is equal to σ_δ, the charge at the beginning of the diffuse double layer, then the potential of the diffuse double layer, ψ_δ, can be calculated from the Gouy-Chapman equation

$$\sigma_\delta = (8 n_i k T \varepsilon)^{\frac{1}{2}} \sinh (z_i e \psi_\delta / 2kT) \qquad (5)$$

Values of ψ_δ for cotton linters and bleached sulphate pulp are given in Table 3. In both cases the larger surface areas obtained from nitrogen adsorption were used, giving the smaller σ_o values, as ψ_δ is to be compared with ζ, the potential at the plane of shear.

Bleached sulphate pulp has a more negative surface charge and hence a more negative surface potential than cotton linters, at the same electrolyte concentration, for all values of the pH.

Cotton Linters			Bleached Sulphate Pulp		
pH	$-\psi_\delta$/mV	$-\zeta$/mV	pH	$-\psi_\delta$/mV	$-\zeta$/mV
10.03	55.6	24.1	10.31	110.8	13.9
8.46	47.4	22.8	8.55	107.5	13.5
7.31	42.0	22.8	6.53	99.5	12.4
6.34	37.2	21.5	5.82	89.2	12.2
6.18	36.3	20.6	4.78	69.7	10.4
6.08	35.5	20.2	4.08	42.4	7.6
4.81	21.7	16.8	3.44	15.8	4.9
4.50	15.7	15.7	2.51	2.2	1.6
3.78	6.9	8.9			
3.10	4.3	4.3			

Table 3. Comparison of ψ_δ from charge/pH isotherms and ζ , from streaming potential measurements for cotton linters and bleached sulphate pulp in 10^{-3} mol dm $^{-3}$ NaCl.

STREAMING POTENTIAL MEASUREMENTS

In streaming potential measurements water is forced through a compacted plug of fibres. Excess counter-ions are removed from the double layer and a 'streaming potential' is induced between either side of the plug. Measurements were made for cotton linters and bleached sulphate pulp over the whole pH range (2-10.5) in 10^{-3} mol dm $^{-3}$ NaCl. The zeta potential was determined from the linear plots of E_s against P. Data for the whole pH range in 10^{-2} mol dm $^{-3}$ NaCl were also determines for cotton linters (6). The variation of ζ with pH is shown in Fig. 4 for cotton linters and in Fig. 5 for bleached sulphate pulp. Electrophoresis data were also determined for cotton linters and the zeta potential so obtained is shown by way of comparison in Fig. 4. The data are in agreement within experimental error.

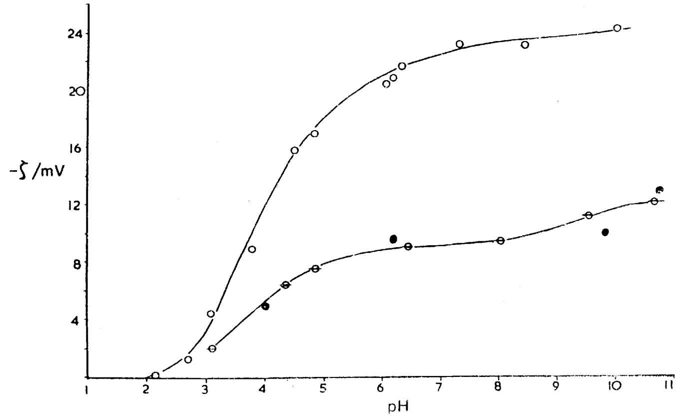


Fig 4—Variation of the zeta potential with pH for cotton linters from measurements of streaming potential. 0, 10^{-3} mol dm^{-3} NaC1; ⊖, 10^{-2} mol dm^{-3} NaC1; ●, 10^{-2} mol dm^{-3} NaC1 (micro-electrophoresis data).

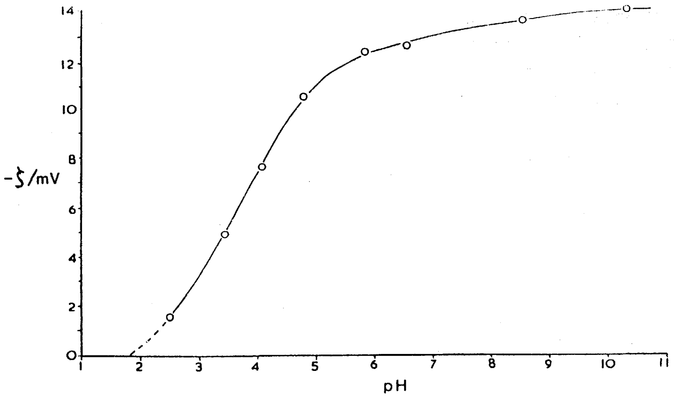


Fig 5—Variation of the zeta potential with pH for bleached sulphate pulp from measurements of streaming potential. 0, 10^{-3} mol dm^{-3} NaC1.

Cotton Linters

The value of the zeta potential in 10^{-3} mol dm $^{-3}$ NaCl and pH 7.0 agrees reasonable well with results obtained by other workers. Zeta potentials of between 25 and 30 mV have been previously determined for cotton (7). The suppression of the double layer on increasing the electrolyte concentration is clearly seen by comparing the zeta potentials at 10^{-3} and 10^{-2} mol dm^{-3} NaCl. As can be seen from Fig.4 the 'isoelectric' point is close to the point of zero charge (pH 2.0 compared with pH 1.5 - 2.5 from the adsorption isotherm), which is good evidence that the adsorption of hydroxide ions is responsible for the double layer. In Table 3 the zeta potential and surface potential are compared over the pH range. Except at very low values of the pH, $|\psi_\delta|$ is larger than $|\zeta|$.

Bleached Sulphate Pulp

Comparison of Fig. 4 and 5 shows that, at the same electrolyte concentration, the zeta potential of bleached sulphate pulp is less than that of cotton linters. The difference in zeta potentials increases as the swelling in the fibre increases with Ph; the swollen volume of bleached sulphate pulp is 2.50 cm^3/g compared with 1.10 cm^3/g for cotton (8). It seems probable therefore that, because of the swelling of amorphous cellulose or perhaps carboxylated cellulose chains at the surface, the potential at the shear plane is shifted further out into the double layer, thereby reducing the zeta potential. This model was first postulated by Goring and Mason (9). Indeed such micro-fibrils at the surface of the cellulose have been found in electron-microscope images of the surface of unswollen fibres. From the values of the zeta surface potentials the distance of the shear plane from the surface can be calculated; at pH 6.5 and in 10^{-3} mol dm^{-3} NaCl, the plane of shear is 18 nm for bleached sulphate pulp but much closer at 5nm for cotton linters. From Fig.2 and 4 it can be seen that there is a good comparison between the 'isoelectric' point and pzc (pH 2.0 and 1.7); this again provides good evidence that the adsorption of hydroxide ions at the cellulose surface is the source of the surface charge and hence double layer (In sodium adsorption experiments (1) it was found that the adsorption of hydroxide ions is balanced by the adsorption of sodium ions. This would not be true if other negative ions were responsible for the surface charge of the cellulose). However the zeta potential is very much smaller than the calculated surface potential (Table 3). Indeed it is lower than in the case of cotton linters in spite of an increased surface charge density. This phenomenon of the zeta potential being lowered on increasing the charge, has previously been observed (10) and has been used as an argument against adsorption of hydroxide ions being the source of the surface charge (9). The weight of evidence for the ionogenic source of the surface charge shown in this work discounts such an argument.

CONCLUSIONS

The pzc and 'isoelectric' point occur at similar values of the pH for cotton linters and bleached sulphate pulp, indicating that adsorption of hydroxide ions is responsible for the diffuse double layer; this is confirmed by sodium ion adsorption experiments. This work shows quite dramatically that the zeta potential is not a measure of surface charge and cannot be used for a comparison of the surface charge of even very similar materials.

ACKNOWLEDGEMENT

I am indebted to S.E.R.C. and to Wiggins-Teape Limited for joint sponsorship of this research. It is impossible to measure my debt to the late Dr Heinz Corte without whose industry, enthusiasm and above all, inspiration this work would not have taken place. It was his original contention in this symposium eight years ago that the zeta potential should not be taken as a measure of the charge of the cellulose/water interface.

GLOSSARY OF SYMBOLS

$B = (z_i^2 e^2 / 2\varepsilon kT)^{\frac{1}{2}}$

e	charge of electron
F	Faraday constant
K	Boltzmann constant
n_i	concentration of co-ion i in bulk solution
S	surface area per gram
T	absolute temperature
ΔV	excluded volume, $\Delta V = \Delta n_i \; V_t/(n_i \omega)$
V_c	total volume of solution
ω	mass of solid
z_i	valency of ion i
Γ	surface excess
ε	electrical permittivity of the medium
ζ	zeta potential
σ_o	charge per unit area at surface
σ_δ	charge per unit area at Stern plane
ψ_o	potential at surface
ψ_δ	potential at Stern plane

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Transcription of Discussion

SESSION 2 FIBRES

Chairman P. Howarth

The Surface Potential of Cellulose

by T.M. Herrington

Dr. T. Lindström STFI, Stockholm, Sweden

(Written contribution) I think you are treating the cellulose fibres as being non-porous latex particles. It is clear that a calculation of the surface potential from the surface charge, as determined by potentiometric titrations on, for instance, non-porous spherical particles, may be comparable to the potential in the plane of shear in a streaming potential experiment.

The potential you determine in a streaming potential experiment stems mostly from the phase boundary of the fibre/water suspension. On the other hand, the total charge as determined from potentiometric titrations comes from all the charged groups in the swollen cell wall. It is not meaningful to calculate a potential from the Gouy-Chapman equation if you have a gel and not a two-dimensional surface. The equation is simply not applicable to the case you are referring to. Maybe the equation would be a reasonable approximation if you do not have overlapping double layers and an even charge distribution on all the internal surfaces, but it is more likely that the charge distribution across the cell wall is not even. So, what I am saying is that both measures, that is charge from potentiometric titrations and zeta potential, are valuable, but calculating one from the other requires a detailed knowledge of both the charge distribution in the cell wall and presumably some knowledge about the surface topography of fibres. In conclusion, I do not think we have that knowledge today and I do not think the Gouy-Chapman equation should be applied in the way you do.

Dr. T. Herrington (Written response) The primary objective of this work was the measurement of the surface charge of cellulose fibres. As a considerable literature exists on the zeta potential of cellulose, but not on its charge, theoretical equations were sought to calculate values of the potential from the charge. The only readily applicable theory is that of Gouy-Chapman assuming point charges. In the absence of any detailed knowledge about the structure of cellulose at the nanometer level the equations for a planar interface and not curved interfaces were used and no allowance could be made for overlapping double layers. All these limitations have been emphasised in reference 6, and yet the experimental data showed that the Gouy-Chapman equation provided an excellent description of the system. One point not mentioned previously is that for a given Ψ_ζ measurement of ζ at a known value of n:, the sodium chloride concentration gives x, the distance of the plane of shear. For a Ψ_ζ of −22 mV the calculated value of the plane of shear for cotton linters is 20 ± 2A in 0.01 mol dm^{-3} NaCl and 24 ± 3A in 0.001 mol dm^{-3} NaCl.

No profit comes from didactic discussion about the applicability of an equation that adequately represents available experimental data on a system, in the absence of a better approximation; rather a positive approach taken and the equation used as a guide for conditons where no experimental data are available.

E. Strazdins Fairfield, USA

The results obtained by your classical analytical approach certainly serves to enrich our understanding of the relationships. The correlation between the zeta potential values obtained by the streaming potential and microelectrophoretic measurements is another notable result. However, rationalization of your titration curves does require certain assumptions and speculations. When dealing with a complex system, such as paper pulps, containing electrolytes, a semi-empirical experimental approach might be even more enlightening from the practical point of view. A lot of work has been published (Tappi, Dec. 1974) that discuss the relationships of zeta potential and cationic demand with paper drainage, change in swollen volume and hydrodynamic surface area of fibers. Clean-cut correlations are shown to exist between the cationic demand and the hydrodynamic surface area. Increase in ionic strength with sodium or calcium chloride increases drainage while decreasing zeta potential and decreases surface area and cationic demand and the swollen volume. This approach provides more orderly understanding of parameters that effect the papermaking process. These other approaches ought to be correlated with your technique.

Herrington Thank you for your helpful suggestions. We will certainly hope to include an approach along these lines in future work.

Prof. R. Atalla IPC, Appleton, USA

I just wanted to comment on the anomalous behaviour of the calcium chloride curve. Some years ago we carried some work trying to understand the unusual effect of calcium chloride on cellulose by doing experiments on complexation of calcium chloride with ethylene glycol. We found that the calcium chloride ion was the only one of the Group II cations to interact strongly enough with the adjacent hydroxyl groups to bring about substantial conversion from the trans to the gauche form. We followed this spectroscopically and it was quite significant.

So I believe one is observing some effects of chelation of calcium ions by adjacent hydroxyl groups. This occurs more with calcium than with any other Group II cation.

Dr. R.W. Davison Hercules, Wilmington, USA

As I understand what you have been doing, you are titrating the total charge throughout the fibre from the outside surface right through the swollen fibre into the interior, but you are carrying out your streaming potential work looking at the hydrodynamic (external) surface only.

Therefore, it seems to me that you are assuming that charge is distributed uniformly over both the external and the internal surfaces of the swollen fibres. However, if this assumption is not valid (and I believe it is not), then I wouldn't expect the charge/pH results you presented to be in agreement with your streaming potential results. It is our experience that the cationic demand of the external surface is quite different from that of the internal surface of the swollen fibre. Could you comment please?

Herrington In the calculation of zeta potential no surface area calculations are involved. When we calculated the surface area for our titration experiments we used the most comparable method available to us, that is the surface area as seen by the ion. The papermaker himself has to decide what are the most fundamental physical parameters that he needs. Where incipient flocculation is concerned, probably the particle mobility is the relevant parameter, whereas once it is actually occurring, the surface charge determined in a titration experiment is more relevant.