Preferred citation: T. Lindström. Some fundamental chemical aspects on paper forming. In **Fundamentals of Papermaking**, *Trans. of the IXth Fund. Res. Symp. Cambridge, 1989*, (C.F. Baker & V. Punton, eds), pp 311–412, FRC, Manchester, 2018. DOI: 10.15376/frc.1989.1.311.

SOME FUNDAMENTAL CHEMICAL ASPECTS ON PAPER FORMING

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ABSTRACT

The fundamental physico-chemical aspects of retention chemistry are reviewed in the light of basic concepts in colloid chemistry.

Special emphasis has been paid to the surface chemistry of cellulose and cellulosic materials, their origin of charge, dispersion force interactions as well as the implication of certain aspects of peculiar cellulosic surfaces, e.g. the influence of their porosity on polymer adsorption.

Charge neutralization, patch flocculation, heterocoagulation, bridging and complex flocculation phenomena are discussed as well as polymer adsorption phenomena at the cellulose/water interface

INTRODUCTION

The papermaker uses a wide variety of synthetic and natural additives in order to retain fines and filler materials and dewater the consolidating wet web during papermaking. Owing to the complex wet-end chemistry, the mode of action of these additives is not well understood.

Modern papermaking systems involve closed white water systems, fast machines and twin-wire forming. These general trends call for an increased use of retention/dewatering agents in papermaking and new combinations and chemical systems are continously being developed for the paper industry.

The present review aims at summarizing some of the fundamental principles in the area of retention chemistry.

THE ELECTRICAL DOUBLE LAYER AND COAGULATION OF CELLULOSE SOLS

Before dealing with electrokinetics and electrical interactions (1-3) of particle dispersions it is illustrative to deal briefly with the structure of the electrical double layer.

A schematic representation of an electrical double layer is pictured in figure 1. The negatively charged surface attracts ions of opposite sign (counter ions) and repels ions of its own sign (co-ions). The ion-distribution of such an atmosphere obeys Boltzmann's law:

$$C_i = C_{i0}\exp(-z_i F\Psi/RT) \quad (1)$$

where C_i is the local and C_{i0} the average ion concentration, R the gas constant, F the Faraday constant and T the absolute temperature. The potential is linked to the charge distribution by the Poisson law:

$$\nabla^2\Psi = -4\pi\rho/\epsilon \quad (2)$$

where $\rho = \sum z_i C_i F$ and ϵ the dieletric constant of the media. Equations (1) and (2) gives the so called Poisson-Boltzmann equation, which can be solved, leading to:

$$\Psi = \Psi_0 \exp(-\kappa x) \qquad (3)$$

for the potential at a distance x from a flat, charged surface with potential Ψ_0.

$1/\kappa$ is the inverse of the so called Debye-parameter and $1/\kappa$ is given by:

$$1/\kappa = (\epsilon\epsilon_0 RT/2F^2)^{\frac{1}{2}}\ 1/\sqrt{I} \qquad (4)$$

where I is the ionic strength:

$$I = \tfrac{1}{2}\sum c_{i0} z_i^2$$

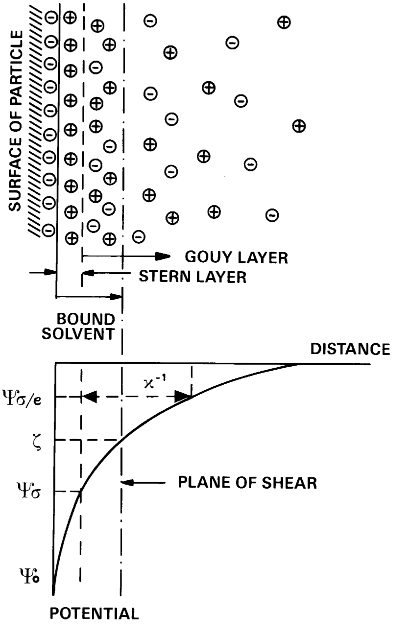


Fig 1 - The electrostatic double layer.

One important aspect of the solution of the Poisson-Boltzmann equation is the occurrence of the quantity, $1/\kappa$ in eq 3. It indicates the order of magnitude of the spatial extension of the ionic atmosphere around a particle.

It is thus instructive (see table 1) to give a short table of values for this parameter at different electrolyte concentrations.

C (mol/l)	$1/\kappa$ in nm
10^{-5}	96
10^{-4}	30
10^{-3}	9.6
10^{-2}	3.0
10^{-1}	0.96

Table 1. Thickness of the electrical double layer for monovalent electrolytes in water at 25°C.

The magnitude of the thickness of the electrical double layer is extremely important when effects of polymers on electrokinetics and in bridging flocculation are considered.

Electrokinetics

The term "electrokinetics" involves the combined effect of motion and electrical phenomena. Electrokinetic phenomena involve processes where there is a relative velocity between two parts of the electrical double layer. This may arise from the movement of charged particles in an electric field (electrophoresis) or from the movement of the solution phase relative to a stationary wall (electro-osmosis or streaming potential). In each case electrokinetic measurements involve a quantity known as the zeta-potential (ζ).

The zeta-potential is the potential in the slip plane or surface of shear between the two phases (see fig 1). The exact location of this slip plane is more or less ill defined, though it is often assumed that $\zeta \approx \psi\delta$, because the thickness of the bound solvent layer in the time frame of an electrophoresis experiment is probably very thin, approximating at most a few molecular layers of bound solvent.

When a polymer is adsorbed onto a particle surface, the slip plane is moved out from the surface a distance which is dependent on the draining properties of the polymer in the adsorbed state. Thus strictly, the notion of zeta-potential loses some of its significance for materials such as swollen gels (e.g. cellulosic surfaces) and polyelectrolytes.

The conversion of the electrophoretic mobility, the experimentally determined quantity in an electrophoresis experiment, to zeta-potential offers some additional problems. The commonly exployed formula relating electrophoretic mobility (μm/s/ V/cm) and ζ-potential:

$$V_e = \epsilon \zeta E / 4 \pi \eta \qquad (5)$$

where E is the applied field strength and η the viscosity of the dispersing media, has the following restrictions (4):

- *The thickness of the double layer must be thin compared with the dimensions of the particle ($\kappa a \gg 1$).*

- *The surface conductance must be small.*

Another effect not included in the above derivation is the so called "relaxation effect", which arises because the electrostatic double layer is distorted under the action of an external electric field. Provided the electrostatic double layer is thin compared with the size of the particle, this effect can however be neglected (4).

The combined effect of variations in double layer thickness and of the shape of the particles on the expression relating zeta-potential and electrophoretic mobility is given in figure 2.

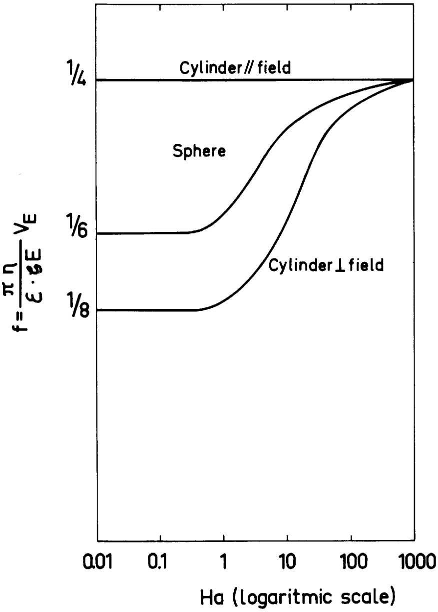


Fig 2 - Dependence of the electrophoretic mobility on the ratio of the radius (a) to the thickness (1/κ) of the double layer.

It can be seen in figure 2 that all three curves merge to the expression given in equation 5 for large κa. It can thus be concluded that if we have particles of arbitrary shape and particles with a thin double layer compared with the particle size, equation 5 can be used. For practical purposes, however, it offers no advantage to convert mobilities into zeta-potentials, as practical papermaking systems are always polydisperse and it is not usually possible to calculate the double layer thickness since the electrolyte composition is not known. This implies that it is not possible to make meaningful statements about an absolute zeta-potential at which coagulation should occur in practical systems, since the degree of validity of equation 5 is uncertain.

Origin of the charge on papermaking fines and fibres

Cellulose, as such, is negatively charged throughout the whole pH-regime. No charge reversal occurs and the zeta-potential is approximately zero at pH-values < 2.7, see fig 3. As shown in the figure, streaming potential values on coarse fibres and electrophoresis measurements on fines particles gave approximately the same result (5, 6).

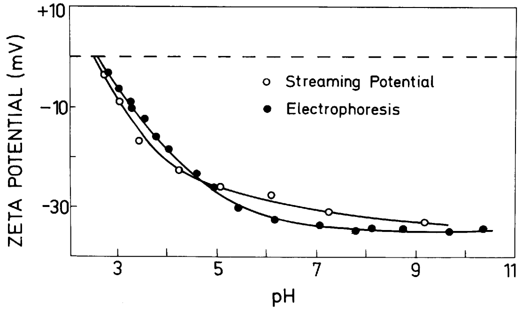


Fig 3 - Zeta-potential for fines and fibres versus pH. (Jaycock and Pearson, 5, 6)

In the early literature there was some controversy as to whether cellulosic fines and fibres exhibit the same zeta-potential (6, 7-12). When results from the streaming potential method on fibres and microelectrophoretic measurements on fines are compared, similar results are often obtained (6, 7, 12,). It should be noted, however, that the fines fraction for many types of fibre material has a higher content of noncellulosic material (13-15) and thus a higher content of acidic groups. Different values ought therefore to be obtained in many cases.

This issue is, however, probably of minor significance in practical papermaking systems.

The charge of dispersed materials originates from one of the following sources (2):

- *Dissociation of ionic groups on the particle*
- *Adsorption of ions*
- *Isomorpous substitution in the crystal lattice*

In the case of cellulose surfaces, the present evidence suggests that the dissociation of the ionic groups is the main source of the charge (7-8, 16). It is not known whether ion adsorption contributes to the charge. This situation may be compared to the origin of the charge on clays, where isomorphous substitution and ion dissociation (silanol, aluminol groups) are important factors, and on $CaCO_3$ where ion adsorption is the potential determining factor at the surface.

The ionizable groups on cellulosic fibres may be carboxyl groups, sulfonic acid groups, catecholic groups, phenolic groups or hydroxylic groups. Under normal papermaking conditions the carboxyl and sulfonic acid groups are the major contributors to the fibre charge.

Most of the carboxyl groups originate either from non-cellulosic components in the wood itself or are created during the pulping and bleaching operations.

Sulfonic acid groups are introduced with the sulfite treatment during Chemi(Thermo)Mechanical (CTMP) or chemical Pulping.

In native wood and in (Thermo-)Mechanical Pulps (TMP) the carboxyl groups stem from uronic acid residues. Most of these groups are present as 4-O-methyl-α-D-glucopyranosyluronic acid bound to the xylan, even if the xylan chain also contains minor amounts of α-D-galactopyronosyluronic acid groups (17-18). Some carboxyl groups are also present in the pectic substances in the fibre cell wall. The number of methylglucuronic acid groups varies in different woods but is usually of the order of 5-15 meq/100 g (17).

One essential fact is that the acid function of some carboxyl groups is blocked owing to lactone or ester formation (19). Lactones and esters are cleaved under alkaline conditions (e.g. during the initial stages of alkaline cooking) and can be formed under neutral or acidic conditions during drying (18).

In the acidic sulphite process, the sulphonation takes place at benzylic carbon atoms in both phenolic and non-phenolic lignin units (20). Lignosulphonates do not generally contain carboxyl groups (21). Thus the sulphonate groups in sulphite pulps are contained in the lignin fraction and the carboxyl groups in the non-cellulosic cell-wall components. The carboxyl group content decreases as a result of lignin and polysaccharide (mainly xylans) dissolution during delignification (see figure 4).

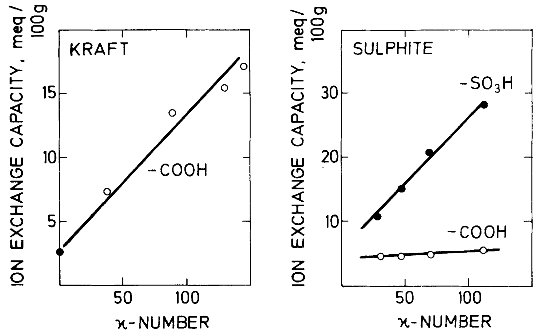


Fig 4 - Ion exchange capacity of kraft and sulfite pulps at various kappa-numbers. (Lindström and Carlsson, 22)

A similar situation arises during kraft pulping. In contrast to lignosulphonates, however, kraft lignins do contain some aliphatic carboxyl groups (23). These are probably formed by atmospheric oxidation or in disproportionation reactions of the Cannizzaro type (23).

During alkaline pulping, peeling reactions are stopped by the formation of metasaccharinic acid types of carboxyl groups, but they constitute relatively few carboxyl groups compared with methylglucuronic acid groups in the xylans (18). During oxidative bleaching, carboxyl groups may be introduced onto the polysaccharides if the bleaching is performed under unfavourable conditions. This is, however, seldom the case during the technical bleaching of paper grade pulps (17).

The classical coagulation theory, DLVO-theory

The classical coagulation theory for the stability of lyophobic colloids, i.e. the DLVO-theory (Derjaguin-Landau-Verwey-Overbeek) (1-3) considers two kinds of forces between dispersed particles

- electrostatic repulsive forces
- van der Waal's (London dispersion) attractive forces

According to this theory, the energy of interaction between two particles is a superposition of the electrostatic and the attractive forces:

$$V_{tot} = V_E + V_A \qquad (6)$$

The mathematical expressions for the total energy of interaction depend on a number of factors such as particle size and shape, chemical compositon of the particle etc.

The repulsive energy term originates from the overlapping of the electrostatic double layers when two particles interact.

For the repulsive energy at constant surface potential, valid at both low electrolyte concentrations (κR low) and relatively long distances (κr large), the following expression may be used:

$$V_R = 32\pi\epsilon_r\epsilon_o R(k_BT/ze)^2\Phi^2(\ln(1+\exp(-\kappa r)) \qquad (7)$$

where

R = radius of particles
r = interparticle distance
z = valency of the electrolyte
e = elementary charge
Φ = tanh $(ze\Psi/4k_BT)$, where
Ψ = surface potential
k_B = Boltzmann constant

The attractive forces can be grouped into the following types

a) Permanent dipole - induced dipole interaction (Debye)
b) Permanent dipole - permanent dipole interaction (Keesom)
c) Induced dipole - induced dipole interaction (London)

For individual atoms, these attractions forces decay rapidly with increasing interatomic distance $(\sim r^{-7})$ but when they are summed for the interaction between particles in the colloidal size range they are of significant wide-range $(\sim r^{-2})$ and strength.

It is convenient to designate the cluster of constants as the Hamaker constant (A_{121}). The attractive energy of interaction may then be written:

$$V_A = - A_{121}/12\pi r^2 \qquad (8)$$

Using equation (6) and appropriate constants the energy of interaction between particles may be calculated. A typical interaction curve for two spherical particles of equal radius (1000Å) is given in figure 5.

Particles having a thermal energy (k_BT) exceeding the barrier will be intercepted (coagulation) during a collision. The DLVO-theory essentially predicts:

- the higher the potential at the surface of a particle, the larger will the repulsion be

- the larger the Hamaker constant, the larger is the attraction between molecules and by extension, between macroscopic bodies.

- the lower the electrolyte concentration the larger is the distance from the surface before the repulsion drops significantly.

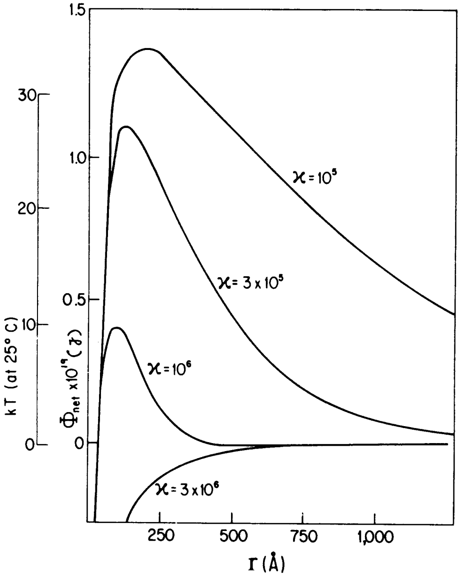


Fig 5 - Energy of interaction between spherical particles (r=0.1 μm) at different κ-values and constant A_{121} (10^{-19} J) and ψ_0 (25.7 mV).

It has long been known that the addition of electrolytes causes coagulation of lyophobic colloids, and this is also the case for finely dispersed cellulose sols. The higher the valency of the counter-ions the higher is their ability to compress the electrostatic double layer. This is the qualitative statement of the Schulze-Hardy rule. Many authors have established similar relationships for cellulosic dispersions (24-26, 27, 28).

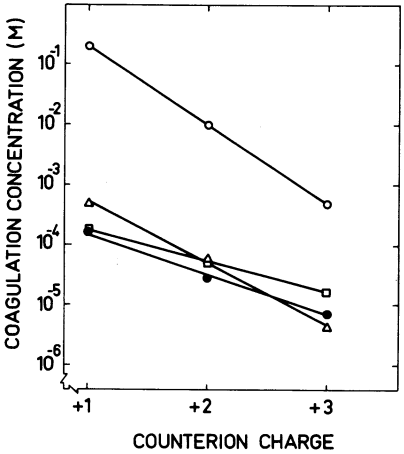


Fig 6 - The influence of the charge of the counterions on the logarithm of the critical coagulation concentration (C.C.C.) for various sols.

o Styrene-butadiene latex, (Force et al, 28)
□ Microcrystalline cellulose, (Rånby, 25)
● Microcrystalline cellulose, (Kratohvil et al, 24)
Δ Microcrystalline cellulose, (Martin-Löf et al, 27)

In figure 6 some data are compiled together with data for a latex disperison. A general feature of this graph is that the Critical Coagulation Concentration (C.C.C.) is lower for cellulosic dispersions than for e.g. latex sols. This behaviour indicates a comparatively high value for the Hamaker constant of cellulose. Generally, the DLVO-theory predicts that the relationship between the C.C.C. and the valency of the counter-ion should be C.C.C. $\sim Z^{-6}$.

Coagulation kinetics

Studies of the perikinetic (particle collisions dominated by the Brownian motion) coagulation of particle sols offer a more powerful insight to the interaction forces of colloids.

If an array of uniform spherical particles, whose motion is totally governed by the Brownian motion, is considered the initial rate of doublet formation can be written:

$$J = k_r N_o^2 \tag{9}$$

where k_r is the second order rate constant and N_o the initial number of spherical particles. The Smolouchowsky theory (3) predicts that:

$$k_r = 8k_BT/3\eta \tag{10}$$

when there is no energy barrier between two interacting particles. η is the viscosity of the dispersing medium. This rate of coagulation is referred to as "fast coagulation", and is fast in the sense that there are no barriers towards coagulation.

For slow coagulation, i.e. in the case when there is an energy barrier ("activation energy for coagulation") towards coagulation, the second order rate constant, k_s, may be written:

$$k_s = k_r/W \tag{11}$$

where W is called the stability ratio.

It can be shown (3) that the stability ratio, W, is related to the energy barrier $(V_A(r) + V_R(r))$ according to the expression:

$$W = 2R\int_{2R}^{\infty} \exp(V_A(r) + V_R(r))/k_BT \; r^{-2}dr \tag{12}$$

where R is the particle radius and r the interparticle distance.

It is also common (1-3) to include a correction term for the hydrodynamic drag during interparticle collisions.

It can be shown that the DLVO theory predicts that the stability ratio for spherical particles should vary with the electrolyte concentration (c) as follows (1-3):

$$\log W = K_1 \log c + K_2 \qquad (13)$$

where K_1 and K_2 are constants. This relationship is indeed also found for spherical particles (e.g. latex)

Experimentally, light-scattering is particulary suited to such kinetic studies and experimental turbidities can be interpreted in terms of the number and size of the particles. A variation is simply to measure the change in absorbance with time, which is proportional to dN/dt, in a stop/flow type of experiment.

Such studies have also been made on microcrystalline cellulose (MCC) sols (29).

Figure 7 shows the logarithm of the stability ratio as a function of the electrolyte concentration for MCC-sols. The critical coagulation concentration (C.C.C.) as defined from stop/flow experiments is not, unexpectedly, higher than the C.C.C.'s obtained from "overnight" sedimentation experiments (fig 6). The interesting feature is that MCC-sols show exactly the same stability features as those predicted from the DLVO-theory. It must however be remembered that MCC-sols are anisotropic particles, for which the theory was not derived.

From such data the Hamaker constant of cellulose (in water) was calculated to be about 10×10^{-20} J for various MCC-sols hydrolysed to various degrees (29).

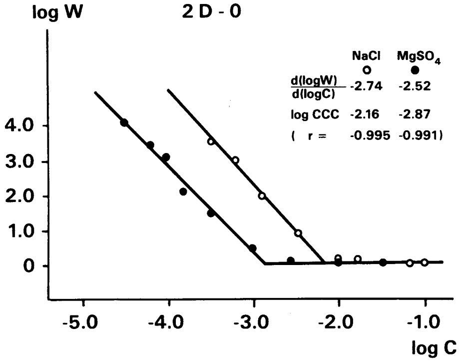


Fig 7 - The logarithm of the stability ratio as a function of the logarithm of the electrolyte concentration determined in stopped flow experiments for microcrystalline cellulose sols. (Winter, L et al, 29)

The Hamaker constant of cellulose may also be estimated from the relationship between the Hamaker constant and the dispersion component (γ^d) of the surface tension:

$$A_{11} = 4\pi/1.2\gamma^d d^2 \qquad (14)$$

where d is the interfacial separation of atomic centres at contact. This method is, however, subject to considerable error depending on the selection of the correct interfacial separation at contact.

A third way of determining the dispersion force of cellulose is by using a statistical mechanics approach (Lifshitz theory) based on the fundamental molecular interactions at different frequencies i.e. the dispersion properties of the polarisation. According to this theory, the dispersion force is the sum of the inductive interactions at different frequencies and it can be directly determined through the dielectric function of the material. The Hamaker constant is calculated by a summation (30):

$$A = 3k_BT/2 \sum_{n=o}^{\infty} \sum_{s=1}^{\infty} (\Delta_{12}\Delta_{32})^s/s^3 \qquad (15)$$

The equation demonstrates the combined Hamaker constant for the materials 1 and 3 immersed in a media 2. Here Δ represents the excess dielectric function between the substance 1 or 3 and the surrounding medium 2. The dielectric function depends on the frequency (ξ) and the dielectric response, (ϵ), of the different materials:

$$\Delta_{kl} = \epsilon_k(i\xi) - \epsilon_l(i\xi)/\epsilon_k(i\xi) + \epsilon_l(i\xi) \qquad (16)$$

The frequency is given by $\xi = n \cdot 2\pi k_BT/h$

The Hamaker constant depends on the difference in dielectric response between the materials and its surroundings over all frequencies. The combined Hamaker constant between two materials can not therefore be calculated from a harmonic or geometric mean value unless the dielectric function Δ is constant over the entire frequency range. It is, however, often sufficient to consider the UV-spectrum since this is the most important range, but even with this approximation a large error is introduced since the characteristic absorption frequencies are different for different materials. For an accurate determination of the Hamaker constant of cellulose it is therefore necessary to determine the dielectric function for cellulose.

The dielectric function can often be expressed by the contributions from different frequency-ranges according to (<u>31</u>):

$$\epsilon(i\zeta) = (\epsilon_O-\epsilon_d)/(1+\xi/\nu_{MW})+(\epsilon_d-n^2)/(1+(\xi/\nu_{IR})^2)$$

$$+ (n^2-1) / (1+(\xi_{UV})^2) + 1 \qquad (17)$$

In this equation ϵ_0 is the static dielectric number, ϵ_D the microwave dielectric number, n is the index of refraction, ν_{MW}, ν_{IR} and ν_{UV} are the characteristic absorption frequencies in the different frequency ranges. For cellulose all of these are known except for the characteristic UV-frequency which has so far not been experimentally determined. Assuming however that this characteristic UV-frequency is close to that of other polymers, a Hamaker constant for cellulose in water can be calculated to be $3 \cdot 10^{-20}$ J (29). Published values for the Hamaker constant of cellulose and some other sols are presented in table 2. From Visser's extensive tabulation of Hamaker constants for various materials A_{121} for cellophane can be calculated to be between 10-18 x 10^{-20} J. A large spread in the experimental values for the Hamaker constant when different methods are compared is however not uncommon (33).

Phase 1	A_{121} x 10^{20} (J)	ref
AgI	0.2-10; 10-70; 3	(32)
Au	6; 0.5-1	"
Se	0.5-5; 2	"
SiO_2	0.2-0.5	"
Arachidic acid	0.03	"
Polystyrene	0.1-1; 0.5-2	"
Paraffin	1.5	"
Cellulose	3, 10-18	(29, 33)

Table 2. Values of the effective Hamaker constant for various sols

AGGREGATION OF CHARGE-STABILIZED DISPERSIONS BY POLYMERS

Fines, fillers, fibers and other miscellaneous colloidal materials used in papermaking are aggregated by the use of various polymers in order to increase their wire retention. The aggregation mechanism for a particular suspension is determined by the physical and chemical surface characteristics of the particles and polymers involved as well as by the suspension concentration, the size distribution of the particles and polymers, and the hydrodynamic mixing conditions etc in a very complex manner.

In spite of the complexity of these aggregation processes it is convenient to classify and group the aggregation mechanisms into various classes. In the following section the following classes will be treated:

* *Charge neutralization and charge reversal phenomena*
* *The patch flocculation mechanism*
* *Bridging flocculation (monopolymer systems)*
  - *adsorption flocculation*
  - *sensitization flocculation*
* *Complex flocculation (multicomponent systems)*
  - *Dual polymer systems of the cationic/anionic type*
  - *Microparticulate flocculant systems*
  - *Network flocculation phenomena*

Charge reversal phenomena

In the simplest case, the charge of a suspension is neutralized by the addition of an oppositely charged polyelectrolyte. If a sufficient amount of polymer is added above the optimum polymer dosage (OPD) restabilization can occur. This may be due to charge reversal of the suspension (charge restabilization) or to steric stabilization (34).

In principle, the London van der Waal's component is the primary driving force causing coagulation in this case. Steric stabilization is due to the protective action of an adsorbed polymer layer on the particle surface. Charge restabilization and steric stabilization may be simultaneous phenomena.

In many cases it is difficult to distinguish between charge neutralization, patch flocculation and bridging flocculation although it is commonly recognized that the latter phenomena are more common the higher the molecular weight of the polymer used (12, 26, 35, 36). This is also indicated by the fact that the OPD for flocculation is shifted from the isoelectric point to lower polymer additions as the molecular weight of the polymer is increased (12, 26, 34-36). In other cases the physical conditions during aggregation determine which mechanism is the predominant one. Thus, in very dilute suspensions, charge neutralization and patch flocculation are more likely to be the predominant aggregation mechanism if the average interparticle distance is longer than the polymer chains or loops protruding out from the particle surface. If the contact time before particle collision is so long that the polymer is adsorbed in a more flat conformation on the particle surface, bridging is also less likely.

Charge neutralization as a polymer aggregation phenomena has been studied by several authors (e.g. 7, 11, 12, 34-43). In the case of charge neutralization, the aggregate structure is expected to be independent of polymer molecular weight or polymer structure of the OPD. If bridging takes place there is a significant dependence on polymer molecular weight (44). It is therefore convenient to discuss charge reversal mechanisms of cellulosic suspensions without specific reference to the particular aggregation mechanism involved.

There are a number of parameters such as the polymer structure, the chemical environment and the fibre properties which affect the amount of polyelectrolyte required to reach the isoelectric point ("cationic demand"). Some data for cellulosic dispersions have been compiled in table 3.

	Parameter (increasing)	Cationic demand	Ref
Polymer Structure	Molecular weight	↘	(38, 39)
	Charge density	↘↘	(38-40)
Chemical Environment	pH	↗	(7, 38-40, 45)
	Electrolyte content	↗	(38-40)
	Anionic wood polymers	↗↗	(38, 39, 46-48)
Fibre Properties	Carboxyl content	↗	(7)
	Hydrodynamic surface	↗	(38-40, 45)

Table 3. The effect of various parameters on the cationic demand for cellulosic dispersions

An increase in the molecular weight of the added polymer decreases the cationic demand. The most likely explanation for this behaviour is the fact that cellulose is a porous substrate. The higher the polymer molecular weight, the less accessible is the cellulose gel to the polymer, or, alternatively, fewer accessible ionic adsorption sites are available to the polymer. Thus it is easier to recharge the surface. Note that under these circumstances the interior of the cellulose gel may be negatively charged while the outer surface is cationic. Another view is that as the polymer molecular weight increases the size of the loops protruding out in solution increases (49). This means that the slip plane, where the zeta-potential is determined, is displaced out from the surface thus decreasing the influence of surface charge on the zeta-potential.

The effect of charge density of the polymer on charge reversal is not only a matter of the number of cationic groups since the extension of the polymer in solution increases due to mutual electrostatic repulsion between the charged groups (50). This extension of the polymer conformation again prevents the polymer from penetrating the porous structure, thus decreasing the cationic demand more than is expected from simple stoichiometric charge relationships (38-40). The effects of the molecular weight and charge density (D.S.) on charge reversal are illustrated in figure 8.

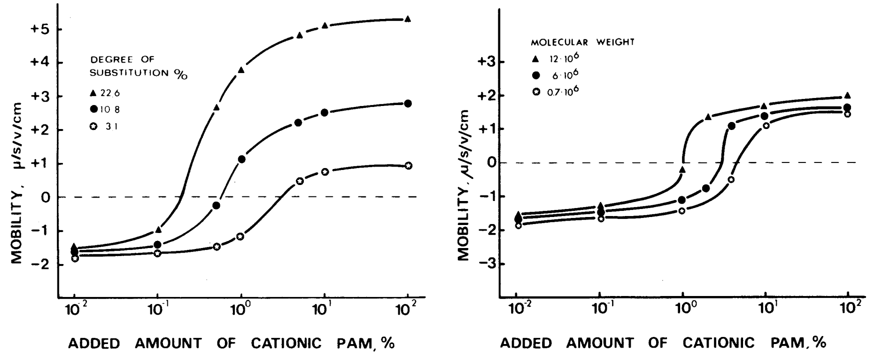


Fig 8 - The effects of degree of substitution (D.S.) (left) and polymer molecular weight (right) on charge reversal of microcrystalline cellulose sols. (Lindström et al, 38)

Electrolyte addition increases the cationic demand since the polymer becomes more coiled and penetrates the porous structure of the cellulosic surface (38-40).

An increase in pH or carboxyl group content increases the surface charge on the cellulose, thus increasing the amount of cationic polyelectrolyte required to reach the isoelectric point.

Increasing the hydrodynamic surface by e.g. beating increases the accessibility of charged groups to the cationic polyelectrolyte and thus increases polymer adsorption and cationic demand.

The "Patch model" of flocculation

An electrostatic mechanism different from the classical mechanism for the flocculation of charged particles by polyelectrolytes of opposite charge has been proposed (51, 52). The difference between this concept and the charge neutralization concept is the suggestion that patches of a charged poly-ion are formed on the oppositely charged surface. The situation is illustrated in fig 9.

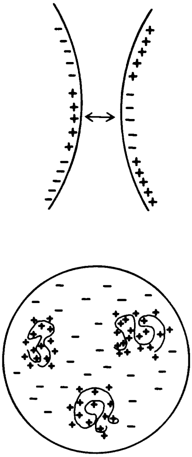


Fig 9 - The "patch model" of polymer adsorption and flocculation.

Thus the surface charge on the particle is not evenly smoothed out when polymer is adsorbed. In this way, a charged patch on one particle is attracted by an oppositely charged patch on another particle.

This is a kind of heterocoagulation mechanism where both attractive van der Waal's forces and attractive electrostatic interactions promote flocculation. The model applies to systems where the attractive forces between the polymer and the particle are high. Under these circumstances it is concluded from theoretical calculations (52) that the polymer is adsorbed in a flattened conformation on the surface so that the polymer loops are too small to bridge over the electrostatic double layer. Optimum surface coverage is not 0.5 and is predicted to decrease with increasing molecular weight. For high molecular weight polymers or high ionic strengths the OPD is predicted to be independent of molecular weight.

In general it is found that systems which work through a patch flocculation mechanism have their isoelectric points very close to the OPD for maximum flocculation (16, 53-55).

The shear strength of flocs formed through patch flocculation is generally greater than the floc strength created through simple neutralization of the charges on the surfaces. This is expected since both attractive van der Waals forces and electrostatic forces cooperate.

It has also been found (51) that an increase in the electrolyte content decreases the rate of flocculation due to a decreased mutual attraction between the patches, as expected from theory. This is a specific feature distinguishing patch flocculation from charge neutralization. It must be emphasized that patch-flocculation can only occur if the characteristic size of the patches and their interspacings are greater than the characteristic size of the electrostatic double layer ($1/\kappa$). Thus under conditions with a very low electrolyte content this mechanism is transferred to a charge neutralization type of aggregation mechanism. Thus, a small amount of electrolyte is usually necessary to sensitize this type of agglomeration. Several authors have also applied this theory to the flocculation of cellulosic dispersions (16, 53-56,).

It is believed that condensation polymer products with a comparatively low molecular weight and high charge density work through a patch type of flocculation mechanism. Typical products of this class are the epihalohydrin type of products (e.g. epichlorohydrin condensed with dimethylamine), quaternized polyamideamines, polyethyleneimines etc.

From a papermaking point of view an important feature of patch flocculants is the reversible flocculation behaviour of suspensions which have been sheared (57). In the case of patch flocculants, the adsorbed polymer is quite firmly attached to the surface in a flat conformation (53). Thus polymer chain breakage is less likely to occur during shearing in this case than in bridging flocculation. Thus they show a reversible flocculation behaviour (57).

This is important since reflocculation can take place after dispersion in the turbulence generator of a headbox. Moreover recirculated polymer in the white water circulations (adsorbed onto fines and fillers) can be "reused". Finally reflocculation on the microscale enhances dewatering in the wire and press section of the paper machine without any severe deterioration in fibre formation.

Heterocoagulation

The term heterocoagulation is assigned to particle-particle interactions, where the particles are unlike charged. The theoretical treatment of heterocoagulation is essentially an extension of the DLVO-theory (58-60).

In papermaking, the deposition of small cationic particles onto larger suspended fibres and fines is quite a common phenomenon for e.g. filler or rosin size deposition and retention. Clearly, in this case, the dispersion forces and mutual electrostatic attractive forces both contribute to the forces of attachment.

Many fillers and pigments are cationic in the acidic region and can thus be deposited onto negatively charged cellulose fibres.

For oxide surfaces hydrogen and hydroxide ions are important potential determining ions, e.g. for α-Al_2O_3 we may write

$$
\begin{aligned}
&AlOH \rightleftharpoons AlO^- + H^+ \\
&H^+ + AlOH \rightleftharpoons AlOH_2{}^+
\end{aligned}
\qquad (18)
$$

Protonization in the acidic region thus leads to cationic charges and deprotonization in the alkaline region leads to negative charges.

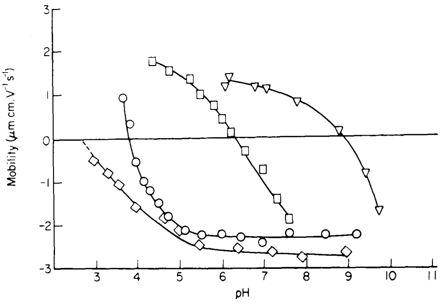
In table 4 the isoelectric point for some minerals used in papermaking has been tabulated.

Mineral	IEP/pH	Ref
TiO_2		
anatase	6.0 ± 0.3	(<u>61</u>)
rutile	6.7 ± 0.1	(<u>62</u>)
α-Alumina	9.3	(<u>61</u>)
SiO_2	2.0	(<u>61</u>)
Kaolin	2.0	(<u>63</u>, <u>64</u>)
$CaCO_3$-calcite	8.3 ± 0.1	(<u>65</u>)

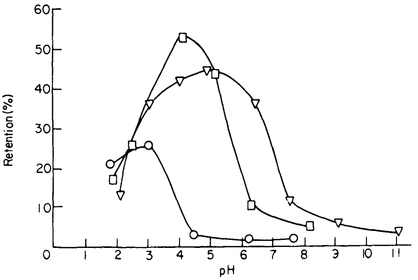
Table 4. The isoelectric (IEP) point of some mineral surfaces

In many cases the IEP-values determined for pure minerals are different from those of commercially supplied materials, either because of surface modification or contamination (e.g. adsorption of phosphates, silicates at the interface).

Figure 10a illustrates how the retention of TiO_2 and α-alumina to cellulose fibers is affected by pH and figure 10b shows their mobility vs pH curves.



(a)



(b)

Fig 10a - Mobility vs pH curves for various fillers and cellulose. -o-, Anatase, ;-∇-, Al_2O_3, Hydral; -□-, Rutile; -◇-, cellulose fibre fines (left). (Jaycock et al, 68)

Fig 10b - Retention (%) vs pH with unbeaten stock in the absence of fibre fines. -o-, Anatase; -∇-, Al_2O_3, Hydral; -□-, Rutile, R-CR (right). (Jaycock et al, 68)

The higher the IEP of the minerals the higher is the limiting pH for good retention. The decrease in retention at low pH-values is due to protonization of the carboxyl groups of the cellulose fibers at low pH-values and the decrease in mutual electrostatic attraction associated therewith.

Heterocoagulation interactions between small cationic particles and cellulose have been studied by several authors. Some illustrative studies with various particles are listed in table 5.

Cationic partic	Ref
TiO_2	(5, 66-69, 83)
α-Al_2O_3	(5, 69, 70)
SiO_2	(5, 69)
Clay	(5, 69, 71)
Cationic latex	(70, 72-74)
Cationic rosin size	(75-81, 130)

Table 5. Some heterocoagulation studies - cationic particle deposition on cellulose

It has, in general, been found that the heterocoagulation theory is in qualitative agreement with the experimentally observed results.

Quantitatively the surface roughness and thus the contact area between the deposited particles and the fibre surface has a profound influence on the force of attachment. Alince, for instance (72), found that soft latexes are more firmly attached to cellulose surfaces than hard latexes.

Naturally, cationic particles are more firmly attached to fibres than homocoagulated particles, but the bond strength is smaller than that obtained with polymers in bridging and patch-flocculation situations.

Technically, heterocoagulation deposition is a more important retention mechanism for smaller particles than for larger particles. This is due to the fact that large (>1 μm) cationic deposited particles are easily detached from the fibre surfaces when subjected to the magnitude of shear stresses common in modern papermaking (82). The strong size dependence of the shear stress required for detachment (TiO_2 attached on cellulose) is illustrated in fig 11 (83).

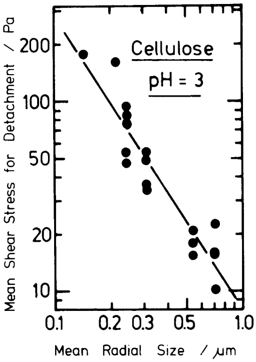


Fig 11 - Size dependence of the shear stress required for detachment. TiO_2 attached on cellulose. (Hubbe, 83)

The maximum shear stress on fibre walls in modern high speed papermaking is of the order of 2 x 10^2 - 2 x 10^4 Pa (84). It should be noted that only a fraction of the fibre population is subjected to these shear stresses. Thus only smaller particles can be retained on fibres subjected to high turbulence. In practice, the cationic charge on additives such as e.g. AlkylKeteneDimer (AKD) dispersions is often provided by polymers, securing a firmer attachment on to the surface than in a heterocoagulation situation with bare particle surfaces.

When functional chemicals are retained by means of a heterocoagulation or heteroflocculation mechanism a uniform deposition onto the fibre surfaces is achieved. This is the reason why heterocoagulation is the preferred mode of deposition for sizing agents and certain functional pigments like TiO_2. Premature agglomeration by e.g. interparticle bridging decreases the efficiency of sizing chemicals and the scattering power of TiO_2.

Interparticle bridging flocculation

The flocculation of dispersions through interparticle bridging was postulated many years ago (44, 85-88). Direct evidence for bridging flocculation was also early obtained by electron microscopy (89).

The literature is replete on investigations of bridging flocculation of cellulosic dispersions (see e.g. 11, 12, 53, 90-100) and other materials. It therefore seems justified to treat the subject together with advances in related fields of colloid chemistry (34, 44, 96, 101-104).

In the bridging theory it is assumed that the polymers have a sufficient chain length to be able to create bridges between different particles.

Bridging may occur through interparticle connections by the ends of a polymeric chain as originally proposed by La Mer and Healy (44) or through loops and tails as proposed by Fleer (104). Experimentally it is, however, difficult to distinguish between the two models.

It is believed (44) that the polymer is first adsorbed onto the particle in an extended conformation on the surface. The loops of the polymer from one particle can then in a second step be adsorbed onto a bare suface on a second particle. This bridge thus induces flocculation.

Naturally bridging is extremely sensitive to the length of the polymer molecule. In the case of polyelectrolytes, the electrostatic repulsion between the charged groups helps the molecule to be stretched out in solution, and the conformation of the polymer is thus sensitive to the charge density of the polymer and the ionic strength of the solution.

In the case of polymers bearing the same charge as the dispersion, bridging flocculation is quite easy to assess, whereas if the polymer bears a charge opposite to that of the particle it is more difficult to distinguish the true flocculation mechanism.

Studies on bridging flocculation kinetics are generally complicated by the fact that polymer adsorption is competing with the flocculation kinetics. Moreover the reconformation rate of the polymer on the surface will be decisive for the type of flocculation occurring.

Thus in dilute suspensions where the interparticle distance is long and the time for adsorption is long compared to the average time for an interparticle collision, the flocculation mechanism is often charge neutralization or patch flocculation instead of bridging flocculation (105).

The probability of building flocs is proportional to the fraction of the surface covered by polymer, θ, on one particle, and to the fraction of the surface that is uncovered, $(1-\theta)$, on another particle. Assuming surface coverage is equal for all particles and that the rate of flocculation, expressed as the decrease in the number of primary particles $(-dN_o/dt)$ can be described as a bimolecular collision process, the following expression can be given for the rate of flocculation:

$$-dN_o/dt = KN_o^2\theta(1-\theta) \qquad (19)$$

According to this expression, the OPD corresponds to half surface coverage ($\theta = 0.5$). It has also been observed that the maximum rate of flocculation often occurs for a surface coverage around 0.5 (44, 106, 107). Thus, for bridging flocculation to occur according to this theory the following requirements are necessary (44):

- extended segments of the polymer must be available on the surface

- the segments must be of sufficient number and length

- free surface regions must be available for adsorption

If the surface becomes so covered that there is insufficient surface for bridging, the dispersion becomes restabilised. This case is referred to as surface saturation stabilization (44). However, this is not the only cause of restabilization, as the extended segments can physically interfere with one another to prevent bridging (steric stabilization).

Restabilization of dispersions with bridging flocculants is in technical situations a rare phenomena.

The necessary length of the extended segments on the surface may be approximated by the concept of "distance of closest approach" (34, 44, 106). If it is assumed that the distance between different particles is limited by the electrostatic repulsion between the double layers, the distance of closest approach is approximately equal to twice the double layer thickness ($2 \cdot 1/\kappa$). Bridging can thus in certain cases be promoted by an electrolyte addition.

The collision frequency between particles is governed both by the Brownian motion of the particles (perikinetic aggregation) and by collisions induced by the shear-field (orthokinetic aggregation).

As all particles, regardless of size, have the same thermal energy, the velocity decreases with increasing particle size, and for large particles the velocity due to thermal motion is negligible.

Thus for small particles the collison frequency is dominated by the Brownian motion, whereas collisions between larger particles are dominated by the shear field.

In order to obtain an idea of the relative importance of particle-particle encounters induced by Brownian motion compared with those induced by the shear field the following simple considerations apply.

If there are initially N_o particles per unit volume the number of collisions occurring in unit volume per unit time is given by

$$J = k_1 N_o^2 \tag{20}$$

where k_1 is the rate constant. For perikinetic aggregation $k_{1,per}$ was given earlier by eq 10 and for orthokinetic aggregation k_1 is given by

$$k_{1\ ortho} = 32/3 \cdot G \cdot a^3 \tag{21}$$

where G is the shear rate (s^{-1}) and a is the particle radius. Calculation of the ratio $k_{1\ per}/k_{1\ ortho}$ gives the results tabulated in table 6.

Particle radii (µm)	Shear field (s^{-1}) 10	 100	 1000
0.1	100	10	1
1	0.1	0.01	0.001
10	10^{-4}	10^{-5}	10^{-6}

Table 6. The ratio between the perikinetic particle collision rate constant and the orthokinetic collision rate constant at different particle radii and shear fields.

The shear fields occurring during the forming of paper are of the order of $6x10^2$-$5x10^3$ s^{-1} (<u>84</u>). Thus for particles smaller than about 1 µm in radius Brownian motion is more important whereas for particles larger than 1 µm the flocculation process is induced by shear.

Generally, polymer-induced cellulose fibre flocculation is very fast (108) (of the order of less than a second) and it is also obvious that for anisotropic materials like cellulose fibers, both mechanical entanglement flocculation and polymer interparticle bridging must be considered as simultaneous phenomena.

Considering flocculation as a reversible process, the floc size is gradually built up until a critical size of the floc (depending on the shear field and the floc strength) is reached where the disruptive forces are stronger than the resistance to splitting of the floc. This is so because the resistance to splitting of a floc increases as the square of the floc diameter whereas the disruptive force due to the shear field increases as the cube of the floc diameter (109). Dynamic models for flocculation in turbulent flow have been considered by Pelton (110).

The size of polymer-induced fiber flocs has been shown (108) to coincide with the macroscale of the turbulence as predicted by theories of flocculation (111, 112). Thus, when the size of polymer-induced fiber flocs from softwood and hardwood pulps were compared, they were found to be of the same size, which was close to the macroscale of the turbulence during the experiment.

In bridging flocculation, disruption of a floc leads to a decrease in interparticle bonding as the polymer segments adsorbed to the second particle or the connecting polymer chains between the particles are disrupted. Then the polymer segments tend to "curl back" and be adsorbed on the first particle (44, 49, 113,). In this way the conformation of the polymer on the particles becomes more flattened and the probability of reflocculation is decreased. Thus the effect of agitation is irreversible. It has been observed that this effect is more pronounced for low amounts of added polymer (114). When porous materials like cellulose are employed, the penetration of the polymer or polymer segments into the porous structure enhances this type of action.

It should be noticed that there is also an effect of agitation on the polymer molecule itself. If a high molecular weight polyacrylamide solution is subjected to shear forces, the flocculating ability of the polymer is reduced (34). This is probably due both to disentanglement of the polymer molecules (107, 115, 116) and to shear degradation of the polymer (115). It has also been suggested that for polyacrylamide the flocculant is an aggregate of molecules rather than an individual molecule (107). Thus the molecular weight of the flocculant is apparently effectively higher, which enhances the bridging capability of the polymer.

When the polyelectrolyte is of opposite sign to the particles, electrolyte addition is usually not necessary, but in the case of nonionic polymers and polyelectrolytes of the same sign as the particles, electrolyte addition is almost always necessary (34). This is usually referred to as sensitisation (117). Deviations from this behaviour have also been reported (118, 119).

Although it is convenient to discuss bridging flocculation as though the surface charge of the particle is evenly spread out on the surface, it must be pointed out that a filler such as clay has both cationic and anionic charges on the surface (63) (depending on pH). In an electrophoretic experiment only the net charge of the particle can be measured. Adsorption of an anionic polymer can thus take place on the cationic charges on the edges of the particle (120) and induce bridging flocculation (121). The presence of electrolyte seems however to be a necessary requirement to induce bridging flocculation even in this case (121).

Adsorption flocculation - flocculation with polyelectrolytes of opposite sign to that of the particle

In this case, the adsorption of the polymer to the particle is promoted by the electrostatic attraction between the polymer and the particle and, moreover, the surface charge is reduced, so that the double layer repulsion between different particles is reduced.

The degree of flocculation increases (34, 102, 122) and the OPD decreases with increasing molecular weight (26, 34, 44). As mentioned earlier, the presence of extended polymer segments able to bridge between particles is necessary in this type of flocculation.

In the case of a polymer with a sign opposite to that of the particle, it has been suggested that the polymer is more likely to be adsorbed in a flat conformation on the surface (52) especially in the case of a low surface coverage.

Under these circumstances, the probability of interparticle bridging is low and the "patch model" of flocculation seems in this case to be more appropriate to describe the flocculation mechanism (52).

It is generally believed that high cationic charge density condensation polymers function through a patch flocculation mechanism, whereas high molecular weight cationic vinyl-addition polymers function through classical bridging concepts (e.g. 53, 123).

The most efficient flocculants of the polyacrylamide type have a charge density in the low D.S-range (34, 99, 106, 124). (D.S. = degree of substitution = molar percentage of charged groups in a copolymer built from one type of charged monomer and one type of uncharged monomer.) It is feasible to suggest that the presence of the nonionic segments in the polymer increases the length of the polymer loops protruding out from the surface in the adsorbed state, thus improving the bridging ability of the polymer.

A more highly charged polyelectrolyte is expected to be adsorbed in a more flattened conformation on the particle surface. On the other hand, if the polymer has too low a charge density, it will not be adsorbed onto the particle surfaces unless the nonionic groups in the polyelectrolyte interact with the surface.

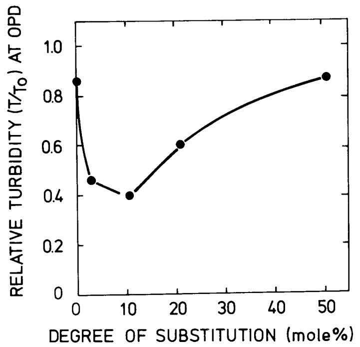


Fig 12 - Optimum degree of substitution of C-PAM for maximum retention of cellulosic fines materials under dynamic retention conditions. (Lindström et al, 124)

Fig 12 shows a typical case where the optimum D.S. of C-PAM for the flocculation of cellulosic fines was around D.S. = 10 mole %. The optimum D.S. for maximum flocculation is shifted to lower D.S. the higher the amount of polymer added (99). The optimum D.S. is dependent on the charge density of the surface.

Generally there is an optimum surface charge density for maximum flocculation (108). Too low a surface charge density leads to poor polymer adsorption, whereas too high a surface charge density leads to too flat a conformation of the polymer on the surface, and this decreases the likelihood of interparticle bridging.

Surface charge moderation by means of alum is a popular tool among papermakers to improve the efficiency of cationic bridging flocculants in certain cases. The mechanism is to decrease the surface charge so that polymer is adsorbed in a less flat conformation on the surface. Too high an addition of alum, however, blocks the surface sites for adsorption (97, 100). The extraneous electrolyte also coils the polyelectrolyte, decreasing its bridging ability.

In conclusion there is generally an optimum surface charge density for maximum flocculation for a given polymer and, vice versa, an optimum polymer charge density for a given surface.

Electrolyte addition is generally not necessary in adsorption flocculation. An increase in electrolyte concentration decreases the thickness of the electrostatic double-layer, but the polyelectrolyte also becomes coiled. Secondly, an increase in electrolyte concentration decreases the adsorption of the cationic polymer. The overall effect of electrolytes is mostly to decrease the efficiency of the flocculant (97, 98, 124).

Flocculation of dispersions with nonionic polymers

The flocculation of particle dispersions with nonionic polymers has been investigated for a wide variety of materials (see e.g. 34, 57, 101, 102, 104, 125-127) including cellulose dispersions (90, 128). The most investigated polymers are polyacrylamide (34, 90) and polyethylene oxide (34, 128). The basic features are generally well understood in terms of classical sensitization concepts (34, 90, 128). As the nonionic polymers are not as stretched out in solution as polyelectrolytes, an addition of electrolyte is usually necessary in order to decrease the thickness of the electrostatic double layer so that flocculation can be induced. Naturally polyvalent counter-ions are more efficient in sensitising the flocculation process than monovalent counter-ions (34, 90, 104).

The degree of flocculation increases with increasing molecular weight of the polymer (34, 90), although an optimum molecular weight has also been reported (44). In the latter case, it has been suggested that this is due partly to steric stabilization, because the extent of steric stabilization increases with increasing molecular weight of the polymer. The OPD decreases with increasing molecular weight (44) or remains unaffected (34).

As the adsorption of a nonionic polymer to a surface is not promoted by electrostatic interactions, the chemical interactions between the surface and the nonionic polymer are extremely important (34).

The adsorption of various nonionic synthetic polymers has been studied to some extent (128, 129). Early work was mostly concerned with various gums and mucilages (130) and it is only recently that the adsorption of synthetic polymers have been studied in more detail (128, 129).

Polyethylene oxide is selectively adsorbed onto surfaces containing phenolic and catecholic groups, and does not flocculate bleached kraft pulps (128). Based on this observation a selective flocculation and fractionation procedure has also been developed (128).

Polyacrylamide does not generally flocculate cellulosic dispersions unless they have been subjected to acid hydrolysis, e.g. microcrystalline cellulose (90). Therefore their ability to function as retention aids is related to their ability to flocculate fillers or other stock ingredients onto which they can be adsorbed.

The effects of pH and electrolyte addition are shown in fig 13 (90) for the flocculation of microcrystalline cellulose with nonionic polyacrylamide. This figure illustrates the effect of chain length of the polymer and the importance of the thickness of the double layer in bridging flocculation.

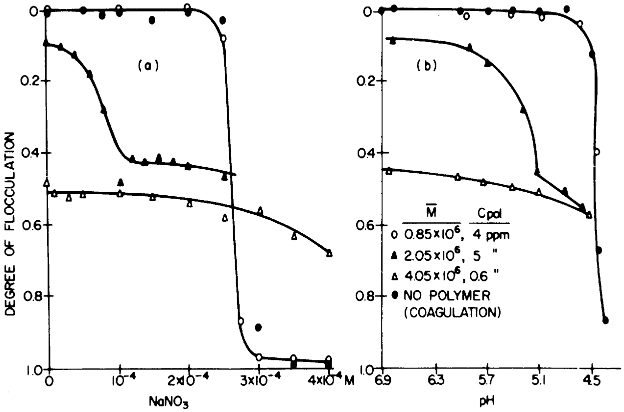


Fig 13 - Degree of flocculation of microcrystalline cellulose (Avicell) with PAM of different molecular weight as a function of a) ionic strength and b) pH. (Böhm and Luner, 90)

The high molecular weight polymer is able to flocculate the cellulose without electrolyte addition at all pH-values. The extension of the polymer is so great that it can bridge between two particles in spite of the thickness of the electrostatic double layer. If the molecular weight of the polymer is decreased, the addition of an electrolyte or a decrease in the pH is necessary in order to compress the double layer thickness so that the polymer is able to bridge the distance between two particles (sensitisation). At a low polymer molecular weight, the polymer is not long enough to bridge so that the critical salt concentration or critical pH coincides with the critical coagulation concentration (C.C.C.).

Flocculation of dispersions with polymers of the same sign as that of the particles

In this case also the presence of an electrolyte seems to be a necessary requirement (103). Besides reducing the thickness of the electrostatic double layer, the adsorption of the oppositely charged polyelectrolyte onto the surface is enhanced by addition of an electrolyte as the electrostatic repulsive forces between the surface and the polyelectrolyte are decreased. Thus the chemical interaction between the polyelectrolyte and the surface is even more important in this case. A typical example is flocculation of clay particles with anionic polyacrylamide (86), where it has been found that optimum flocculation occurs for a moderate charge density of the polymer around 30 % molar per cent anionic groups. It has been found that the nonionic segments of the polymer are responsible for the adsorptive forces to the clay plate edges (131). On the other hand, an increase in charge density increases the size of the polymer. Thus, in order to obtain a good flocculant a polyacrylamide with a medium charge density should be chosen. Similar findings have been obtained for other systems (34, 103), although there are other mechanisms which may also be responsible for polymer adsorption.

It is often observed that the flocculation of particle suspensions by means of anionic polyacrylamide is enhanced by calcium ions (e.g. 98, 126, 132, 133). There are at least 3 different mechanisms known to explain the role of multivalent counterions in promoting flocculation.

The role of the calcium ion may be to compress the electrostatic double layer i.e. sensitization or to guide polyelectrolyte adsorption.

It has also been suggested (133) that the mechanism by which polymer adsorption occurs involves a complex in the vicinity of the interface between multivalent counter-ions and functional groups of the particle and the polyelectrolyte. Thus multivalent ions accumulate in the double layer and facilitate adsorption of the polymer onto the surface. Interparticle bridging is also considered to be the mechanism leading to aggregation in this case.

A third mechanism, complex flocculation, where intermacromolecular complexes are inducing flocculation will be discussed below.

Flocculation of dispersions involving multicomponent systems

The largest and most important class of retention aid systems within this group are the dual polymer systems.

Complex flocculation phenomena involving polyelectrolytes and multivalent counter-ions as well as polymer systems involving more than two components are, however conveniently treated in this section. Therefore these systems will collectively be grouped under the term multicomponent systems. Synergistic additions of up to at least three polymeric components have been documented in the literature (e.g. 134).

Multicomponent interacting systems may be classified in systems with mutually interacting or non-interacting polymeric components. This means that synergistic flocculation effects may be obtained by the simultaneous use of 2 different polymeric components which do not interact. Systems of this type were early recognized (95, 135). In these systems the two polymers interact with different specific sites on the particle surface, securing more interparticle bridges and thus a stronger floc.

Another type of synergism may arise from the use of two cationic polyelectrolytes in sequence. The synergism may in this case be due to surface charge moderation, treated previously or may be due to better conditioning of the floc structure by the build up of flocs with e.g. patch flocculation and bridging flocculation characteristics.

The most commonly used dual flocculation systems are however systems containing two mutually interacting components.

Dual retention aid systems (cationic/anionic type)

One specific type of system is the system where a cationic polyelectrolyte is added prior to an anionic polyelectrolyte in order to promote adsorption of the anionic polyelectrolyte to the negative surface (or vice versa) (see e.g. 37, 91-93, 95, 136, 137).

In this case the first cationic polyelectrolyte is usually a highly charged condensation type of polymer e.g. polyamines or cationic polyamideamine products followed by a high molecular weight anionic vinyl-addition type of product, usually anionic polyacrylamide (95, 136).

The two-stage sequential treatment is usually superior to a single cationic addition. In the two-stage treatment the anionic polyelectrolyte is attracted to a positive patch, but the chain ends can protrude out in solution due to the electrostatic repulsion between the polymer and the surrounding negatively charged surfaces on the particle (138).

A highly charged condensation type of cationic polyelectrolyte is usually preferred over high M_w cationic vinyl-addition products (95, 136) in this type of sequential addition. A low charge density cationic vinyl-addition product forms less accentuated patches on the surfaces allowing the anionic polyelectrolyte chains to curl back on the surface, thus reducing their ability to bridge between different particles.

The efficiency of these combinations is thus governed by the charge density combinations of the particle surface and the added polyelectrolytes. As in all bridging types of system the flocculation efficiency is increased with an increased M_w of the bridging components. An increase in electrolyte concentration in such systems coils the polyelectrolytes and decreases the interaction between the oppositely charged components, generally decreasing their bridging ability (137). Again the hydrodynamics and the kinetics of flocculation have a decisive influence on the extent of flocculation and on the floc structure. The rate of flocculation is generally very fast (137). The contact time between the addition of the cationic polyelectrolyte and the anionic addition should generally be minimized, while still allowing for pre-flocculation before the addition of the anionic polyelectrolyte (95).

Owing to penetration of the cationic polyelectrolyte into the porous cell wall of cellulosic fibres, the contact time between the polymer and the fibers must not be too long and the molecular weight of the cationic polyelectrolyte must not be too low.

The cationic/anionic types of flocculant system are generally less efficient if the anionic component is added prior to the cationic polyelectrolyte. An intermacromolecular complex is then formed between the two polyelectrolyte components in the aqueous solution phase. Generally particles may be intercepted in this network but this mechanism leads to inferior flocculation (137). In this context the term complex flocculation will be designated to this latter type of flocculation phenomenon.

Dual retention aid systems employing negative microparticles

A specific category of dual retention aids is represented by the microparticle-containing flocculant systems. Examples in this category are the use of cationic starch in conjunction with anionic colloidal silica (139) or colloidal anionic aluminium hydroxide (140) and cationic polyacrylamide together with Na^+-montmorillonite (141, 142).

These systems are characterized by the addition of a cationic polymer followed by the addition of an anionic submicron particle suspension. They can therefore be classified as microparticulate retention/dewatering aids.

Although there is a lack of systematic scientific information on the mechanism of action of these systems, there is a solid body of practical papermaking experience stemming from their wide industrial use. Compared with conventional dual retention aid combinations, the microparticulate retention aid/dewatering combinations show the following characteristic distinguishing features:

* *Reflocculation takes place after dispersion of a particle suspension treated with a microparticulate retention aid combination. The systems may be classified as reversible or at least partially reversible flocculants.*

* *A strong positive dewatering effect is experienced both in the wire section and in the press section.*

* *The formed and dried sheet often exhibits a higher porosity when a microparticulate retention/dewatering system has been used.*

The (partially) reversible nature of the microparticulate systems is probably due to the fact that bridging flocculation takes place with the aid of anionic particles instead of anionic long-chain polyelectrolytes.

When long-chain polymers are used, chain cleavage and reconformation of the polyelectrolyte on the particle surfaces take place, but neither of these processes can take place when microparticles are used as the bridging aid.

A reversible flocculation is important for the dewatering effect, because a small scale reflocculation after initial web forming leads to a higher permeability of the web, and this leads to better dewatering and pressability as well as to a more open sheet structure (higher porosity).

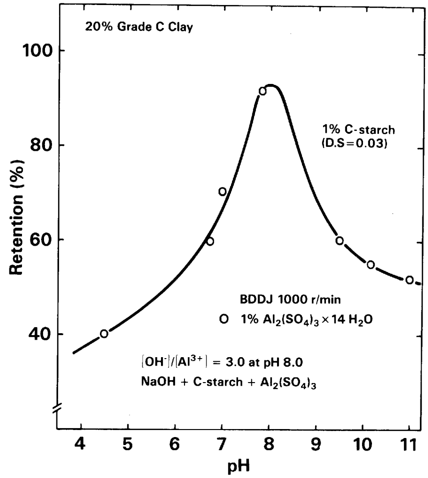


Fig 14 - The effect of pH on fines retention in a Britt Dynamic Drainage Jar at 1000 rpm. 1 % cationic potato starch (D.S.=0.03) was added followed by 1 % aluminium sulphate. (Lindström et al, 140)

A typical example of a microparticle system is the combination of cationic starch and anionic colloidal aluminium hydroxide (140). Fig 14 shows the effect of pH on fines retention in a system where cationic starch was followed by the addition of aluminium sulphate.

In the acidic pH-regime anionic aluminium hydroxide is not formed, and in the alkaline regime $NaAl(OH)_4$ is formed provided the pH is sufficiently high. Thus the sharp maximum in fines retention may be understood.

Complex and network flocculation phenomena

In the systems discussed so far, the more important physical chemical interactions are believed to occur on the particle surface. There are also, however, a multitude of systems where the second component causes gelation coacervation or precipitation of an intermacromolecular complex in which the particles can be intercepted (complex flocculation). Thus in these systems the interaction between the components takes place in solution rather than on the particle surface, although in most practical cases hybrid types are usually found.

Here the second component acts as a crosslinking agent and may be a simple ion (143-146), an aluminium salt (147), or a second polymer (37, 91-93). The formation of the complex is usually aided by electrostatic interactions but hydrogen-bonded complexes are also known to act as strong flocculants. It has also been observed in certain systems (146) that flocculation takes place when incipient phase separation of the formed complex occurs, which is analogous to current concepts of the destabilization of sterically stabilized dispersions (148). The aggregation mechanisms considered here may be referred to as polymer network flocculation (149), sweep flocculation, or enmeshment (150) in order to distinguish them from classical interparticle bridging concepts.

In the simplest system of this class, flocculation may be viewed as an enmeshment of the colloidal particles in the network formed. Network formation induced by self-association (149) or during hydrolysis of certain metal salts (151-152) may be considered as homotype systems within this general class of flocculation phenomena.

From a technical point of view the most important sub-group within this general class of phenomena is the network flocculants.

This sub-group is characterized by a number of very specific features and has been explored in some detail during recent years (153, 154). In this group we find the polyethylene oxide (PEO)-phenolformaldehyde (FPR) system (153, 155, 156) and related systems (157-159) and the anionic polyacrylamide (A-PAM)/Na^+-montmorillonite (Na^+-Mont) system (160).

In both of these cases it is envisioned that the particles are intercepted in a diluted three dimensional network formed by the interaction between the components.

In the PEO-FPR system it is well known that hydrogen bonding interactions take place e.g. between the ether oxygen in (161) the PEO-molecule and the phenolic protons in the FPR-resin. For the A-PAM/Na^+-Mont system the small montmorillonite particles form adsorption sites for the A-PAM molecular, forming a network schematically pictured in fig 15.

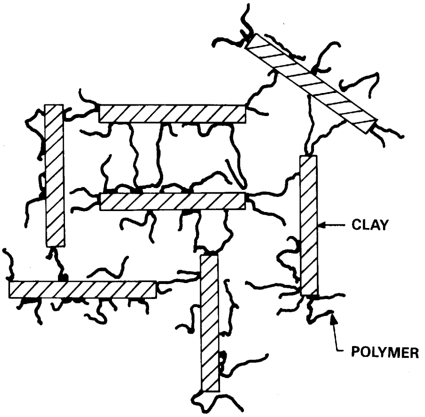


Fig 15 - Schematic representation of a transient clay-polymer network structure (Wågberg, unpublished).

These flocculant systems show at least the following three characteristic features (153, 154).

* *It is necessary to have a collector present to sensitize the flocculation process. In papermaking systems the collector is often cellulose fibers, but may also be for instance air bubbles in flotation processes.*

* *Above a specific flocculant dosage particle separation takes place according to the size of the particles instead of particle surface, as is usually observed for most adsorptive flocculants.*

* *The relative particle removal is independent of the specific surface.*

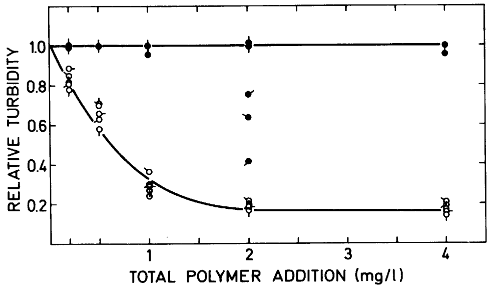


Fig 16 - The effect on latex (0.945 μm) removal of the total quantity of (PEO + FPR) polymer added. PEO/FPR ratio = 1.0. Open symbols (cellulose fibers (1 g/litre) added before flocculants): latex conc. (ȯ) 2.5, (o-) 5, (ǫ) 25, (ρ) 100, (ò) 200 mg/litre. Filled symbols: (●) Cellulose fibers (1 g/litre) added after the flocculants. (●) No cellulose fibers present. (●) Cellulose fibers (0.2 g/litre) added before the flocculants. (●) Cellulose fibers (0.4 g/litre) added before the flocculants. (●) Cellulose fibers (0.6 g/litre) added before the flocculants. Latex conc. 25 mg/litre if not otherwise stated. pH 5.2. (Lindström and Glad-Nordmark, 153)

Fig 16 illustrates two of these features. In this case a stabilized latex (to prevent PEO-latex interactions) was flocculated by means of PEO and an FPR-resin (1:1 weight ratio).

The results are given as the residual relative turbidity after flocculation versus total polymer dosage. This figure illustrates that the latex particles were not removed from the aqueous phase unless cellulose fibers (collector) were present during flocculation. Secondly, incipient particle removal is independent of latex particle concentration (particle surface) over two orders of magnitude in particle concentration.

The following mechanism has been suggested to explain these and other features (153, 154):

Polymer networks formed at these polymer concentrations are usually unstable, due to the fact that they are formed below the critical overlapping concentration ($\sim 1/[\eta]$) of the polymer in solution. A transient network is, however, formed shortly after mixing and this phenomenon can be observed as a peak in solution viscosity before syneresis or phase separation of the intermacromolecular complex.

It is the transient nature of this network which explains why the presence of the cellulose fibers (collector) is necessary in order to achieve latex removal. It is believed that the function of the collector is to sweep the transient network and thereby collect the dispersed particles before the network breaks apart (syneresis) and ceases to exist. For the collector, the inertial forces are larger than the viscous forces under a given set of hydrodynamic conditions, and a relative motion of the collector toward the aqueous phase can be induced. In a sense this is a type of shear-induced flocculation process. If only smaller particles, for which the viscous forces are larger than the inertial forces, are present, the transient network cannot be swept before syneresis occurs and accordingly no particle removal takes place under such conditions. When the fibers were added after the two flocculating components, no latex removal took place, the reason being that syneresis of the network took place during the mixing process before the fibers had been added.

After flocculation has taken place, the network is concentrated and the aggregates are stabilized toward shear forces by the greater number of junction points formed between the complexing components because of the higher local concentration of the complex in the floc.

The simple view that the latex particles are mechanically enmeshed in the network is substantiated by the finding that the polymer dosage required for particle removal is independent of the latex concentration over a wide concentration range. Such a behavior is expected if neither of the two complexing components alone is adsorbed onto the available particle surfaces in the system.

In practice some interaction takes place in most technical systems. If the transient network is anchored in this way onto the collector or particle surface particle removal will be more efficient (154).

It is also interesting to find that latex removal takes place according to particle size, thus manifesting the network character of the transient complex and the apparent mesh-size distribution in the formed network. Typical results are given in fig 17 for a number of different network flocculation systems.

These systems are not totally non interactive with their collector surfaces, but they can still be used to fractionate latex particles according to their size, proving the network character of the systems of this class (153, 154).

Some of these systems have gained wide industrial popularity in the papermaking industry (see e.g. 155-159) for use in systems with high loads of dissolved and colloidal materials interfering with retention aids based on electrostatic interactions.

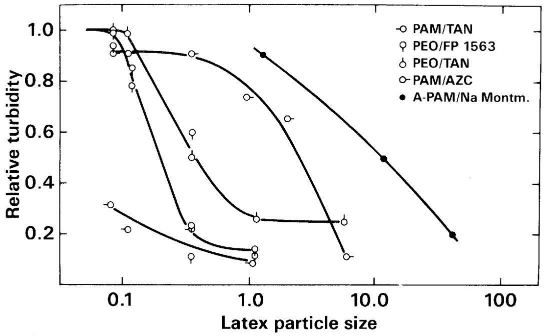


Fig 17 - The apparent mesh size distribution in a number of different network flocculation systems.

-O Polyacrylamide-Tannic Acid (PAM/TAN)
♀ Polyethyleneoxide - Phenolic Resin (PEO/FP1563)
ó Polyethyleneoxide - Tannic Acid (PEO/TAN)
O- Polyacrylamide - Ammonium Zirconium Carbonate (PAM/AZC)
● Anionic Polyacrylamide - Na$^+$-montmorillonite (A-PAM/Na$^+$-Montm.)

The influence of dissolved and colloidal material on polymer flocculants

It is widely recognized that the dissolved and colloidal materials present in paper machine white waters have a detrimental influence on many retention and dewatering agents used in the paper industry (see e.g. 38, 162-171,). These substances are often referred to as "anionic trash" among papermakers. Although these substances and their interfering action are widely recognized their chemical composition and physicochemical properties have not been the subject of deeper studies, though some information (e.g. 172, 173) is available in the literature.

The dissolved and colloidal substances in paper machine process waters originate from the mechanical or chemical pulping process, from broke and waste paper, and from various additives or auxiliaries.

The substances originating from the pulps are released from the fiber cell walls during stock preparation operations such as beating and refining. They are also slowly released from the fibre cell wall during pulp storage etc. The level of these substances in the process waters will be dependent on the extent of water closure, chemical conditions etc. The accumulation of these substances is limited by their solubility characteristics and they may redoposit onto various surfaces on the paper machine when the chemical conditions are changed.

One important aspect of dissolved and colloidal materials in paper machine process waters is that the negatively charged anionic substances interact with cationic additives, forming polyelectrolyte complexes (PEC).

The interaction between oppositely charged polyelectrolytes has been investigated by several authors (e.g. 174-179). These reactions may be both stoichiometric and non-stoichiometric. Several factors such as electrolyte concentration, charge density, chain flexibility etc influence the stoichiometry. It is generally found, however, that under electrolyte-free conditions, the reactions are stoichiometric, whereas deviations from stoichiometry occur in the presence of electrolytes (see e.g. 180-181). The stoichiometric reactions taking place between oppositely charged polyelectrolytes under electrolyte free conditions is the principle underlying the colloid titration technique (182, 183) which is widely employed in the paper industry. Thus the basic route of interference of cationic additives by anionic substances is through the formation of inactive PEC's, although it must be emphasized that non-ionic interactions may play a more important role than has hitherto been believed (164).

Table 7 lists a few references to specific studies on the effects of dissolved substances on the efficiency of cationic retention aids.

Substance	Reference
Lignosulfonate	(38, 164, 184-187)
Wood extracts	(164, 188)
Humic acid	(47, 164, 167)
Kraft lignin	(64, 184)
Sodium silicate	(164)
Carbohydrates	(38, 184, 189)
Carboxymethylcellulose	(184)
Starch	(184)
Fatty acids and resin acids	(184)
Spent liquors	(190, 191)

Table 7. Some studies on the effects of dissolved substances on cationic retention aids

It has generally been found that the highly charged anionic polyelectrolytes e.g. lignosulfonates and silicates, have a stronger inactivation effect on cationic retention aids than e.g. starches and xylans.

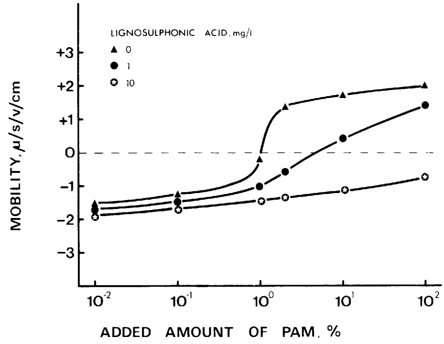


Fig 18 - The effect of lignosulfonic acid on charge reversal of a microcrystalline cellulose sol with cationic polyacrylamide. (Lindström et al, 38)

The effect may be illustrated by the effect of lignosulphonic acid on a charge reversal curve of microcrystalline cellulose with cationic polyacrylamide (38) in fig 18.

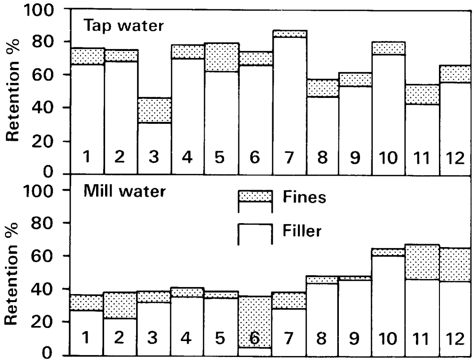


Fig 19 - Comparison of the performance of different retention aids and combinations (BDDJ experiments at 1000 rpm) in tap water and process water from a stone groundwood mill. (Conc of dissolved organics = 1.2 g/l and inorganics = 0.5 g/l, Si-conc 80 mg/l) Magazine paper stock: 20 % S.W. kraft + 80 % SGW pulp; 25 % clay.

1) 0.05 % Percol 292 (C-PAM)
2) 1 % Alum + 0.05 % Percol 292 (C-PAM)
3. 0.05 % Percol E24 (A-PAM)
4. 1 % Alum + 0.05 % Percol E24 (A-PAM)
5. 0.2 % PAC + 0.05 % Percol E24 (A-PAM)
6. 0.1 % Polymin SN.
7. 0.1 % Polymin SN + 0.05 % Percol E24 (A-PAM)
8. 0.05 % Organopol (A-PAM)
9. 0.15 % AZC + 0.05 % Organopol (A-PAM)
10. 0.5 % Organosorb (Na^+-montmorillonite) + 0.05 % Organopol (A-PAM)
11. 0.05 % WSR 301 (PEO)
12. 0.05 % WSR 301 (PEO) + 0.05 % FP 1563 (Phenolic Resin).
(Lason et al, 192)

In fig 19 the performance of a number of selected retention aids and combinations are compared in experiments performed in tap water and in a process water from a stone groundwood mill. In tap water all retention aids and combinations except No. 3 (A-PAM) showed a good effect on the fines and filler retention. When the process water from the stone groundwood mill was used, only the network flocculant combinations (No. 10, 11, 12) showed a good performance. This example illustrates the beneficial use of retention aids which function by means of a hydrogen bonding interaction mechanism instead of an electrostatically based retention mechanism in certain systems with a high load of anionic substances.

Effects of hydrodynamic shear forces on particle detachment

In modern high-speed papermaking, high shear forces are generally unavoidable. High shear forces are also deliberately used in headboxes in order to break up macroscale flocs and improve paper formation.

It is generally known that flocs created by certain retention aids have a higher ability to withstand high hydrodynamic shear forces than those created by other retention aids.

Thus it is of interst to know how different parameters affect the shear stresses required for particle detachment when different retention aids and different retention aid combinations are used.

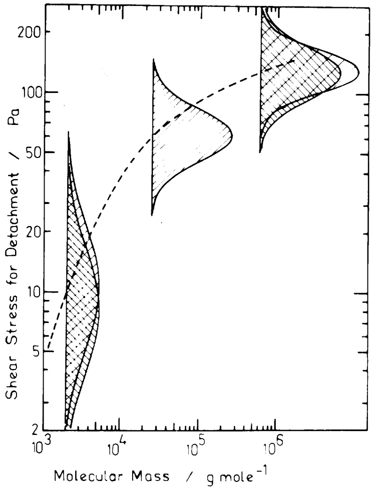
It was early recognized that pure colloidal forces, i.e. electrostatic and attractive London van der Waal's forces, were of less significance than mechanical entanglement interactions for the dispersion and flocculation of papermaking fibers (193, 194).

The effects of polyelectrolytes on the adhesive forces between particles have been measured in some cases (see e.g. 195-202).

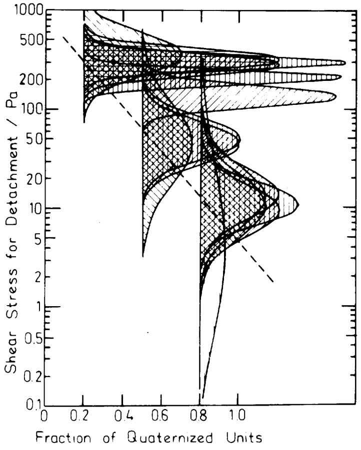
The common technique used is to measure the rate of detachment of spherical particles (attached to the surface by means of polymer) from flat surfaces when subjected to controlled fluid shear fields.

It has been found that the higher the adsorbed amount of polymer the higher is the bond strength (201- 203).

As expected longer polymer molecules give rise to a higher bond strength than shorter polymer molecules (201- 204). The effects of polymer molecular weight (PEI) and degree of substitution (C-PAM) on the shear stress required for detachment of TiO_2 particles on polymer-pretreated cellulose surfaces are illustrated in Fig 20a and 20b (201).



(a)



(b)

Fig 20a - Effect of molecular mass of PEI on the adhesion of TiO_2 spheres to pretreated cellulose (left). (Hubbe, 201)

Fig 20b - Effect of the proportion of cationic monomer units (D.S.) on the shear stress required for detachment from glass pretreated with C-PAM (right). (Hubbe, 201)

The effect of the D.S. of C-PAM on the shear stress for detachment is related to the fact that the higher the D.S. the lower is the amount of C-PAM adsorbed on the cellulose surface.

The effect of various cationic retention aids on the shear stress required to detach filler particles from cellulose has been investigated by Hubbe (82, 201, 204,). Typical results are tabulated in table 8.

Retention aid	Particle radius 0.1 µm	 0.5 µm
None, pH = 7	84	6
None, pH = 3	510	34
C-starch	990	75
PEI	2600	190
C-PAM	6700	510

Table 8. Shear stress (s^{-1}) *to detach filler particles of various radii from cellulose pretreated with cationic retention aids (82).*

Thus stronger bonds are formed with C-PAM than with PEI or C-starch, which in turn form stronger bonds than those due to the London van der Waal's interaction.

These results are in good agreement with the generally experienced sequence of floc strength created by different retention aids:

Dual polymer systems > Single high M_w bridging flocculants > Patch-flocculants> Heterocoagulation (pure electrostatic) > Charge neutralization

The maximum shear stresses on the surface of papermaking fibers in flocs on a paper machine have been estimated by Tam Doo et al (84) and d'Incau (205). These values were also compared with the shear stresses in a Britt Dynamic Drainage Jar, a British STD sheet-machine and a freeness tester. Typical values obtained (84) are shown in Fig 21, which indicates that the maximum fibre wall shear stress occurs in the fan pump and in the pressure screen on a Fourdrinier paper machine (operating at 760 m/min).

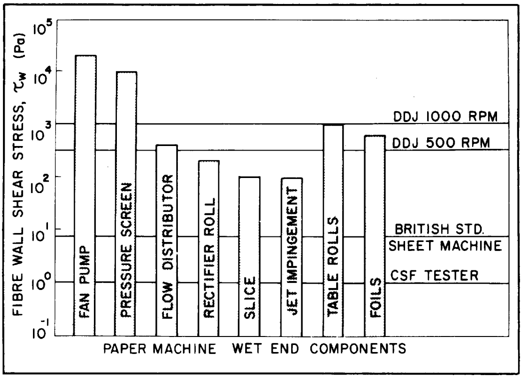


Fig 21 - Maximum shear stresses on the fibre walls for various wet end components of a paper machine operating at 760 m min^{-1}. Also shown are the shear stresses produced in some commonly used laboratory testers. (Tam Doo et al, 84)

This is in line with general practical experience that polymeric retention aids should be added after the fan pump and pressure screen to be most effective.

Again, it should be emphasized, that only a small percentage of the fibers (<10 %) are subjected to these high shear rates. The situation is essentially similar in a BDDJ-Jar, and the larger the stirring time the lower will the fines and filler retention become.

Kinetics of polymer-induced fibre flocculation

There is, generally, little fundamental understanding of polymer adsorption and flocculation under dynamic conditions. Most studies have paid little attention to the dynamic aspects. The complexity stems from the fact that in most technical situations polymer adsorption and flocculation occur simultaneously. When adding polymer to a suspension the following steps must at least be taken into consideration (206).

- *Mixing of the polymer solution and the suspension.*
- *Adsorption of the polymer onto the particles.*
- *Rearrangement of the adsorbed chains on the particle surface.*
- *Collisions between particles, (having adsorbed polymer on their surfaces) leading to aggregation.*
- *Break-up of flocs in the suspension.*

In practice these processes are simultaneous, occurring at rates depending on a number of chemical and physical factors.

Depending on particle size, concentration and shear rate, flocculation is induced by orthokinetic or perikinetic collision processes. Thus for particles around 1 μm in size and shear rates above about 10 s^{-1}, adsorption of high M_w polymers occurs predominantly by fluid motion rather than by diffusion (206), and polymer adsorption is slow compared with the rate of flocculation.

The kinetics of polymer-induced flocculation has not been extensively studied. More recently, however, newly developed techniques, have been used for such studies (207-209). They are all based on optical or laser-optical transmission or backscattering techniques. The optical signal is then more or less transformed to suitable numbers for the monitoring of the state of aggregation.

Wågberg (208) utilized the power spectrum concept, originally developed by Norman and Wahren (210, 211) to characterize the state of flocculation in flowing pulp suspensions.

Wågberg used a laser optical back-scattering technique to monitor the local fibre concentration and transformed the signal to a wavelength power spectrum. By monitoring the power spectrum before and after polymer addition it was possible to evaluate both the degree of polymer-induced flocculation and the size of the flocs (see fig 22).

To characterize the degree of polymer-induced fiber flocculation by a single quantity, the coefficient of variation V_A of the signal with polymer addition and V_B without addition were used to calculate the flocculation index, F, according to the equation

$$F = \sqrt{(V_A^2 - V_B^2)} / V_B \qquad (22)$$

The variances V_A^2 and V_B^2 are equal to the areas below the curves A and B as shown in figure 23.

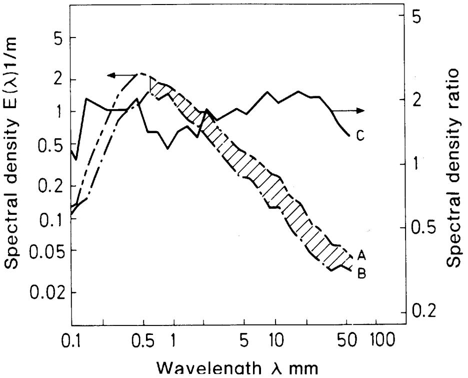


Fig 22 - Wavelength power spectra from fibers of a bleached softwood kraft pulp showing the effect of addition of C-PAM. Curve A with and curve B without polymer addition. Curve C shows the ratio between the two spectra. (Wågberg, 108)

The ratio of spectrum A to spectrum B in Figure 22 is given as curve C, which provides information about the induced flocculation over the whole floc size range of interest. The average wavelength, λ, is defined as the wavelength which divides the area between curve A and curve B into two equal parts. The average floc diameter, d, was then calculated as being equal to half the average wavelength, λ.

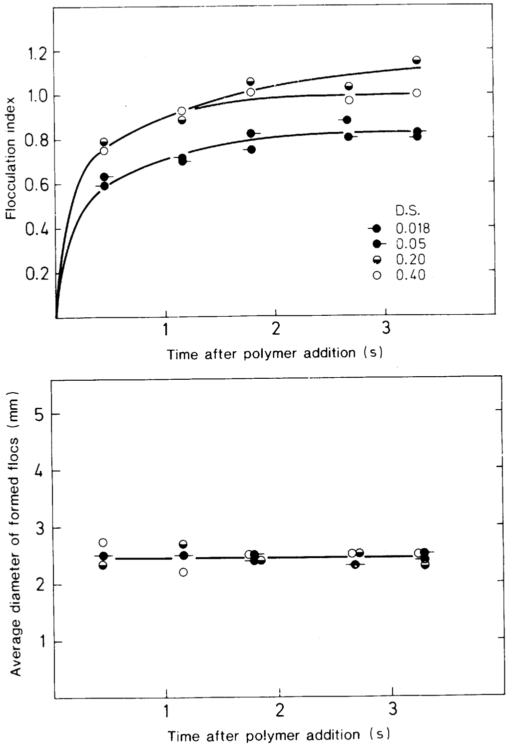


Fig 23 - (a) Flocculation index (upper diagram) and (b) the average diameter of flocs (lower diagram) formed as a function of time after polymer addition for differently charged MAPTAC polymers. Addition level of MAPTAC was 0.3 mg/g and fiber concentration was 1 g/l. (Wågberg, 108)

Typical results are shown in fig 23a and 23b. This figure illustrates that the flocculation process is very fast, whereas the floc size was not so sensitive to the flocculation intensity. The size of the flocs found was to a large extent related to the size of the macroscale of the turbulence (108).

POLYMER STABILIZATION MECHANISMS AND FORMATION AIDS

Generally, particle dispersions may be stabilized electrostatically, sterically (103, 217) or through depletion stabilization (103, 217). All these stabilization mechanisms are relatively well understood from a theoretical point of view. Electrostatic stabilization was discussed earlier and naturally electrostatic repulsive charges may also be introduced onto the particle surface by means of an adsorbed polyelectrolyte.

"Steric stabilization" involves the adsorption of a polymer onto a particle surface and forming a protective layer preventing particle interaction. This subject will be treated later. "Depletion stabilization" refers to a mechanism in which stabilization occurs through the presence of a polymer in the solution phase. During a collision between two particles a zone is formed between the particles from which the polymer is physically excluded. The exclusion of the polymer decreases the solution entropy of the system, resulting in a repulsive force between particles. Theoretically this type of mechanism is only important for more concentrated polymer solutions. This type of stabilization is not known to occur in pulp suspensions, and will therefore not be further discussed.

It has been recognized for many years that certain natural (gums and mucilages) and synthetic (A-PAM etc) water dispersible polymers have a significant deflocculating effect on papermaking fibres (212). The use of formation aids goes back to ancient japanese papermaking methods (see e.g. (214) or Dard Hunter in "A papermaking pilgrimage to Japan, Korea and China" 1936). Swanson has reviewed early literature (212) and Lindström and Lee (213) have more recently discussed the mechanism of action of formation aids.

The action of formation aids can, however, not be understood in terms of generally accepted theories of polymer stabilization and the concepts suggested by Lindström and Lee (213) will therefore also be discussed in this context.

Formation aids

The following general observations can be made when formation aids such as anionic polyacrylamides are used.

* *There will be a marked reduction in the drainage rate of the suspension (213, 215, 216).*

* *Formation aids have an insignificant effect on the shear viscosity of the suspending medium (213).*

* *It is not necessary that the polymer be adsorbed onto the particles in the suspension (213, 215).*

The reduction in drainage rate is probably the major reason why the use of formation aids has been limited to certain special applications e.g. some nonwoven products.

Formation aids are effective at very low polymer concentrations of the order of ppm. A 10 ppm solution of A-PAM with a relative viscosity of 10 dl/g would increase the shear viscosity of the aqueous phase by 1 %. It is therefore difficult to explain the decrease in drainage rate when the A-PAM molecule is not adsorbed onto the fibres (see e.g. 218).

Early investigators (e.g. 216) suggested that vegetable extracts were adsorbed and formed lubricating layers on the surfaces of fibers.

This mechanism is clearly not applicable, as the adsorption is not necessary for dispersion. Likewise "depletion stabilization" cannot explain the dispersion behaviour because the polymer concentration is too low.

Lindström and Lee (213) suggested instead that the elongational viscosity characteristics of high polymer solutions were responsible for the decrease in drainage rate. These high molecular weight polymers greatly increase the flow resistance through porous media, where the fluid shows elongational flow characteristics.

When the polymer solution is accelerated through the interstices of a porous media, the polymer molecules elongate in the direction of flow, absorbing energy and increasing the fluid viscosity. The polymer will be effective in increasing the flow resistance if it is subjected to a strain rate for a period of time sufficient for stretching to occur. This effect can be treated as follows.

The relaxation time for a polymer molecule is (219-221):

$$T = [\eta]\eta_S M/RT \qquad (23)$$

where $[\eta]$ is the intrinsic viscosity of the polymer, η_S is the solution viscosity, M the relative molecular mass of the polymer, R the gas constant and T the absolute temperature. Provided the strain rate, ϵ $(= k_1 \upsilon/r)$; (r = radius of curvature of a pore, υ = average fluid velocity, k_1 = a constant depending on the flow geometry) is larger than the inverse of the relaxation time of the molecule, stretching occurs:

$$\mathrm{Deb} = T \cdot \dot{\epsilon} \qquad (24)$$

Condition for stretching to occur is Deb > 1

Fig 24 illustrates that the elongational viscosity of a solution of anionic polyacrylamide increases by two orders of magnitude in the transition region (Deb ~ 1).

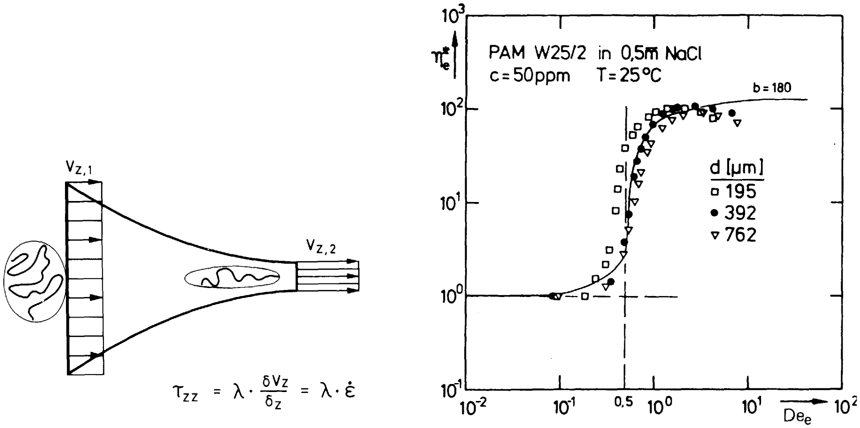


Fig 24 - Stretching of a polymer molecule in elongational flow (left). Experimental results showing the elongational viscosity for A-PAM at various Deborah numbers. (Pressure drop experiments over a column with glass beads.) (Durst and Haas, 219)

If the flow through a fiber mat is considered, the characteristic radius of curvature is larger than the characteristic fibre dimension (fibre width) and the fluid velocity equals the dewatering velocity. Table 9 shows that it is possible to reach high Debhora-numbers in papermaking.

		2 x radius of curvature	
		50 μm	500 μm
Fluid	0.2 m/s	10^2	10
velocity	0.04 m/s	20	2

Table 9. Estimation of the Debhora-number for flow in a fibre mat

Lee (222) has also shown that high molecular weight A-PAM could increase the flow resistance of water through papermaking pads by a factor of 10.

Decreased drainage is also a commonly observed phenomenon under industrial conditions where high molecular weight retention aids are added under conditions in which they are not sufficiently adsorbed to the fiber and fines and remain in solution. (For instance during conditions of overdosage of a retention aid.)

This behaviour may explain the decreased drainage in the presence of a polymer in the solution phase.

The following hypothesis may explain the improved formation.

It is well known that a few ppm of dissolved high M_w macromolecular can reduce the turbulent drag of their solution (see e.g. 223). This can be understood from the large body of knowledge showing that polymer molecules in turbulent fluids can damp the bursts of turbulent energy which normally propagate tranversely from the near wall region to feed and sustain turbulence in the bulk flow. This process is most effective when the relaxation time of the viscoelastic macromolecule is approximately the same as the duration of the turbulent burst. Based on these facts, Lindström and Lee (213) suggested that the reduction in fibre flocculation is due to the ability of a polymer to reduce the turbulence intensity in the suspension. Under these conditions the fibers will be less bent and the fibre entanglements which form under these conditions will consist of fibers with less strain energy. Thus the flocs will be weaker and more easily disrupted.

Steric stabilisation

Steric stabilization is the general term for stabilization of colloidal particles by non-ionic polymers (103, 217). If a particle surface is covered with a polymer layer protruding out in solution the motion of the polymer segments prevents the particle from adhering to another particle. The polymeric layer on the particle surface acts as a steric barrier towards aggregation. The phenomenon is usually referred to as "protection" of the colloid. In this type of stabilization, the solvency of the adsorbed polymer on the particle surface is the prime factor responsible for the stability of the dispersion (217).

Sterically stabilised dispersions cannot be flocculated by the addition of electrolytes unless the polymer is first desorbed from the particle surface. Displacement of the polymer from the particle surface may lead to flocculation and this is referred to as displacement flocculation.

Flocculation can also be induced by reducing the solvency of the dispersing medium for the stabilising moieties. This is called incipient flocculation. The simplest way to flocculate a sterically stabilised dispersion is to change the temperature. When the solvency is reduced, the dispersions exhibit a very sharp transition from long-term stability to instability. Depending on the polymer - solvent interaction, instability can be induced by either heating or cooling. The strong temperature dependence of many sterically stabilised dispersions is a characteristic feature which markedly contrasts with the relative insensitivity of electrostatically stabilised dispersions to changes in temperature. In the DLVO theory for electrostatic stabilization, the electrostatic repulsive forces are equated with the London van der Waal's attraction force. This theory may be modified by adding an extra term which takes the steric interactions into consideration.

$$V_{tot} = V_A + V_E + V_{steric} \tag{25}$$

In the DLVO theory, the van der Waal's attraction is the driving force towards coagulation. However, for sterically stabilised dispersions, the van der Waal's forces can usually be neglected as long as the molecular weight of the stabilising moieties is reasonably high and the surface is completely covered with polymer. Furthermore, in systems with a high electrolyte content, the electrostatic repulsive forces can be neglected and thus the stability of the dispersion is dependent only on the steric term. The steric term can also be subdivided into one term which takes care of mixing of the polymer segments with solvent (ΔG_M) and another term which take care of the elasticity of the polymeric layer (ΔG_{el}).

The elastic term originates from the "spring effect" during a collision between two particles.

It can be shown that the change in free energy, ΔG_M, during interpenetration of the polymeric chains can be written (50, 148) as:

$$\Delta G_M = \psi_1 (1 - \theta/T) \times (\text{Geometric term}) \qquad (26)$$

where ψ_1 is an entropy parameter, T the absolute temperature and θ the Theta-temperature of the polymer (Flory-temperature). There is also a geometric term in this expression which we do not need to consider as long as we are only looking for the sign of ΔG_M. ΔG_M is positive for stable and negative for unstable dispersions. As it is well known that polymer segments become self-attracting in solvents worse than θ-solvents* for the polymer, it appears that the segmential interaction with the solvent is responsible not only for the stability of the dispersion but also for incipient flocculation.

Thus the stability or instability of the dispersion is dependent on neither the nature of the particles nor the particle size but only on the inter-

---

* A θ-solvent is a solvent for the polymer where the second virial coefficient vanishes, i.e. there is no polymer-polymer interaction in the system.

action of the polymer with the solvent. When the polymeric segments on the particle are soluble in the solvent the dispersion is stable, whereas when the segments are insoluble the dispersion will flocculate. It has been shown for a number of systems that there is a close relationship between the θ-temperature of the polymer and the critical flocculation temperature.

In order to analyse further the temperature dependence of flocculation we may write:

$$\Delta G_M = \Delta H_M - T\,\Delta S_M \tag{27}$$

If both ΔH_M and ΔS_M are positive but $\Delta H_M > \Delta S_M$ the enthalpy change on close approach opposes flocculation. This is referred to as enthalpic stabilization. By increasing the temperature, ΔG_M can become negative and the dispersion flocculates. If, however, both ΔH and ΔS are negative and $\Delta H < T\,\Delta S$ the entropy term opposes flocculation and the dispersion is said to be entropically stabilised. Flocculation can in this case be induced by cooling the dispersion.

These different types of steric stabilization are summarized in table 10.

ΔH_M	ΔS_M	$\Delta H_M/T\Delta S_M$	ΔG_M	Type	Flocculation
+	+	>1	+	Enthalpic	On heating
-	-	<1	+	Entropic	On cooling
+	-	$\lessgtr 1$	+	Combined enthalpic entropic	Not accessible

Table 10. Comparison of different types of steric stabilization (148).

Dispersions stabilised with polyacrylamide are entropically stabilised, whereas those stabilised with polyethylene oxide are enthalpically stabilised (148).

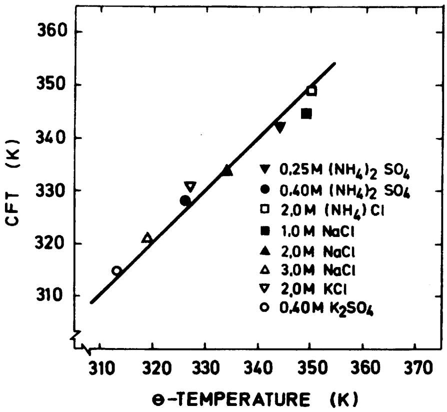


Fig 25 - Critical flocculation temperature for a kraft lignin sol stabilized with polyethylene oxide (PEO) versus θ-temperature for PEO. (Lindström, 224)

Fig 25 shows the close relationship between the θ-temperature for polyethylene oxide and the critical flocculation temperature for a lignin dispersion stabilised with polyethylene oxide.

Steric stabilization is also known to play an important role on the stability of wood resins in newsprint manufacturing (225).

POLYMER ADSORPTION ONTO CELLULOSIC SURFACES

The understanding of the adsorption of polymers and polyelectrolytes onto cellulosic fibres and fines, fillers etc is one of the keys to a better understanding of papermaking wet-end chemistry.

Our theoretical understanding of the adsorption of polymers onto surfaces has advanced considerably during recent years (226, 227). The Scheutjens-Fleer (227) theory of polymer adsorption constitutes a landmark in this context. Modern polyelectrolyte adsorption theories also follow suit (226). The Hesselink adsorption theory (228, 229), now considered old in the field, still offers a simple qualitative theoretical framework. This theory is, however, inconsistent as it does not allow for changes in the conformation during minimization of the free energy of adsorption, and more modern approaches have followed using the Roe and Scheutjens-Fleer approach (226).

In general, a cationic polymer is better adsorbed on an anionic surface than is a non-ionic or anionic polymer. However, it is also necessary to consider that the net energy of adsorption (ϵ) of the non-ionic segments on the polymer also contributes to the adsorption pattern. In general, an increase in the net adsorption energy of the non-ionic segments increases the adsorbed amount. Increasing the charge density of the polymer decreases the amount of adsorbed polymer when the surface bears the same charge as the polymer or if the surface is non-ionic. When the charge density of the polymer increases, the polymer expands and becomes stiffer and polymer adsorption decreases as the fraction of segments in trains increases. When the polymer bears the same charge as the surface, the electrostatic repulsive forces between the polymer and the surface charges increase with charge density, thus decreasing polymer adsorption. In the case of adsorption to a non-ionic surface, the polymer charges the surface to an increased extent with increasing charge density, which decreases further polymer adsorption. Also, the amount of non-ionic segments decreases as the charge density increases, which lowers the attractive forces between the polymer and the surface.

There is generally little systematic information available on the adsorption of non-ionic polymers onto cellulosic surfaces (129, 153). The adsorptive properties can, however, to some extent be understood in terms of the proton donating/accepting properties of the cellulosic surface and the polymer

(129, 153). Except for polyethylene oxide (PEO) and polyacrylamide (PAM), non-ionic polymers are generally not used as retention aids. As discussed in a previous section, PEO has a strong affinity to phenolic groups but not to a cellulose surface. PAM has generally no affinity to cellulosic groups (153), which is of importance when discussing the adsorption of cationic polyacrylamides onto cellulose.

Therefore, the major emphasis here will be to discuss the adsorption of cationic polyelectrolytes onto cellulosic surfaces.

The adsorption of cationic polymers such as polyacrylamides (53, 230-234), PEI and wet strength resins (7, 53, 232, 235-246) and other materials onto cellulose (16, 40, 232, 247-249) has been studied by a number of authors.

There are a number of peculiar problems in polymer adsorption when relating theory to experiments (226). Thus, there is to be considered the problem of (ir)reversibility of adsorption. Essentially this is a hysteresis problem arising from multipoint attachment of a polymer onto a surface and is a time-dependent phenomenon, leading to the question of applicability of equilibrium thermodynamics. Related is the problem of adsorption and desorption kinetics. The kinetics of adsorption is slow due to the low diffusion coefficient of polymers and the slow rate at which polymer molecules rearrange on surfaces. With polydisperse polymers, equilibrium times are even longer due to the process by which smaller molecules are being replaced by the preferentially adsorbed larger molecules.

For cellulosic surfaces, the porosity problem and the exchange (leaching) of liquid material across the interface may be added, to mention just a few experimental obstacles.

The characteristic feature which distinguishes monomers from polymers is that the polymer is adsorbed in "loops" and "trains" on the surface rather than in a flat conformation. The runs of segments lying in the layer immediately adjacent to the surface are called trains and the runs of segments extending into the bulk solution are called loops or tails. The fraction of loops will be denoted p. The adsorption isotherm is expected to be of the high affinity type i.e. the first molecules brought into solution are totally adsorbed and a measurable quantity of polymer in solution is found only when an appreciable amount of the surface is covered (228). Thus the adsorption isotherm is expected to be very sharp. In practice, however, a more or less rounded type of adsorption isotherm is obtained for cationic polyelectrolytes adsorbed onto cellulosic surfaces (see e.g. 53, 230, 233, 249). Characteristically, they are however, most often of the high affinity type.

Discrepancies between theory and experiments are most likely due to the polydispersity of the polymer. Polydispersity in the adsorbing polymer causes rounding of the isotherm because higher molecular weight polymer fractions may displace lower molecular weight adsorbed polymers (250).

Rounded isotherms also arise because of the fact that polymers with different chain lengths have different accessibilities to the porous cellulose surface. With low molecular weight polyelectrolytes, accessible to all anionic charges in the fibre cell wall, less rounded isotherms are generally obtained (249).

It was early recognized that the adsorption of a cationic polyelectrolyte onto cellulose was related to the number of negative charges on the fibres (235, 239). Generally an increase in surface charge was found to increase the polyelectrolyte adsorption (7, 53, 233, 235, 239, 240, 244, 247).

More recently, the charge stoichiometry has been explored in somewhat more detail. Thus it has been found that there is a quantitative charge stoichio-

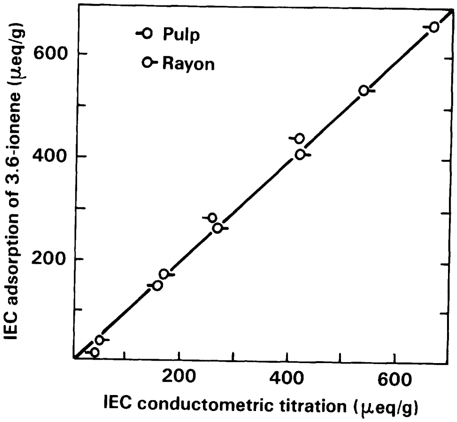


Fig 26a - Ion-Exchange Capacity (IEC) evaluated from adsorption isotherms of 3.6-Ionene on carboxymethylated pulp and rayon fibers as a function of charge on the fibers. The charge was evaluated by conductometric titration (left). (Wågberg et al, 248)

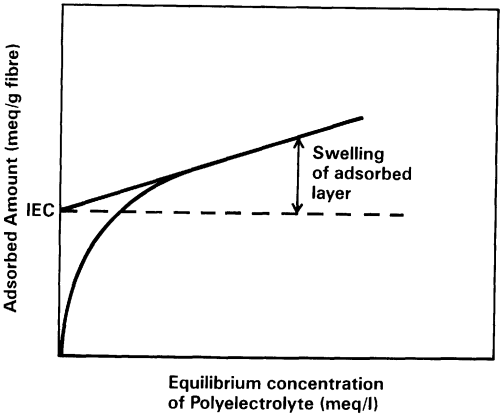


Fig 26b - Procedure for estimation of the ion-exchange capacity of a pulp from a polyelectrolyte adsorption isotherm, provided the polyelectrolyte is accessible to all charged groups in the fibrous substrate (right).

metry between the number of adsorbed cationic charges and the number of ionic charges on the cellulosic substrate, as exemplified in fig 26a (248).

In this case the charge stoichiometry was evaluated by extrapolating the plateau value of adsorption to zero polymer concentration in solution and taking the Y value as an estimate of the ion-exchange capacity of the fibre material as shown schematically in fig 26b.

This relationship holds only if the polyelectrolyte has full accessibility to the charged groups in the cell wall. This requires that the polyelectrolyte have a sufficiently low molecular weight for accessibility to the charged groups in the fibre cell wall. Alince found that the adsorption of polyethyleneimine (PEI) to cellulose increased in the very low molecular range (244). Thus it is probable that the cationic polyelectrolyte has to have a certain molecular weight to have a sufficiently high affinity to the fibre material before the above arguments are valid. This is predicted by the polyelectrolyte adsorption theory (228). In the high molecular weight region ($>10^4$) the adsorption is generally found to decrease with increasing molecular weight (40, 53, 230, 236, 244, 251) as expected from the decreased accessibility to the charges in the cell wall.

Stoichiometric polyelectrolyte adsorption is thus only observed under certain conditions of good accessibility of the polyelectrolyte to the charges in the cell wall.

Moreover, it is only observed in solutions with a low ionic strength, with thick electrostatic double layers. As soon the electrolyte concentration increases, the double layers are compressed requiring a much better geometric fit between the individual charges on the polyelectrolyte for stoichiometry to be observed. These are the same arguments as those previously discussed for the stoichiometry of polyelectrolyte complexes.

Theory (228) predicts that the first polymers are adsorbed in a rather flat conformation (i.e. p is low) whereas at higher surface coverage the adsorbed polymers have segments protruding out into the bulk solution. As the fraction of the segments in the loops increases at high surface coverage, the thickness of the adsorbed layer increases.

This behaviour has also recently been observed for the adsorption of 3-6-Ionene onto cellulose (249). Wågberg et al (249) found from counter-ion release experiments that at the plateau level of the adsoption isotherm the adsorption increased, although no more counter-ions were released from the fibers. The amount of counter-ions released during adsorption increased steeply up to the knee in the adsorption isotherm and then stayed constant. The total number of released counter-ions also corresponded to the ion-exchange capacity of the fibre material. This behaviour can be interpreted in terms of a lower fraction of "bound" segments corresponding to an increased swelling of the surface layer of the adsorbed polyelectrolyte (as shown in fig 26b).

Theoretically, adsorption is expected to increase with increasing electrolyte concentration (228) due to coiling of the polymer (=increased flexibility) and due to the decreased electrostatic repulsion when the surface and polyelectrolyte bear the same charge. Only when the polymer and the adsorbent carry opposite charges do the electrostatic conditions promote adsorption. The adsorption decreases with increasing electrolyte concentration when the charge interaction is the main reason for adsorption. When the nonionic adsorption energy drives the adsorption, an increase in electrolyte concentration tends to increase the adsorption.

For the adsorption of cationic polyelectrolytes onto cellulose it is generally observed that electrolytes decrease the adsorption of the cationic polyelectrolyte (233, 244) or that there is an optimum in the adsorbed amount (232, 234, 239). The latter behaviour is shown in fig 27b (234).

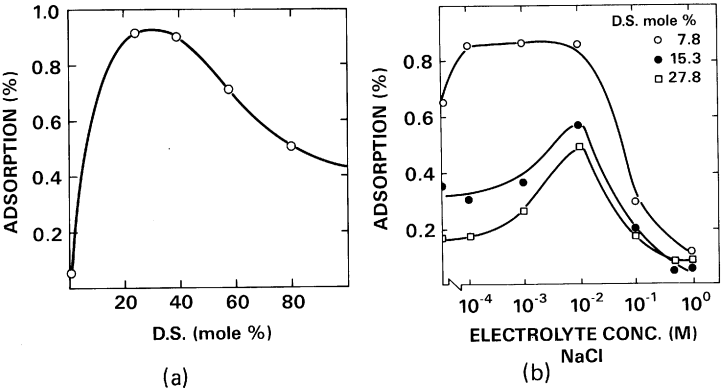


Fig 27a - The effect of charge density (D.S.) of high M_w C-PAM on the adsorption to bleached kraft pulp (left). (Lindström and Wågberg, 234)

Fig 27b - The effect of electrolyte concentration on the adsorption of high M_w C-PAM to bleached kraft pulp (right). (Lindström and Wågberg, 234)

Initially the polymer coils thus increasing the flexibility and decreasing the size of the polymer, which promotes adsorption, whereas at higher ionic strengths the decrease in charge interaction decreases adsorption. It should be noted that the initial increase in adsorption may be due to the higher accessibility of the polymer to the porous structure of cellulose as the radius of gyration of the polymer decreases. Naturally these effects depend on the pore size distribution of the fibre material and on the molecular weight of the polymer.

The effect of the valency of the electrolyte present is shown in fig 28 (233). The higher the valency the lower is the adsorption. Similarly cationic aluminium species have been found to have a strong effect in depressing the adsorption of C-PAM to cellulose (98, 233). These effects are readily understood from the decreased charge interaction between the C-PAM and the cellulose surface when the cation valency is increased.

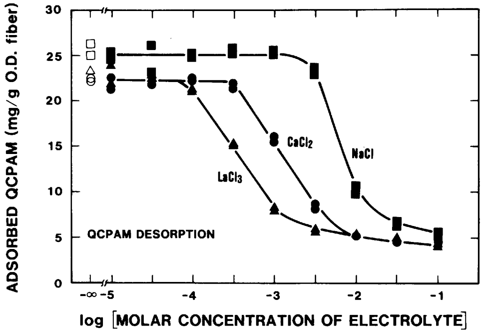


Fig 28 - Amount of adsorbed C-PAM after exposing fibers saturated with adsorbed polymer to various concentrations of $LaCl_3$, $CaCl_2$ and NaCl at pH 5. (Pelton, 233)

When the surface is oppositely charged to the polymer, the theory predicts that optimum adsorption occurs at a low charge density of the polymer provided the polymer affinity to the surface is dominated by charge interactions. This is natural, firstly, because a low amount of charge promotes adsorption due to electrostatic attraction. As the charge density of the polymer increases, however, the ability of the polymer to recharge the surface increases and, as soon as the dispersion is recharged further adsorption of the polymer is limited by the electrostatic repulsive forces between the surface and the polymer. Thus an optimum charge density for maximum adsorption exists.

This is also what is experimentally observed for the adsorption of cationic polyelectrolytes to cellulose (232, 234) though most commonly the decreasing slope is observed (7, 16, 40, 53, 230). A typical example is shown in fig 27a for the adsorption of C-PAM to bleached kraft pulp (234).

Polymer reconformation and transient electrokinetic phenomena

It is recognized and common practice in papermaking to add the retention aid fairly close to the headbox position. With these short contact times between the polymer and the stock, equilibrium adsorption is probably not attained as discussed in previous chapters. Moreover, it takes a certain time for the adsorbed polymer on a surface to reach its equilibrium conformation.

For high molecular weight polymers it can be expected that adsorption takes place by a series of individual attachments at various points along the polymer chain over a finite period of time. As more contacts are made, the polymer conformation becomes flatter and loops become less extensive until some equilibrium state is reached (105, 195, 200, 225, 228, 252-255).

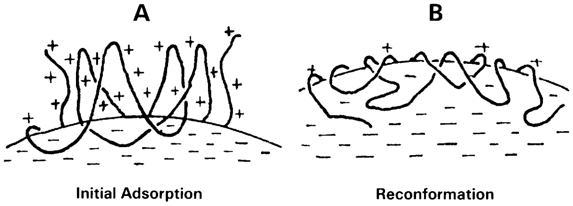


Fig 29 - Models for (a) initial polymer adsorption (b) reconformation of polymer on a surface. (Unbehend, 252)

This situation is schematically illustrated in fig 29, where a) represents the conformation of the polymer at the surface after short contact time and b) represents the state of adsorption after longer times. It is obvious that the likelihood for bridging flocculation is higher when the polyelectrolyte is in a more expanded conformation on the surface.

Corroboratory evidence for such reconformation processes for polyelectrolytes on cellulosic surfaces has been presented by Wågberg et al (253).

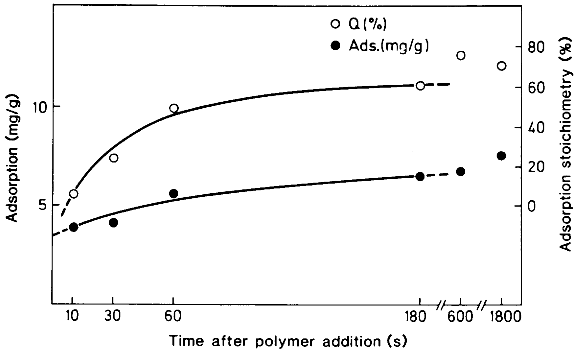


Fig 30 - Kinetics of adsorption and adsorption stoichiometry, for the C-PAM ($M_w = 4 \times 10^6$) polymer on cellulosic fibers with D.S. = 0.065. Amount of added polymer: 15 mg/g. (Wågberg et al, 253)

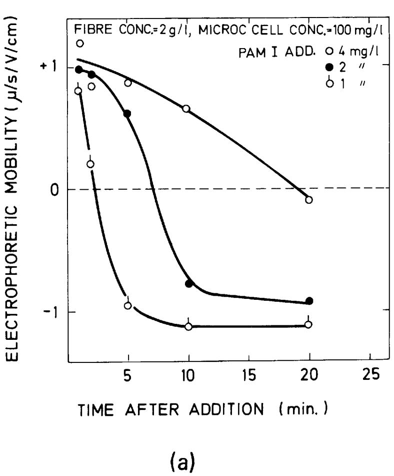
This behaviour is illustrated in figure 30 where the adsorbed amount of a low charge density polyelectrolyte (C-PAM) and the adsorption stoichiometry (fraction of cationic groups bound to the cellulose surface, as determined from counter-ion release experiments) is given versus time after the addition of polymer.

Initially less than 10 % of the cationic groups are bound to the surface, whereas after 60 min, 80 % of the cationic groups were found to be bound to the charged surface sites on the cellulose surface.

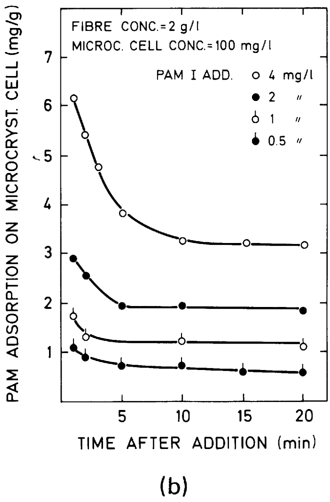
For a highly cationic low molecular weight (6×10^3) polyelectrolyte 3,6-Ionene, the adsorption stoichimetry was initially high and changed only little with time, although adsorption was comparatively slow because of pore diffusion into the cellulose cell wall.

It may be expected that the reconformation of cationic polyelectrolytes on anionic particles would also be reflected in changes in the net zeta-potential, as the shear plane is being moved closer to the particle surface with time.

A transient surface potential has indeed been observed by many authors when subjecting fibre suspensions to cationic polyelectrolytes (7, 45, 124, 230, 256-258). It is generally observed that if the zeta potential of the fines fraction (fillers or cellulosic fines) is monitored as a function of time after the addition of a cationic polymer, there is initially a rapid change towards a positive surface potential before the zeta potential again gradually drops towards negative values again. It must be stressed that experimentally this behaviour has been observed in microelectrophoresis experiments on the fines fraction sampled from a fibre suspension.



(a)



(b)

Fig 31a - The electrophoretic mobility of microcrystalline cellulose (MCC) sampled from a suspension of bleached kraft fibers (2 g/l) and microcrystalline cellulose (100 mg/l) different times after addition (left). (Lindström, 258)

Fig 31b - Corresponding C-PAM adsorption measured on the MCC-fraction (right). Experiments with H^3-C-PAM. (Lindström, 258)

A typical example is given in fig 31a where the electrophoretic mobility of microcrystalline cellulose, MCC (model for fines fraction) sampled from a suspension of bleached kraft pulp (coarse fiber fraction, 2 g/l) and MCC (100 mg/l) is given versus time after addition.

At first sight this behaviour may be attributed to conformational changes of the polyelectrolyte on the cellulose fibre surface and/or to pore penetration of the polymer into a porous substrate. This behaviour is not however noted unless the fiber fraction is present in the experiemnt. The decrease in the zeta potential of the MCC corresponds instead to a decrease in the amount of C-PAM on the MCC. In fact, polymer is being transferred from the MCC to the cellulose fibres (see fig 31b). This behaviour is most likely due to the difference in size and morphology of small sized material (e.g. MCC) and the cellulose fibers.

The average diffusion distance of the polymer into a smaller porous particle is small compared with the thickness of the cell walls of fibers. Thus adsorption is slower on the fiber fraction than on the fines fraction. The fines fraction is initially saturated with polymer but as the polymer diffuses into the cell walls of fibers, surface sites become available on fibers so that a polymer transfer from fines to fibers can occur (230, 258).

Tanaka (256) has observed that the zeta potential of PEI-treated non-porous particles like polystyrene latex decreased with time after addition. This was attributed to the conformational change of the polyelectrolyte on the surface. With this observation in mind it therefore appears as if there are at least two different phenomena which can explain the observed transient zeta potentials. The relative magnitude and importance of these two effects varies depending on the physical and chemical conditions during the experiment.

ACKNOWLEDGEMENTS

The Mo och Domsjö AB is greatly thanked for allowing the author to publish this manuscript.

The author is indebted to Dr Anthony Bristow for the linguistic revision of the manuscript and to Mrs Lena Westin-Eriksson for typing the manuscript.

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Transcription of Discussion

SOME FUNDAMENTAL CHEMICAL ASPECTS ON PAPER FORMING

T. Lindstrom (Review Paper)

Dr. M.J. Jaycock, Roe Lee Paper Chemicals Ltd, U.K.

Thank you for a most interesting paper. I have two comments to make.

The diagram you give on Gouy double layers and Stern layers - may I criticise the population of the Stern layer? If you calculate what the population must be by (a) calculating charge densities by Zeta potentials, and (b) doing an adsorption isotherm to determine how much is there - the conclusion from the six or eight studies I have looked at so far is that if the Stern layer is negative this is accompanied by at least 80% of that number of the opposite charge ions. So the population of the Stern layer is almost never just one single ionic species as it stands, it is always both. I think that on simple electrostatic grounds you would expect this, repulsion of a layer that was composed of ions of one type would result in it blowing apart very quickly.

Prof. T. Lindstrom

I agree with what you say. There is a population distribution of both species - this is obvious.

Dr. M.J. Jaycock

Could I make one other comment on hemicellulose? You suggested that when we looked at the isoelectric points of fillers that they were different, and I think that is correct when they are measured on their own, but once they appear in a papermaking system the hemicelluloses etc. that are present make them all look the same - so in fact it does not matter if it is clay or TiO_2 or anything else, they get coated with hemicellulose and act as if they are little hemicellulose particles in terms of their electrophoretic behaviour. This work was done in Loughborough with Joe Pearson and Basharat Nazir some years ago and we are pretty convinced that surfaces do not remain as anything other than hemicellulose and that therefore all surfaces in the system look the same.

Prof. T. Lindstrom

It will of course depend on what systems we are talking about. For instance the degree of machine backwater closure in the mill, different kinds of pulp etc. So I think you are probably right - this could be the situation in many practical mill systems, but I would not say that all situations are like that.

Dr. J.G. Penniman, Paper Chemical Laboratory Inc. USA

I would like to add my compliments on your paper, I hope it turns into a book soon. I don't think it is fair to characterise the isoelectric point of TiO_2, for example, at one specific value because it can be surface treated and Rutile TiO_2 can have an isoelectric higher than a pH of 9. This means that it is cationic in conventional papermaking systems. My other comment is that we have added to Michael's (Jaycock) earlier work on streaming potential and while the data you showed is, I believe, true as a special case, if you do add cationic chemicals to a conventional papermaking furnish you find that the curve that you get if you measure the streaming potential is linear as opposed to the cationic demand plateau on both sides of the plateau that is observed with conventional microelectrophoresis. I would appreciate hearing your thinking on this and ask if you could give a reason for it?

Dr. T. Lindstrom

In reply to your first question, I agree you can of course change the IEP if you change the surface chemistry. My experience with streaming potential measurement is limited. I do not recall that the charge reversal curves should be linear instead of the usual shape.

Prof. J. Marton, SUNY, USA

Most of the publications relating to the polymer furnish interactions relate to acidic papermaking. We are all involved at present in alkaline papermaking conditions. We are using cationic calcium carbonate, anionic calcium carbonate, anionic clay etc. If you called a retention aid supplier into the mill, one would recommend an anionic retention aid another would recommend a cationic retention aid. I would like to hear comments or some guidelines on the driving forces involved and the best systems to use?

Prof. T. Lindstrom

Mineral particles are both cationic and anionic and therefore we can in principle add any type of retention aid and it will work to some extent. It is just a matter of how strong the floc will be. If you know the chemistry of the system you can construct certain guidelines but I would suggest the use of multivariate analysis for finding the conditions where certain polyelectrolytes are more efficient than others in different paper mill systems. I think this is the way chemical suppliers should work and learn about their systems. They should pick out certain parameters like the type of particles present, the chemical environment, anionics, pH, electrolytes, etc. Chemical suppliers already have many "rules of thumb", but in my opinion if they adopt a more systematic approach it will be much more useful. I am afraid there is no universal answer to your question.

Dr. J.C. Roberts, Session Chairman - UMIST

I feel that this review is the most comprehensive there is in the field and I think Tom has done an excellent job in producing it and I will certainly be recommending it to all my students.