

ELECTROSTATIC AND STERIC EFFECTS OF CATIONIC POLYMERS ADSORBED ON CELLULOSE FIBRES

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Introduction

THE use of cationic organic polyelectrolytes as drainage and retention aids in the papermaking process and as flocculants in sewage treatment is steadily increasing. Therefore, there has been a growing interest in a better understanding of the mode of action of these additives.

There are two basic concepts discussed in the current literature which can be briefly described in terms of bridging and of charge neutralisation, respectively.^(1–6) Of particular interest is a variety of the latter, the ‘patch charge model’, which was introduced recently.⁽⁷⁾ In general the discussions are based on the data of electrophoretic mobility and of flocculation, drainage, or retention.^(8–14)

Clearly, in all cases the adsorption of the polymers from the bulk of the solution onto the dispersed particles is of prime importance for the discussion of the mechanism of action. There have been, however, only a few attempts to study the adsorption and the adsorption kinetics of cationic polymers in cellulose systems.^(15–18)

The object of this investigation was to study the influence of molecular weight and of charge density on the adsorption of polyethyleneimines (PEI) and of cationic polyacrylamides (PAA) in cellulose systems, in conjunction with electrokinetic and flocculation measurements.

Experimental

Materials

The data of the cellulose used are summarised in Table 1. After refining in a laboratory refiner the bleached sulphite pulp was freeze-dried for storage.

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TABLE 1—CHARACTERISTICS OF PULP

Ash content	0.50 per cent
SiO ₂	0.03 per cent
Ca	850 ppm
Mg	100 ppm
Fe	< 10 ppm
Carboxylic content	0.9 mequiv/100 g
BET Specific surface area	$\left\{ \begin{array}{l} S_{N_2} = 3.0 \text{ m}^2/\text{g} \\ S_{H_2O} = 141 \text{ m}^2/\text{g} \end{array} \right.$

The polyethyleneimines (PEI) were specifically made and had a mean molecular weight of 400, 1 500, 2 200, 4 300 and 22 000 according to the degree of polymerisation of 10, 35, 50, 100, and 500 respectively. The cationic modified polyacrylamides (PAA) denoted as A, B, and C had molecular weights in the range from 0.2×10^6 to 2×10^6 .

All experiments were performed in a 10^{-4} molar KCl solution in twice distilled water.

Methods

The polyelectrolyte charge density was determined by using a colloid titration technique based on the observation that cationic polyelectrolytes will react stoichiometrically with anionic polyelectrolytes.⁽¹⁹⁻²¹⁾

The equivalence point was determined by the metachromatic colour change⁽²²⁾ of o-toluidine blue with a 50 per cent esterified poly(vinylalcohol) sodium sulphate (NaPVS) as a chromotropic titrant. Details of the optical double beam titration technique will be published elsewhere.⁽²³⁾ The detection limit was 1×10^{-7} mequiv cm^{-3} .

The same method was used to determine the adsorption isotherms and the adsorption kinetics by measuring the residual polymer concentration after contact times between 30 seconds and 60 minutes.

The adsorption experiments were performed at a fibre concentration of 2 g/dm³, and a total volume of 3 dm³. The freeze-dried cellulose samples were dispersed by a 5 seconds treatment with a high speed disperser (Ultra-Turrax) followed by a half hour period of magnetic stirring at 500 rpm. The pH-value of the samples was adjusted to 4.5 or 7.0 by small additions of HCl and NaOH, respectively.

After this preconditioning procedure the polymer solution was added and, in the case of the kinetics experiments, the first sample collected through a screen (200 mesh) after 30 seconds, while the suspension was stirred at 500 rpm with a blade stirrer.

In a separate series of similar experiments equilibrium adsorption isotherms were measured. The residual polymer concentration was determined after a contact time of 30 minutes.

All adsorption experiments were performed in polypropylene ware to reduce polymer loss due to wall effects at low polyelectrolyte concentrations.

The extent of flocculation was determined by measuring the residual absorbance

of the supernatant liquid after a settling time of 24 hours. A Cary 14 spectrophotometer was used in the high sensitivity mode using 5-cm cells.

Electrophoretic mobility measurements were conducted on the undiluted suspensions in a semi-automatic microelectrophoresis apparatus, Laser-Zee-Meter, Model 102, manufactured by Pen-Kem-Company, Croton-on-Hudson, USA.^(11, 12) The instrument was calibrated with Min-U-Sil (Pennsylvania Glass Sand Corp.) a substance with well-defined mobility ($-2.14 \mu\text{m s}^{-1}/\text{V cm}^{-1}$ at 22.5°C).

Results

THE charge densities of the polyethyleneimines and the polyacrylamides investigated are summarised in Table 2.

TABLE 2—CHARGE DENSITIES OF POLYELECTROLYTES (mequiv/g)

	PEI					PAA		
	10	35	50	100	500	A	B	C
pH 4.5			24.6 ± 1			1.4	1.6	1.9
pH 7.0			19.1 ± 1			1.2	1.2	1.5

Within each group of polymers the charge density is almost independent of the molecular weight. It increases significantly with decreasing pH values.

Some typical results of the adsorption kinetics measurements of the PAA's

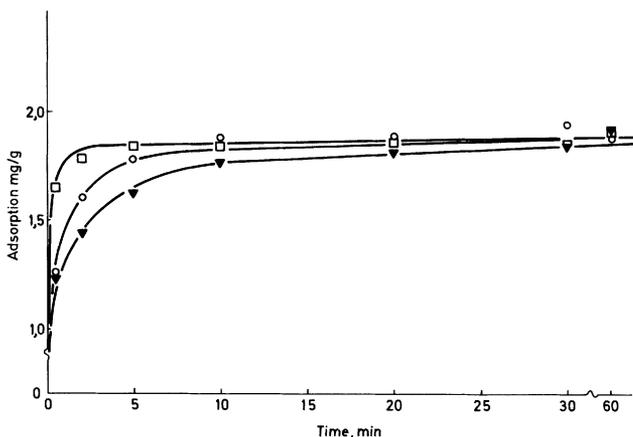


Fig. 1—Adsorption versus time of polyacrylamides of different molecular weights onto cellulose (2 g/dm^3) at an addition of 0.2 per cent. pH: 4.5

□ PAA A, ○ PAA B, ▼ PAA C

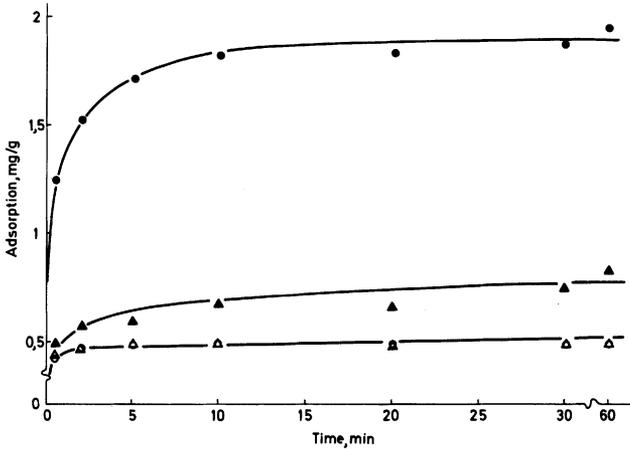


Fig. 2—Adsorption versus time of polyethyleneimines of different molecular weights onto cellulose (2 g/dm^3) at a dosage of 0.05 per cent and 0.3 per cent, respectively. pH: 4.5
 ○ (PEI 10) and △ (PEI 500) at 0.05 per cent
 ● (PEI 10) and ▲ (PEI 500) at 0.3 per cent

and the PEI's are shown in Figs. 1 and 2. In all cases of the PAA measurements the dosage of polymer was 0.2 per cent. As can be seen from Fig. 1 it takes an appreciable amount of time before maximum adsorption is reached. The speed of approach towards total adsorption depends clearly on the molecular weight.

With polyethyleneimines the adsorption kinetics is the same within experimental error for all species. This is shown in Fig. 2 where the adsorption of PEI 10 and PEI 500 is plotted as a function of time at two levels of addition. At a level of 0.3 per cent the accessible degree of adsorption depends on the molecular weight; it increases with decreasing molecular weight. The same is true for polyacrylamides if the level of addition is raised to values above 0.4 per cent.

From Fig. 3 it can be concluded that the saturation level of adsorption of the polyethyleneimines increases with decreasing charge density of the polymers.

As shown in Figs. 1–3 in all cases the process of adsorption was completed after 30 minutes. Therefore, equilibrium adsorption isotherms were deter-

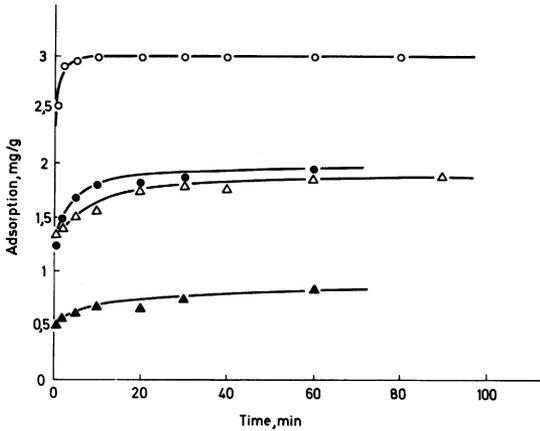


Fig. 3—Adsorption versus time of PEI 10 and PEI 500 onto cellulose (2 g/dm^3) at pH 7.0 as and pH 4.5 (for charge densities see Table 2); level of addition 0.3 per cent
 ● (PEI 10) and ▲ (PEI 500) at pH 4.5
 ○ (PEI 10) and △ (PEI 500) at pH 7.0

mined after half hour contact time. Fig. 4 shows the results of the experiments with the molecular weight series of PEI.

The same data are plotted as equilibrium adsorption isotherms in Fig. 5.

All the isotherms are of the high-affinity type. The saturation level decreases with increasing molecular weight.

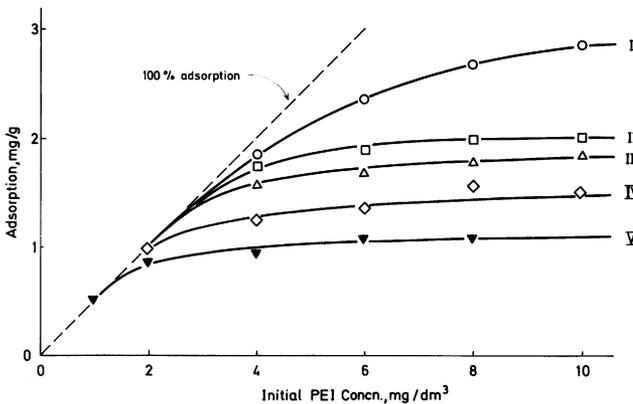


Fig. 4—Adsorption of polyethyleneimines of different molecular weights onto cellulose (2 g/dm^3) at pH 4.5, contact time 30 min
 I: PEI 10, II: PEI 35, III: PEI 50, IV: PEI 100, V: PEI 500

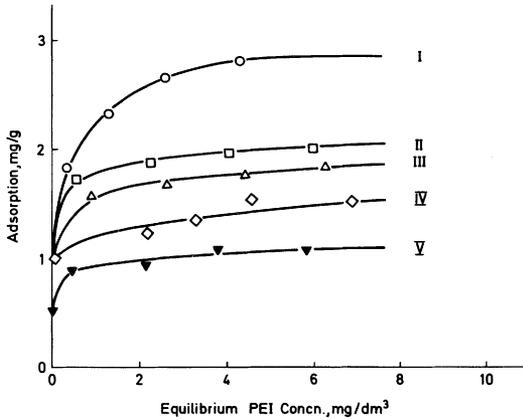


Fig. 5—Equilibrium adsorption isotherms of PEI's; effect of molecular weight
 I: PEI 10, II: PEI 35, III: PEI 50, IV: PEI 100, V: PEI 500

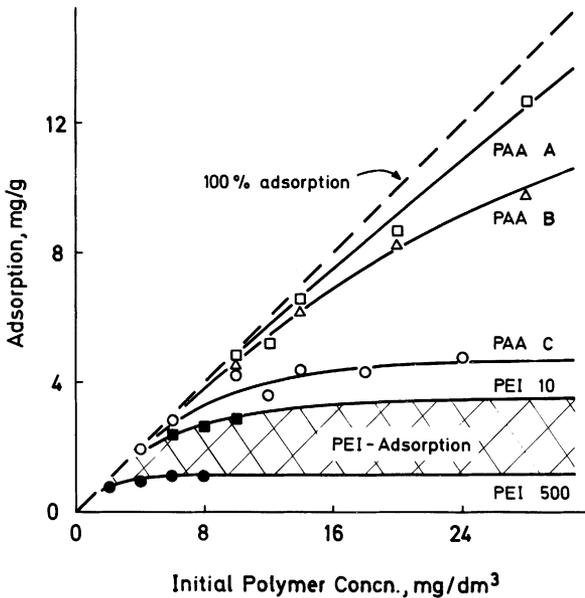


Fig. 6—Adsorption of polyacrylamides and polyethyleneimines of different molecular weights onto cellulose (2 g/dm^3) at pH 4.5 MW of PAA A, B, and C is increasing from the order of 2×10^5 to 2×10^6

The same pattern of molecular weight dependence is observed with the adsorption of polyacrylamides. Fig. 6 shows the results in comparison with the polyethyleneimine data.

It is noteworthy that the level of adsorption of all polyacrylamides is well above the level of saturation reached by the polyethyleneimines. Sample C, the polyacrylamide with the highest molecular weight comes in its adsorption characteristics close to the lowest molecular weight polyethyleneimine PEI 10. With the low molecular weight polyacrylamide PAA A there is total adsorption over almost the entire range of initial polymer concentration investigated in this study.

The electrophoretic mobilities of cellulose fines with polyethyleneimines are shown in Fig. 7.

The mobility data relate directly to the adsorption data of Figs. 4 and 5. Both measurements were carried out on the same samples. It follows from Fig. 7 that there is a strong dependence of the charge reversal capability on the molecular weight. Despite the fact, however, that the level of adsorption is increasing with decreasing molecular weight, as indicated in Figs. 4 and 5, the pattern of charge reversal shows the opposite trend. This becomes particularly evident in Fig. 8 where the zeta-potential is plotted as a function of the adsorbed amount of the PEI's of different molecular weights.

As to the state of adsorption, the results of successive adsorption

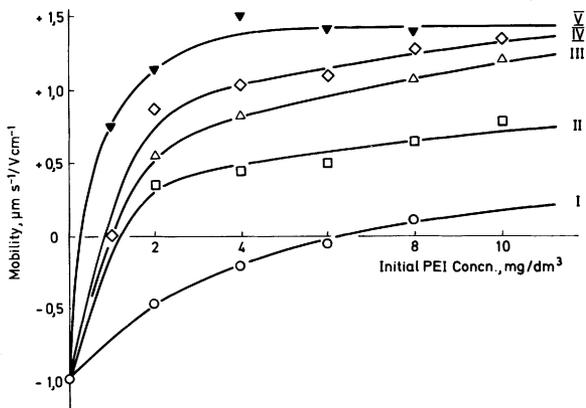


Fig. 7—Mobility of cellulose fines at equilibrium of the adsorption experiments with polyethyleneimines of different molecular weights, pH: 4.5

I: PEI 10, II: PEI 35, III: PEI 50, IV: PEI 100, V: PEI 500

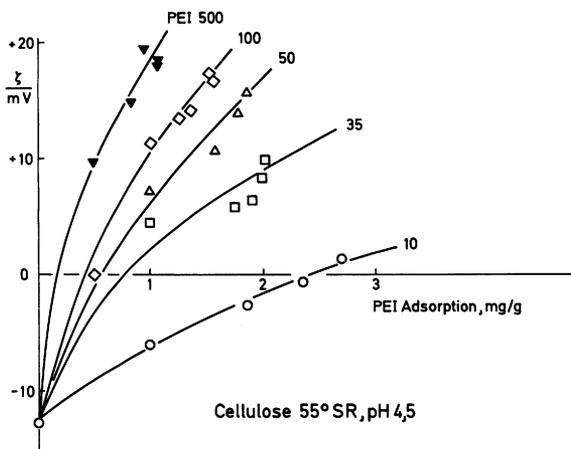


Fig. 8—Zeta-potential of cellulose fines as a function of the adsorbed amount of polyethyleneimines, pH: 4.5

experiments are quite informative. In Fig. 9 the adsorption of PEI 500 to almost saturation was followed by the adsorption of PEI 10.

Neither is the adsorption of the low molecular weight species inhibited nor is the already adsorbed high molecular weight polymer replaced. On the contrary, the adsorption of PEI 10 seems to be almost undisturbed.

The results of a similar experiment with reversed order of addition are plotted in Fig. 10.

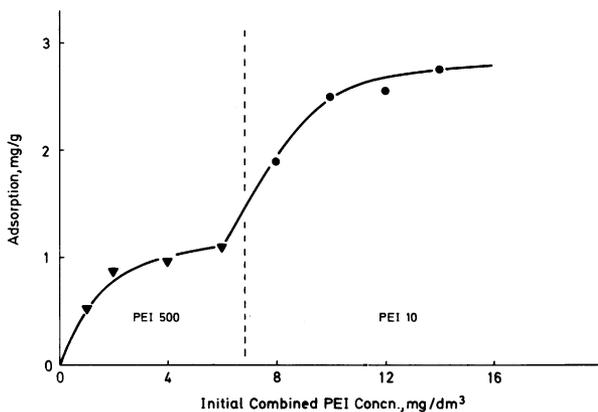


Fig. 9—Adsorption of polymers in successive adsorption experiments. PEI 500 followed by PEI 10

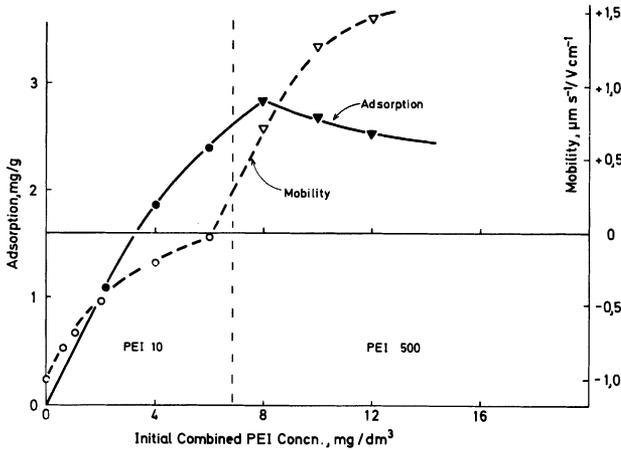


Fig. 10—Adsorption of polymers and mobility of cellulose fines in successive adsorption experiments. PEI 10 followed by PEI 500

The findings are quite different to the results of the preceding experiment. The total amount of polymers adsorbed eventually decreases when the PEI 10 covered cellulose is exposed to the PEI 500 solution. The significant increase of mobility, however, indicates that extensive replacement of the low molecular weight polyelectrolytes by the high molecular weight species is taking place.

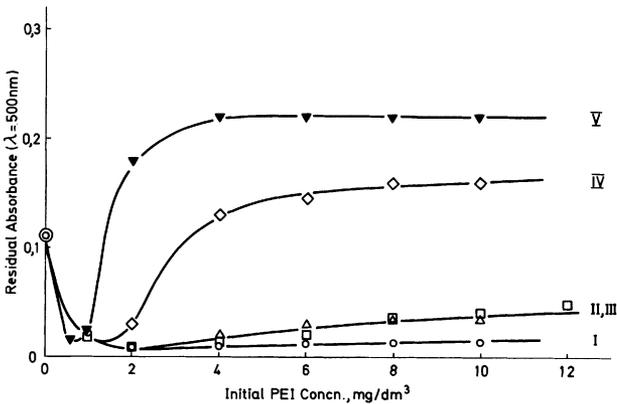


Fig. 11—Flocculation of cellulose suspensions (2 g/dm³) containing polyethylenimines of different molecular weights, pH: 4.5. I: PEI 10, II: PEI 35, III: PEI 50, IV: PEI 100, V: PEI 500

Parallel to the adsorption and mobility measurements, the extent of flocculation, induced by the addition of the polymers, was determined by measuring the residual absorbance of the supernatant liquid. A survey of the results of the PEI-series measurements is shown in Fig. 11.

Only the curves with high molecular weight polyethyleneimines exhibit a critical polymer concentration for optimum flocculation which is correlated to the point of zero mobility of the cellulose fines as indicated in Fig. 12.

Optimum flocculation is achieved in the mobility range of -0.5 to $+1.0 \mu\text{ms}^{-1}/\text{V cm}^{-1}$. In the case of high degrees of charge reversal the adsorbed polymers act as dispersants rather than as flocculants, as indicated by a level of residual absorbance well above the value obtained with plain cellulose suspensions.

In case of PEI 10 there is also a rapid decrease of residual absorbance associated with decreasing values of negative mobility. Due to the fact that

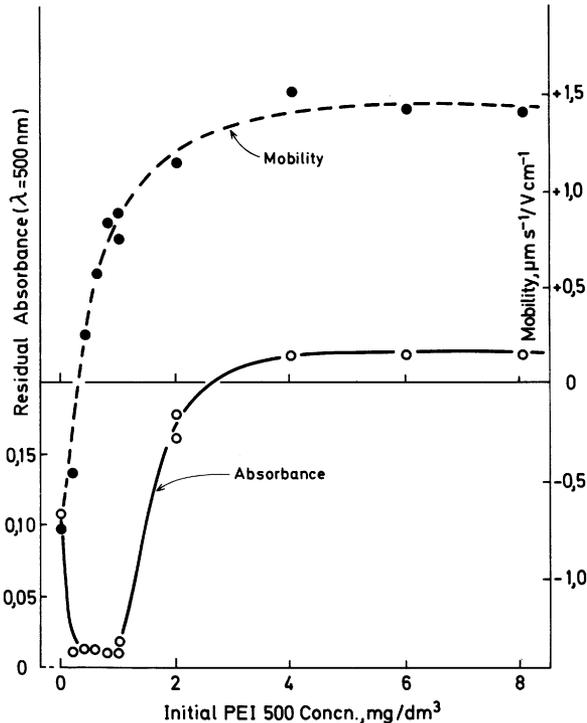


Fig. 12—Flocculation and electrophoretic mobility of cellulose suspensions (2 g/dm^3) containing PEI 500, pH: 4.5

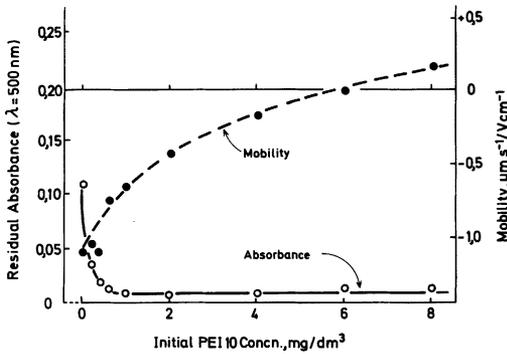


Fig. 13—Flocculation and electrophoretic mobility of cellulose suspensions (2 g/dm³) containing PEI 10, pH: 4.5

there is no charge reversal to an appreciable degree within the investigated range of polymer dosage, the state of flocculation stays constant. This is shown in Fig. 13.

The polyacrylamides exhibit a very different pattern of flocculation. As shown in Fig. 14, despite a comparable degree of charge reversal there is no indication of a close correlation between the mobility and the extent of flocculation.

The basic difference in the mechanism of action between polyethyleneimines

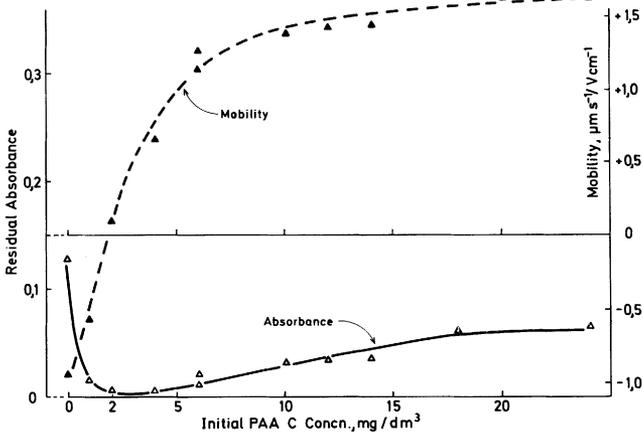


Fig. 14—Flocculation and electrophoretic mobility of cellulose suspensions (2 g/dm³) containing PAA C

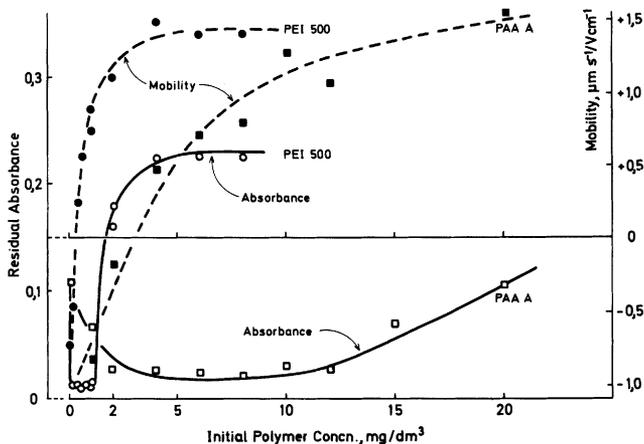


Fig. 15—Comparison of flocculation and mobility data of cellulose suspensions containing PEI 500 and PAA A, respectively

and polyacrylamides is clearly displayed in a direct comparison of flocculation and mobility data as shown in Fig. 15.

Discussion

SEVERAL conclusions may be drawn from the results of this study, which appear to corroborate some basic views of the mechanism of action of these polymers.

1. For both types of polyelectrolytes the extent of adsorption increases with decreasing molecular weight. The same phenomenon has been observed with different polymers by other authors.⁽¹⁵⁻¹⁸⁾

It reflects the differences in accessibility due to the porous structure of the adsorbent. At least for the low molecular weight PEI's the surface area accessible for adsorption is much larger than the nitrogen BET-area and perhaps close to the H₂O BET surface area.

2. This view is strongly supported by the results of the mobility measurements. Here it was observed that the efficiency of charge reversal increases with increasing molecular weight despite lower saturation levels of the adsorbed amount. As expected, with the generally smaller PEI-polymers this observation is particularly conspicuous.

The adsorption of the low molecular weight PEI's occurs to a large extent on the electrokinetically ineffective 'inner surface' of the pore structure.

3. The decreased tendency of adsorption with increasing charge density combined with earlier findings of an enhanced charge reversal efficiency,⁽¹⁴⁾ are in

accordance with the present state of knowledge of the conformation of poly-electrolytes.⁽²⁴⁾ The more extended configuration of the highly charged polymers results perhaps in two effects, one of a higher degree of mutual steric hindrance by electrostatic repulsion in the adsorbed state and another of a stoichiometric neutralisation reaction between positive and negative sites at the interface. From the experience of the already mentioned colloid titration technique it can be conjectured that the adsorption process is largely governed by the concentration of negative anchoring sites at the cellulose surface. The highly charged PEI's will tend to be adsorbed in a flat configuration with an increasing tendency towards a one-to-one correspondence of opposite charges with decreasing molecular weight.

Due to the low charge density of the PAA's their adsorption will lead towards a more protruded configuration. The saturation level of adsorption will generally be higher, as found in the present study.

4. With these conclusions in mind it seems justifiable to interpret the flocculation results with the PEI's as indicative of a charge neutralisation mechanism, while the findings with the PAA's strongly support bridging as the prevailing mode of action.

In the case of the higher molecular weight PEI's the point of zero mobility and correspondingly of optimum flocculation is always associated with an adsorbed amount far below the saturation level. This fact together with the observation of a fairly extended range of mobility, within which optimum flocculation occurs, supports the idea expressed in the 'patch charge model'.

In order to further elucidate the proposed modes of action, detailed studies of the configuration of the adsorbed polymers and of the kinetics of flocculation are in progress.

Acknowledgments

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Transcription of Discussion

Discussion

Prof. J. T. G. Overbeek I would like to make a remark both about the difference you find between high molecular weight and low molecular weight polymers. With low molecular weight polymers you would expect that in the adsorption they stay within the bounds of the original electrical double layer and the high molecular weight polymer will stick out further and cover up the original double layer. In this respect the adsorption of the same amount of positive charge may have a different effect because you do not only change the surface charge properties but you also shift the plane of shear to the outside.

Horn Yes, I agree with this interpretation. This is the case when for example you compare polyethyleneimine 500 with polyethyleneimine 10 and their adsorption layer behaviour as far as the electrokinetic effects are concerned. I still think that we have to also consider the adsorption of the very low molecular weight species in the internal structure of the cellulose to get the total picture.

Prof. G. G. Allan I suppose that one of the benefits of coming to these meetings is the possibility of pointing out some of the misconceptions that can arise and I would like to draw to Dr Horn's attention the fact that the adsorption of polyethyleneimine on cellulose has been elucidated in a 19-paper series from the University of Washington. In that work it has been very clearly established that the adsorption of polyethyleneimine on cellulose is a function of the molecular size, and these experiments when integrated with the very elegant studies of Stone and Scallan show that the PEIs fit into the cellulose fibres directly according to the fibre pore structure and they generate accessibility curves more or less identical with those generated by the U.S. Forest Products Laboratory using polyethylene oxides and by the Canadian workers using the sugar series. I think that it ought to be made clear to the meeting that polyethyleneimines are unequivocally retained by cellulose fibres by ionic forces and this was established a long time ago and the amount

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retained exactly corresponds to the number of negative charges. I believe this would also apply in the case of the cationic polyacrylamides which in your slides are not clearly shown to be cationic, and I am here assuming that you have been using cationic rather than uncharged polyacrylamides to achieve this retention. The question I have for you relates to the fact that I wonder why you ran the experiments in 10^{-4} molar potassium chloride and would you comment on the surfactant used in the latex system which would of course have a profound effect on the adsorption of any positively charged polymer.

Horn It has to be pointed out that in this paper we are referring to electrostatic and steric effects of adsorbed polycations with respect to the flocculation mechanism and *not* with respect to the mechanism of adsorption.

The reason why we used 10^{-4} KCl solution has to do with the fact that we started out with streaming potential measurements to determine the zeta potential of cellulose fibres. For the interpretation of these data by, for example, Goring–Mason-plots we wanted to have well defined conductivity values to transform the streaming potentials into zeta potentials. If you apply higher salt concentrations the general pattern of adsorption is not basically changed, however the degree of adsorption is somewhat modified.

As to the polyacrylamides they are cationic modified and this is stated in Table 2. The charge density of the polyacrylamides is about one tenth of the charge density of the polyethyleneimines.