

## DISSOLVED AND COLLOIDAL SUBSTANCES (DCS) AND THE CHARGE DEMAND OF PAPERMAKING PROCESS WATERS AND SUSPENSIONS: A REVIEW

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Dissolved and colloidal substances (DCS) in the process waters of paper machine systems can interfere with the retention of fine particles, retard the drainage of water from the wet web, and generally hurt the intended functions of various polyelectrolytes that are added to the process. This review considers publications that have attempted to characterize the nature and effects of different DCS fractions, in addition to some of the ways that paper technologists have attempted to overcome related problems. The consequences of DCS in a paper machine system can be traced to their ability to form complexes with various polyelectrolytes. Such tendencies can be understood based on a relatively strong complexing ability of multivalent materials, depending on the macromolecular size and charge density. Continuing research is needed to more fully understand the different contributions to cationic demand in various paper machine systems and to find more efficient means of dealing with DCS.

*Keywords:* Cationic demand; Charge demand; Dissolved and colloidal substances (DCS); Interferences to polymeric retention aids; Polyelectrolyte complexes; Fines; Retention; Drainage

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## INTRODUCTION

The goal of this article is to review published work related to the presence, characteristics, behavior, and strategies for overcoming the adverse effects of ionically charged Dissolved and Colloidal Substances (DCS) in the process streams of paper machine systems. DCS can be defined as the sum of the polyelectrolytes, other dissolved substances, and very small (at least one dimension  $< 1 \mu\text{m}$ ) suspended particles present in process water of paper mills. These substances are of concern to papermakers, especially when their level is either relatively high or changing over time, due to various adverse impacts on paper machine operations and products. For example, high levels of negatively charged DCS (sometimes called “anionic trash”) can interfere with the efficient usage of cationic additives, including retention aid polymers. The term “anionic” is often associated with the term DCS due to the fact that substances released from wood typically contain carboxylic acid groups, and such groups will dissociate to their negatively charged carboxylate form under the conditions of pH typically encountered in paper machine systems (Holmbom and Sundberg 2003). Other sources of DCS include waste paper, coating materials, and even chemicals that papermakers intentionally add to the fiber slurry during the manufacturing process. In addition, because papermakers face somewhat similar problems when there is an excess of positively charged colloidal system in the process water (Horn and Melzer 1975; Gruber and Ott 1995), the present review also considers what happens when positively charged multivalent ionic species are present in excess. The term “charge demand” can be defined as the amount of a standard high-charge polyelectrolyte required to neutralize the net ionic charge of DCS. The term “cationic demand” is used to express the amount of high-charge cationic additive added to achieve the neutral system.

The present review article was motivated, at least in part, by a realization that DCS is not just one thing. Rather, ongoing research continues to reveal ways in which different components of DCS can contribute to effects that are observable in the laboratory and during the production of paper (Medvecz 1993; Holmbom and Sundberg 2003). Presumably, if these factors can be understood, there is potential to further improve the efficiency of papermaking operations (Sundberg *et al.* 2000a;b; Sjöström *et al.* 2006; Valto *et al.* 2010). In addition, new strategies are emerging, some of which appear to be aimed at dealing with particular components of DCS.

### Background Concerning Polymers, Ions, and their Interactions

The concept of the “charge demand” or “colloidal charge” of a sample of process water or fiber suspension presupposes some knowledge of polyelectrolytes, multivalent ions, and how they interact with ionically charged matter or various types. Some brief background is given here. Readers seeking additional background are urged to consult the following sources (Eklund and Lindström 1991; Fleer *et al.* 1993; Hiemenz and Rajagopalan 1997).

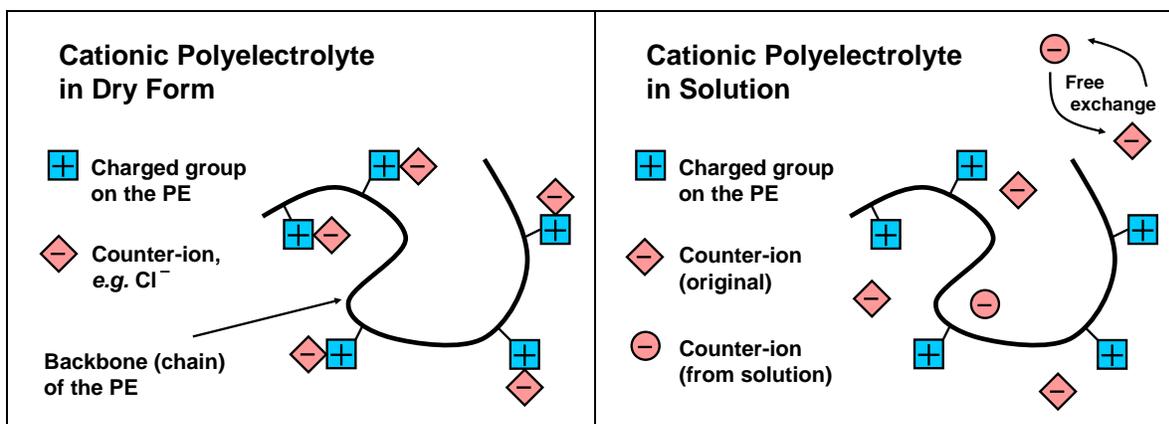
#### *Polymers and ions in solution*

Water is an excellent solvent and/or suspending medium for materials that have the ability to dissociate into ionic forms. Such substances include, for instance, NaCl,

NaOH, HCl, *etc.* These examples dissociate fully in water, forming their simple component positive and negative ions, which are stabilized due to the polar nature of the water molecule. The present article is particularly concerned with certain classes of substances that can dissociate in a specific way: A surface charge arises on wetted surfaces when small ions such as  $H^+$ ,  $Na^+$ , or  $OH^-$  dissociate from something larger, giving rise to a multi-charged ion (multivalent ion or particle) in the solution or suspension (Hiemenz and Rajagopalan 1997). The multivalent substances can be classified as being monomers, polymers (*i.e.* polyelectrolytes), colloidal particles, or larger objects such as cellulosic fibers or cellulosic fines.

The types of multi-valent substances mentioned in the previous paragraph all have one thing in common: they have a tendency, at least to some extent, to interact with high-charge density polyelectrolytes of opposite net charge. When a polyelectrolyte or other multivalent ion interacts strongly with a polyelectrolyte of opposite net charge, the result is called a polyelectrolyte complex, or a coacervate system (see next). If the interaction of the polyelectrolyte is with suspended solid material, then the process is called adsorption.

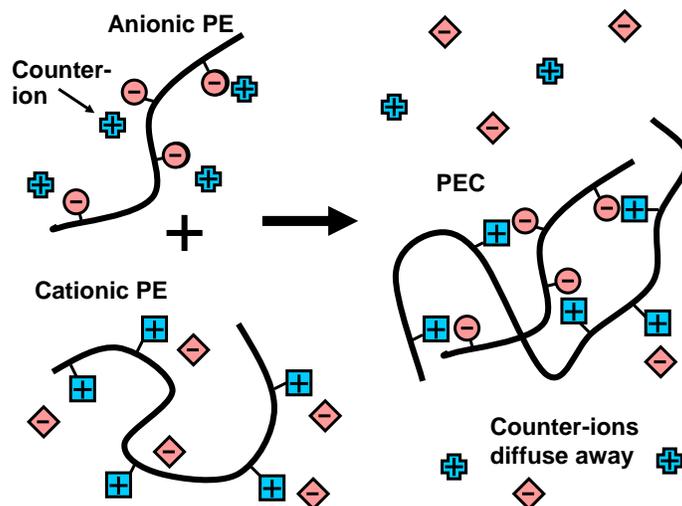
The behavior of polyelectrolytes in solution can be a key to understanding how they interact with other charged entities, including surfaces (Mandel 1985; Fleer *et al.* 1993). Figure 1 presents a simplified view of what happens when a dry, purified sample of a polyelectrolyte is added to water that contains a relatively low concentration of simple ions. As depicted in the figure, the counter-ions (in this case chloride ions) are able to gain some greater freedom in the course of dissolution, since they are no longer constrained to remain associated with the macro-ion. The increased disorderliness of the counter-ions provides part of the driving force leading to dissolution of the polyelectrolyte (Lu *et al.* 2011). The resulting decrease in the free energy of the system as a whole is greater than what might result from the re-adsorption and re-association of the counter-ions onto the macromolecule.



**Fig. 1.** Schematic illustration of the increase of freedom of counter-ions upon dissolution of a polyelectrolyte (PE). Left: Counter-ions are tightly associated with the PE's ionizable groups in the dry state. Right: Counter-ions can diffuse away from the PE's charged groups in the dissolved state and even change their position with other like-charged ions in the system, giving greater disorder.

### Polyelectrolyte complex (PEC) formation

Both electrostatic attractions between opposite charges (enthalpy's component of free energy) and a further freeing up of counter-ions (entropy's component of free energy) work together in favoring the formation of complexes between oppositely charged polyelectrolytes of sufficiently high charge density. The idealized interaction is illustrated schematically in Fig. 2.



**Fig. 2.** Idealized schematic diagram representing interaction of a segment of strong poly-acid and strong poly-base in aqueous solution. Only the counter-ions (not any other salt ions that may be present) are shown. The polyelectrolyte (PE) segments are shown as forming an approximate ladder structure with ion pairs, allowing the counter-ions to diffuse into the bulk of solution, thus increasing the entropy of the system and favoring dehydration of the polyelectrolyte complex (PEC).

As shown in Fig. 2, formation of a PEC results in creation of ion-pairs between the bound groups on the oppositely charged macro-ions. This event allows the counter-ions to freely diffuse away into the bulk of solution (Michaels *et al.* 1965). In typical cases an insoluble PEC will have a nearly 1:1 stoichiometry of charge interactions (Michaels *et al.* 1965; Ström *et al.* 1982; Thornton 1994; Dautzennbert *et al.* 1996; Webster and Huglin 1997; Horvath *et al.* 2006; Mocchiutti and Zanuttini 2007; Pelton *et al.* 2007), such that its net charge is near to zero, at least in its interior regions (Chen *et al.* 2003). Being uncharged, such a PEC can be expected to have a weaker interaction with surrounding water molecules in comparison with the polyelectrolytes from which it was formed. As a consequence, PEC formation often entails precipitation from solution or deposition of the material onto fiber surfaces, *etc.* (Kekkonen *et al.* 2001; Lofton *et al.* 2005). Several authors have discussed ways in which the mechanism of polyelectrolyte complexation can help explain the functions of various additives in the course of a typical papermaking operation (Cundall *et al.* 1979; Linhart *et al.* 1987; Sundberg *et al.* 1993; Kekkonen *et al.* 2002; Vanarek and van de Ven 2006; Aimi *et al.* 2010).

Evidence supporting the predominance of 1:1 charge stoichiometry during a typical polyelectrolyte titration includes both titration results and analysis of precipitates:

- It has been shown that the results of polyelectrolyte titration can be independent of the direction of titration (Chen *et al.* 2003). In other words, the same stoichiometry is associated with the endpoint if the polyelectrolytes used as the sample and as the titrant are switched. Even in the presence of increasing salt concentrations, test results support a model in which the central parts of the resulting complexes engage in an approximate 1:1 complexation. Haronska *et al.* (1989) were able to induce non-stoichiometric interactions by selecting pairs of polyelectrolytes having sharply different charge densities and relatively high molecular mass; their findings show that the polyelectrolyte used as the titrant tended to be “inefficient”, requiring more than the stoichiometrically predicted amount to reach the endpoint.
- Studies of precipitated materials following interactions between solutions of oppositely charged polyelectrolytes have repeatedly shown an approximate 1:1 stoichiometry (Cundall *et al.* 1979; Argüelles-Monal *et al.* 1990; Dragan and Cristea 2002). Among such studies, some of the most interesting are those in which the researchers set up conditions intended to make the 1:1 complexation more challenging (Webster *et al.* 1997; Mende *et al.* 2002). For instance, Kötzt *et al.* (1992) found that the stoichiometry of precipitated complexes was a function of the macromolecule structure, as well as the order of addition.

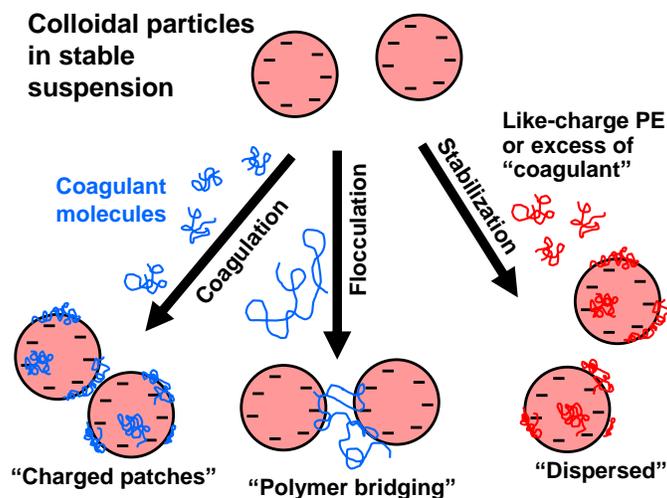
There appear to be some minimum requirements that need to be fulfilled in order for PECs to form and precipitate. One of these is molecular size. For a given combination of materials and aqueous conditions, one can expect there to be a threshold of either molecular size or the number of net ionic charges below which polyelectrolyte complexation becomes weak or even insignificant (Ström *et al.* 1979, 1982; Bottéro *et al.* 1980; Thornton 1994; Liu *et al.* 2010b). Likewise, there can be a concentration of salt which, once exceeded, effectively prevents the formation of PECs (Fleer *et al.* 1993).

#### *Polyelectrolyte adsorption, flocculation, and steric stabilization*

The adsorption of a polyelectrolyte from a solution onto suspended material is in many respects analogous to the interaction between one polyelectrolyte and another, as just described. Again, the process can depend on both enthalpic (heat-generating) and entropic contributions to free energy. The subject of polyelectrolyte adsorption onto cellulose and related materials has been well reviewed (Fleer *et al.* 1993; Wågberg 2000).

Depending on various details, adsorption of a polyelectrolyte onto suspended particles within an aqueous suspension can have a variety of results, including coagulation, flocculation, and dispersion or stabilization. These three idealized possibilities are illustrated in Fig. 3.

As illustrated, the effects of polyelectrolyte addition on colloidal stability can depend on such factors as their sign of charge, their charge density, their molecular mass, and most importantly, their level of addition. If the polyelectrolyte has a relatively low molecular mass and a sign of charge opposite to that of the suspended particles, then it is reasonable to expect coagulation to result from neutralization of the surface charge (Chang and Robertson 1967; Lindström *et al.* 1974; Sandell and Luner 1974; Horn and Melzer 1975; Strazdins 1977; Horn and Linhart 1996; Hubbe *et al.* 2007b).



**Fig. 3.** Schematic illustration of three ways in which the addition of a polyelectrolyte may affect the colloidal stability of negatively charged particles in an aqueous suspension. Note that if cationic polymers having high charge density and low-to-moderate molecular mass are added in such excess that they can cover all of the surfaces, then the result can be the same as shown at the far right, *i.e.* stabilization. Color coding: Pink or red indicates negative charge; blue indicates positive charge.

It is a common observation among papermakers that high-charge cationic polyelectrolytes tend to become more effective for retention and drainage enhancement with increasing molecular mass. Such a trend can be understood in terms of a “charged patch” model (Kasper 1971; Goossens and Luner 1976; Dickinson and Eriksson 1991; Horn and Linhart 1996; Tripaththaranan *et al.* 2004). A defining feature of a charged patch mechanism is that the polyelectrolyte adsorbs tightly onto one surface, with a relatively flat molecular conformation; the “patch” thus formed is able to attract the uncovered areas of other particles in the suspension. Evidence that a system has been coagulated by either charge neutralization or a charged patch mechanism can be provided by observations that the system can coagulate again readily if the particles happen to be knocked apart by hydrodynamic shear (Tripaththaranan *et al.* 2004).

The central part of Fig. 3 illustrates a polymer bridging mechanism, which is characteristic of the class of very-high-molecular-mass acrylamide copolymers that are commonly employed as retention aids in papermaking systems (Swerin and Ödberg 1993, 1997; Pelzer 2008). The bridging mechanism assumes that the macromolecules, even in a randomly coiled conformation, are long enough to bridge the distance between suspended particles, overcoming such effects as repulsive electrostatic forces and lubrication effects that otherwise would slow down or inhibit sticking collisions between the solid surfaces (La Mer and Healy 1963; Gregory 1973). Further evidence in support of such a mechanism was provided more recently by experiments involving transmission electron microscopy and gold nanoparticles to confirm the location and form of macromolecular chains (McNeal *et al.* 2005). According to the definition introduced by Unbehend (1976), bridging flocculation generally gives rise to “hard flocs.” Such flocs feature polymer-induced attachments that are strong but which can break irreversibly. A number of review articles have discussed the implications of polyelectrolyte interactions in papermaking systems, with emphasis on the role of retention aids (Swerin and Ödberg

1993, 1997; Smith-Palmer and Pelton 2002; Hubbe 2007c; Hubbe and Rojas 2008; Pelzer 2008).

The right-most part of Fig. 3, in which the arrow is marked “stabilization”, requires some explanation. Though it is theoretically possible to bring about flocculation of a charge-stabilized system by use of a same-charged polyelectrolyte (Fleer *et al.* 1993), there are two situations in which such a polyelectrolyte will reliably contribute to the stabilization of the suspension: First, if the molecular mass of the polyelectrolyte is too low for it to act as an effective bridging agent (*e.g.*  $\ll 10^6$  g/mole), then the dispersing effects are expected to dominate. Second, if a sufficient amount of hydrophilic polyelectrolyte has been added to cover essentially all of the surfaces, then a highly stabilized system can be achieved, regardless of the sign of charge or other attributes.

#### *Different classes of substances suspended in water solutions*

Substances suspended in aqueous medium may be present in different forms, such as dissolved, colloidal, or macroscopic suspended matter. Due to the small size of the colloidal material (at least one dimension  $< 1 \mu\text{m}$ ), the interactions between surfaces play a dominant role in its behavior (Adamson and Gast 1997; Hiemenz and Rajagopalan 1997). The emulsion droplets or particles formed by extractives are often prominent in this size range (Ekman *et al.* 1990; Puro *et al.* 2011). Liang *et al.* (2011) carried out lab simulations of water re-use in a papermaking operation and found a substantial amount of lignin-derived matter in the colloidal fraction. Dunham *et al.* (2002) carried out a study to compare the cationic demand of the colloidal fraction of a mechanical pulp suspension, versus the entire “dissolved and colloidal” fraction. Removing the colloidal fraction (by use of filter paper) decreased the charge demand by about half in the systems considered. When running this kind of analysis, it is important to include a blank experiment to account for the amount of titrant sorbed by filter paper.

Furthermore, one can discriminate between different states of matter, *e.g.* true solutions, impenetrable hard materials (*e.g.* calcium carbonate or clay particles), and gels. The gel category includes such materials as the amorphous regions in cellulosic fibers. These regions are able to change their state of swelling, *i.e.* their water content, depending on aqueous conditions (Scallan and Tigerström 1992; Park *et al.* 2007). The gel category also includes some polyelectrolytes and their complexes (Miao *et al.* 2008; van der Gucht *et al.* 2011). Various ionic materials can permeate and interact with charged groups within gel materials, depending on time, molecular masses, and other factors (Horvath *et al.* 2008; Wu *et al.* 2009). By contrast, dissolved materials can interact only with the exterior surfaces of impenetrable hard materials such as crystalline minerals and the crystalline regions of cellulosic fibers. It also should be noted that certain DCS components released from wood, *e.g.* glucomannans, gactoglucomannans, and most lignans, are not ionically charged. However, in many typical process water samples from paper mills using mechanical pulps the dissolved component of DCS can be expected to account for a greater proportion of cationic demand, compared to colloidal and particulate materials; the greater contribution of the dissolved fraction to charge demand in those cases can be attributed to various factors such as greater accessibility of the charged groups in dissolved macromolecules.

## Overview of Methods to Evaluate Charge Demand

As will be discussed more fully later in this article, several methods have been used to determine the tendency of DCS in paper machine process water to neutralize the charge of polyelectrolytes. Such tests are usually carried out with standard titrants. The results of charge demand tests can be used to control of the flows of additives that are being used to achieve fine-particle retention, promotion of dewatering, or development of paper strength and other properties. Some of the most prominent experimental approaches are summarized in Table 1, which also provides selected references. Polyelectrolyte titration methods involving either a streaming current device or colorimetric detection of the endpoint are the most widely used approaches. Online systems to monitor and control charge demand in paper machine systems also are widely used (Veal 1997; Bley 1998; Rantala *et al.* 1999; Rice and Roeraade 2003).

**Table 1.** Methods to Evaluate Charge Demand of Process Water Samples

Experimental Approach	Selected References *
Polyelectrolyte titration with streaming current endpoint	Hubbe & Chen 2004; Cui <i>et al.</i> 2008; Hubbe 2008
Polyelectrolyte titration with color (toluidine blue dye) endpoint	Terayama 1952; Halabisky 1977; Hubbe 1979; St. John & Gallagher 1992; Carrasco <i>et al.</i> 1998; Mocchiutti & Zanuttini 2007
Polyelectrolyte titration: electrokinetic endpoint (streaming potential or microelectrophoresis)	Strazdins 1994; Hubbe 2001; Wang & Hubbe 2002
Potentiometric or conductometric titrations to determine carboxyl group content	Herrington & Petzold 1992; Laine <i>et al.</i> 1996; Fardim <i>et al.</i> 2002; Koljonen <i>et al.</i> 2004

\* For a fuller selection of cited references, please refer to later sections in this article; only some key references are cited in this table.

The fact that the methods listed in Table 1 have been found useful in optimizing paper machine additive programs helps to shed light on the nature of the papermaking processes themselves. A paper machine operation can be compared to a giant polyelectrolyte titration (Vannerberg 1992). To the extent that this model is true, one wants to be able to adjust the dosages of charged additives so that they are kept in an optimal state of balance. While many papermakers have reported favorable running conditions, as well as paper quality, when the system has a near-neutral or slightly anionic charge (Lindström *et al.* 1974; Strazdins 1977; Linhart *et al.* 1987), it is even more important that the sign of colloidal charge in a paper machine system should remain stable over time (Rantala *et al.* 1999). Each of the tests listed in Table 1 (or a related automated, online version) can be used to take the guesswork out of what is done at production scale.

## Some Key Sources of DCS in Paper Machine Systems

Table 2 lists some of the most prominent contributors to charge demand of DCS in various paper machine systems. The entries in Table 2 can serve as a springboard for important questions, some of which will be a main focus of later sections in this article. For instance, one may ask why peroxide bleaching of mechanical pulp can greatly increase the cationic demand of the process water. Other key components to be discussed in later sections include the silicates used to stabilize hydrogen peroxide in the presence of transition metal ions (Linhart *et al.* 1987; Nyström *et al.* 1993; Saastamoinen *et al.*

1996; Larnicol *et al.* 2001; He *et al.* 2004), various dissolved substances of lignin and hemicelluloses present in black liquor (Silvestre *et al.* 2000; Sjöholm *et al.* 2000; Lisboa *et al.* 2005; Ribe *et al.* 2010; Jansson and Brännvall 2011; Magaton *et al.* 2011), wood resin, and various binders and dispersants in coating formations that happen to get repulped and sent back to the paper machine system (Järnström 1993; Rantala *et al.* 1999; Nikkinen *et al.* 2001; Monte *et al.* 2011).

**Table 2.** Key Sources of Dissolved and Colloidal Substances Leading to Charge Demand in Paper Machine Process Waters

Source of DCS	Selected References *
Peroxide bleaching/alkali-treatment of mechanical pulping (e.g. pectic acids)	Thornton <i>et al.</i> 1994a; Sundberg <i>et al.</i> 2000a; He <i>et al.</i> 2004; Pranovich <i>et al.</i> 2003; 2005; Pruszyński <i>et al.</i> 2011
Chemimechanical pulping and bleaching (CTMP, APMP, etc.)	Xu 2001; Xu and Zhou 2007; Liu <i>et al.</i> 2011
Peroxide bleaching/alkali treatment of mechanical pulps, CTMP, etc.	Thornton <i>et al.</i> 1993; Thornton <i>et al.</i> 1994b
Carry-over from unbleached kraft pulping (e.g. fatty & resin acids, lignin products)	Alber <i>et al.</i> 1998; Sjöholm <i>et al.</i> 2000; Lisboa <i>et al.</i> 2005; Pirttinen <i>et al.</i> 2007; Aimi <i>et al.</i> 2010
Bleached kraft pulps	Lindström <i>et al.</i> 1978; Holmbom <i>et al.</i> 1999; Sjöström <i>et al.</i> 2000
Coated broke (dispersants, latex, etc.)	Neimo 1993; Nikkinen <i>et al.</i> 2001
Other oxidative bleaching methods (e.g. oxidation of carbohydrates)	Ristolainen & Alén 1998; Sjöström <i>et al.</i> 2006; Cadena <i>et al.</i> 2009; Kukkola <i>et al.</i> 2011
Wet-end additives, e.g. dyes, dispersants	Medvecz 1993; Hubbe 1999; Hubbe 2007b
Recycling, including the de-inking of recovered paper	Holmbom 1997; Eisenschmid and Stetter 1998; Mou and Qin 2006; Li <i>et al.</i> 2008; Miao <i>et al.</i> 2010

\* For a fuller selection of cited references, please refer to later sections in this article; only some key references are cited here. APMP stands for Alkaline Peroxide Mechanical Pulping.

#### *Wood as a main source of charge demand*

Given the fact that wood-derived fibers constitute over 70% of the dry mass of most paper products, it is reasonable to look towards wood as probably being the most important source of charged substances in paper machine systems (Medvecz 1993). Though fresh water also can be a source of charge demand, especially if it contains a significant amount of humic acids (Hubbe 2007a), most fresh water is clarified or pretreated before it is delivered to a paper machine system.

Studies have shown that mechanical pulping processes result in the release of substantial amounts of DCS even when pure, neutral water is used as the medium (Thornton *et al.* 1994a; Cesek and Milichovsky 1996; Örså *et al.* 1997; Valto *et al.* 2009). Greater amounts of such materials tend to be released when pulping is carried out under alkaline pH conditions (Thornton *et al.* 1994b; He *et al.* 2004; Maximova *et al.* 2004; Mou and Qin 2006; Lehmonen *et al.* 2009). The reason for such increased release with increasing pH can be traced, in part, to the presence of carboxylic acid groups in most wood-derived materials. With increasing pH in the range of about 2 to 6, such groups go from an uncharged state to a negatively charged, dissociated state (Herrington and Petzold 1992; Laine *et al.* 1996). Since the negatively charged carboxyl groups are

attracted to water, increased pH favors the release from the wood and dissolution of relatively small molecules that contain carboxylic groups. Furthermore, high alkali will also induce swelling to the wood fibers, as well as cleavage of hemicelluloses and pectins, resulting in increased release, plus demethylation and deacetylation reactions. Some negatively charged species, which will be covered in more detail later, include fatty acids, resin acids, released hemicelluloses and pectins, and fragments of lignin. In addition, various processes related to sulfite pulping, as in chemi-thermomechanical pulp (CTMP) production, tend to produce sulfonate groups, which then contribute to the charge of the associated paper machine process waters (Ström *et al.* 1979; Nyman and Rose 1986; Sjöström 1990; Zhang *et al.* 1994; Vanerek *et al.* 2006). When present in the colloidal material, the sulfonate groups provide a contribution of charge demand that is independent of pH.

#### *Peroxide bleaching of mechanical pulp*

Studies have shown that peroxide bleaching of mechanical pulp can greatly increase the cationic demand of the corresponding process water (Nyström *et al.* 1993; Thornton *et al.* 1993; Sundberg *et al.* 2000a; Bräuer *et al.* 2001; He *et al.* 2004; Pranovich *et al.* 2005; Mou and Qin 2006; Miao *et al.* 2006; Ni *et al.* 2011; Pruszynski *et al.* 2011). As will be discussed later in more detail, the charge demand contribution can mainly be attributed to the demethylation of uronic groups in pectins, giving rise to solubilization and release of the corresponding pectic acids or polygalacturonic acids (PGAs) (Sundberg *et al.* 1993, 1994a, 2000a; Pranovich *et al.* 2003). Unlike kraft pulping and its associated bleaching operations (see next), there is usually no washing stage after mechanical pulps have been subjected to peroxide bleaching (Medvecz 1993). For this reason it is perhaps not surprising that some authors have rated peroxide bleaching of mechanical pulp as the largest and most serious source of charged DCS and associated problems affecting paper machine operations (Ni *et al.* 2011). Recently the alkaline peroxide mechanical pulping (APMP) or the Pre-conditioning Refiner Chemical (P-RC) APMP, has become popular, particularly in China. The charge demand of the resulting pulp would be similar to that of peroxide bleached mechanical pulps (Hou *et al.* 2010).

#### *Black liquor carry-over*

Spent liquor from the kraft pulping process also contains components that can contribute significantly to cationic demand (Alber *et al.* 1998; Bikova *et al.* 2000; Vu *et al.* 2003; Lisboa *et al.* 2005; Neto *et al.* 1999; Sjöholm *et al.* 2000; Rautiainen and Alén 2010; Jansson and Brännvall 2011; Magaton *et al.* 2011). Even though kraft pulping systems invariably employ devices called brown-stock washers to remove black liquor from the pulp before it arrives at the paper machine system, the washing process is never 100% complete (Hart 2011; Pacheco *et al.* 2006). Advances in implementation of brownstock washing technology have the potential to reduce the amount of such carry-over (Lappan *et al.* 1996; Richardson 2005; Lind 2011). In addition, there is evidence that even after extensive washing, additional black liquor solids continue to be squeezed out of the cell walls of pulp fibers during such processes as refining (Sjöström *et al.* 2006) and wet-pressing (Donat *et al.* 2003). Black liquor in the process water of paper machine systems is known to cause problems with process efficiency (Alber *et al.* 1998). The

severe conditions during kraft pulping will, however, degrade most of the pectins and also a large part of the hemicelluloses.

#### *Deinking, recovered fiber*

Paper recycling processes are of particular concern relative to charge demand due to variability. Variability of the incoming material can be expected to cause large fluctuations in the charge demand remaining in the pulp after pulping, as well as after any de-inking of subsequent bleaching operations. As noted by King (1992), one of the primary goals of controlling colloidal charge levels on paper machines should be to improve the stability of operations, an approach that also tends to make product quality more uniform over time. A wide variety of substances have been identified in process water related to de-inking of pulp (Holmbom 1997; Eisenschmid and Stetter 1998; Li *et al.* 2008). For instance, Orblin and Fardim (2011) found evidence that palmitic acid salts, which are used in the de-inking of recovered fibers, can be found in the de-inked pulp even after washing. Additional DCS can be released when secondary fiber is bleached (Mou and Qin 2006; Miao *et al.* 2010). Charged additives, *e.g.* cationic starch, are also present in most samples of recovered fibers.

## CONSEQUENCES OF DISSOLVED AND COLLOIDAL SUBSTANCES (DCS)

Numerous published articles have documented the presence and consequences of DCS in papermaking process systems (see, for instance Holmbom and Sundberg 2003; Sjöström *et al.* 2006; Ni *et al.* 2011, Hu *et al.* 2004; Chen *et al.* 2012a,b). In order to provide an introduction to the subject, this section will review publications that deal with charge demand in general, without reference to different components of DCS.

A conventional approach that papermakers use to deal with DCS involves the addition of high-charge polyelectrolytes having an opposite charge. Thus it is common for papermakers to employ high-charge cationic additives such as aluminum sulfate (papermaker's alum), polyaluminum chloride (PAC), or synthetic polyelectrolytes such as poly-diallyldimethylammonium chloride (poly-DADMAC), poly-ethyleneimine, poly-vinylamine, and a range of other polyamines and copolymers. In principle, an optimized and relatively steady charge demand of the process water in a paper machine system can be expected to yield benefits in terms of reduced costs of some other chemical additives, increased operating speeds of paper machines, lower frequency of process interruptions, and greater reliability with which the papermakers can meet quality specifications.

## Retention of Cellulosic Fines and Fillers during Papermaking

### *Decreased retention efficiency*

Very-high-mass cationic copolymers of acrylamide (cPAM) are the class of additives most frequently used in papermaking systems throughout the world (Kleman 2008). The primary purpose of the cPAM is to flocculate fine particles – including filler particles, cellulosic fines, emulsified sizing agents, *etc.* – so that they stay with the wet web of paper, rather than leaving with the filtrate or “white water” as the paper is being formed (Hubbe *et al.* 2009). As a result of cPAM addition, the fines either stay attached to fibers or become agglomerated together. Though the cPAM also forms bridging

attachments between the fibers, tending to form fiber flocs, the system can be optimized so that such flocs are sufficiently redispersed by hydrodynamic shear before the sheet is formed (Hubbe 2007c).

The efficacy of a cPAM molecule may be at least partly destroyed before it can perform its intended function in a paper machine system that contains an excess of anionic DCS. There are many reports documenting such adverse effects (Auhorn and Melzer 1979; Pelton *et al.* 1980a; Ström *et al.* 1982; Alince 1987; Nurmi and Eklund 2000; Reid and Ricard 2000; Polverari *et al.* 2001; Zhang *et al.* 2007; Ordonez *et al.* 2009; Ni *et al.* 2011; Pruszynski *et al.* 2011). The decrease in effectiveness of cationic retention aids in such situations has been attributed to formation of polyelectrolyte complexes between cPAM and DCS (Mikkonen and Eklund 1998; Nurmi *et al.* 2004).

#### *Adverse effects on performance of wet-end additives*

Anything that reduces retention efficiency on a paper machine will also tend to increase the cost of chemicals. In the first place, it may be necessary either to use a higher dosage of the retention aid polymer, or alternatively the dosage of high-charge cationic additives (scavengers, fixatives, or “anionic trash” catchers) may need to be increased (Glittenberg *et al.* 1994). As noted by Mikkonen and Eklund (1998), if the retention aid polymers interact with dissolved and colloidal anionic substances, then they will not be able to adsorb effectively onto the suspended solids and they will not be effective for retention. In addition, one needs to bear in mind that a relatively large proportion of the functional additives such as sizing agents and strength-enhancing polymers can be expected to be adsorbed on the surfaces of cellulosic fines and filler particles (Marton 1980a,b; 1991). An effective retention aid system therefore can be critical to the performance of other wet-end additives. An unbalanced charge in the wet end also tends to be associated with an accumulation of unretained pitch and other colloidal matter in the process water. Greater deposition of colloidal matter onto the wetted surfaces of the paper machine can take place, especially if the colloidal matter remains within the stock system for an extended time before it is retained (Allen 1980; Petander *et al.* 1998; Hubbe *et al.* 2006). Adverse effects of DCS on sizing, wet-strength treatments, and other paper properties have been reported (Auhorn and Melzer 1979; Sjöström *et al.* 2006; Ni *et al.* 2011).

#### **Rates of Water Removal**

High levels of DCS in paper machine systems also have been found to adversely affect rates of dewatering in the forming zones of paper machines. Such effects have been widely reported (Auhorn and Melzer 1979; Ström *et al.* 1979; Linhart *et al.* 1987; Bobu *et al.* 1999; Polverari *et al.* 2001; Dunham *et al.* 2002; Pruszynski and Jakubowski 2002, 2006; Kokko *et al.* 2004; Miao *et al.* 2006; Pruszynski *et al.* 2011). The effect sometimes has been attributed to adverse effects of DCS on the performance of chemicals used to promote dewatering (Ström *et al.* 1982; Maltesh and Shing 1998).

#### *Fines clogging drainage passages in the wet web of paper*

The mechanism by which DCS tends to inhibit dewatering of papermaking stock appears to be at least partly related to the effects of high levels of cellulosic fines. Studies have shown that drainage tends to become slower with an increasing level of such

finer (Przybysz and Szwarcsztajn 1973; Gess 1991; Liu *et al.* 2001; Hubbe 2002; Cole *et al.* 2008; Hubbe *et al.* 2008; Chen *et al.* 2009). The inhibition of dewatering is seen most strongly when the basis weight of the paper being formed is relatively high (Gess 1991). The effect is often attributed to the relatively high hydrodynamic surface area of fines compared to their mass (Carman 1937; Ingmanson 1952; Marton 1980a,b; Hubbe and Heitmann 2007). In addition, it appears that during the formation of a sheet of paper, unattached fine particles are able to move relative to the fibers in the mat and plug up channels through which water might have passed (Hubbe *et al.* 2009). Studies have shown that such effects can be overcome, at least in part, by retention aid strategies that hold fine particles to fibers in the furnish or which agglomerate the fine particles together. Either of these actions of retention aids will tend to reduce the adverse effect of fines on dewatering and also help to retain the fines in the web of paper (Hubbe *et al.* 2008).

The reason that DCS and cellulosic fines can have similar effects on dewatering may be a consequence of interactions of DCS with various coagulants and flocculating chemicals in the system; a negative effect on dewatering can be expected when the DCS is precipitated in such a way as to form particles having a size range that tends to plug up the drainage channels within a wet web of paper (Ström *et al.* 1979, 1982; Linhart *et al.* 1987). The effect is compounded if some of the fine material is enriched through multiple passes of the white water through the forming zone (Bobu *et al.* 1999). Studies have shown, on the other hand, that precipitation of DCS into relatively large-sized particles can lead to faster dewatering (Auhorn and Melzer 1979; Dunham *et al.* 2002).

#### *Drainage consequences of the chemical nature of fines*

In addition to their relatively high effective surface area per unit mass, cellulosic fines in papermaking systems often have distinctly different composition than the fiber portion of the stock. For instance Koljonen *et al.* (2001) found that fines in mechanical pulp tended to have a higher proportion of lignin at their surfaces in comparison with the fibers. Mosbye and Moe (2002) found that the fines fraction had a higher proportion of negatively charged ionic groups at their surface, compared to the other particle size fractions. However, Sundberg *et al.* (2003) showed that the composition was not uniform when considering different types of fines present in the same freshly prepared mechanical pulp. The pulp was fractionated into microfines, fibrils, flakes, ray cells, and fibers. The flakes were identified as coming mainly from the middle lamella, whereas the fibrillar fines mainly could be attributed to the primary cell wall and the outer portions of the secondary wall. These origins were consistent with the higher lignin content of the flakes and the higher cellulose content of the fibrils. High levels of arabinogalactans, xylans, and pectins were found in the flakes and ray cells. The fibrils contained high proportions of arabinogalactans and pectins. The pectins can be a source of cationic demand if the furnish is subjected to alkaline treatment, causing demethylation of the pectins.

#### **Deposit Control and Runnability Issues**

Dissolved and colloidal substances also have been reported to be a root cause of paper machine runnability problems, including deposit formation on wetted surfaces, filling of the void spaces in press felts, showing up as spots in the product, and often causing the paper web to break. The wood pitch component of DCS is of particular concern with respect to deposits and related runnability problems (Nurmi and Eklund

2000; Strand *et al.* 2011; Prinsen *et al.* 2012). Such situations are complicated by the fact that pitch particles can be stabilized in suspension by hemicelluloses, especially mannans, or pectic acids (Holmbom and Sundberg 2003; Saarimaa *et al.* 2006b). Reducing the pH of kraft pulp after brownstock washing tends to precipitate both extractives (*i.e.* wood pitch) and lignin degradation products (Koljonen *et al.* 2004), though much of the dispersed lignin tends to precipitate right back onto the fibers. Similarly, any reduction in pH tends to destabilize pitch particles that are likely to be suspended in mechanical pulp furnishes (Lehmonen *et al.* 2009).

Another class of depositable materials to be concerned with are the polyelectrolyte complexes that form between high-charge cationic polymers and DCS components. For instance Kekkonen *et al.* (2002) traced certain deposit problems to precipitation of complexes that had been formed between poly-DADMAC and pectic acids. Such deposition was promoted by the presence of calcium ions. Vanerek and van de Ven (2006) likewise showed that interaction between cationic polyacrylamide (*i.e.* a retention aid polymer) and sulfonated kraft lignin yielded coacervate complexes, the properties of which depended strongly on the mixing ratios and other experimental conditions.

### Some Strategies for Dealing with DCS

Though the ultimate goal in this review article is to consider different components of dissolved and colloidal substances in paper machine systems, it is important first to consider what might be regarded as “conventional” approaches that have been used to mitigate the effects of DCS. The subject has been discussed from various perspectives in earlier review articles (Auhorn and Melzer 1979; Linhart *et al.* 1987; Medvecz 1993; Sundberg *et al.* 1993; Gratton and Pruszyński 1995; Leiviskä and Rämö 2008).

#### *Enrichment of non-retained substances; mill water circuit closure*

The presence of extensive and multiple recirculation loops for process water within a typical paper machine system can have a profound impact on the amounts of DCS present, as well as on measures that may be taken to control DCS. Because the DCS materials tend to remain suspended, rather than being efficiently retained in the paper web, they tend to build up in the whitewater system. An article by Orcotoma *et al.* (1999) gives an example that demonstrates how the ratio of fine matter to fibers, on a solids basis, can be many times higher in the thin stock of a paper machine in comparison to the same ratio in the incoming stock or in the product. Many studies have documented the enrichment of DCS in paper machine systems (Lüttgen and Götsching 1979; Bourgogne *et al.* 2001; Bräuer *et al.* 2001; Lehmonen *et al.* 2009; Miranda *et al.* 2009a). Bobu *et al.* (1999) re-created the enrichment effect in the laboratory by multiple recirculation of filtrate back to a laboratory drainage test device. Bourgogne *et al.* (2001) reviewed what can happen in extreme cases in which papermakers choose to use so little fresh water that a paper machine system can be called “fully closed”. In other words, in ideal cases there is no liquid effluent water leaving the paper machine system. The levels of various salt ions and organic materials dissolved or suspended in the process waters from such mills have been reported (Pietschker 1996).

The fact that DCS tends to be enriched within the forming zone of a paper machine has some important implications regarding the implementation of various kinds

of control measures. When considering possible addition of a charge-control agent, it may be misleading to base one's estimates of the required dosages of various treatment chemicals on the level of DCS that happens to be present with fibers within the primary recirculation of a paper machine. Rather, it makes sense that, at steady state, the addition level of a control chemical should ultimately be in line with the amount of DCS present with the pulp slurry that is being delivered to the paper machine system within a specified time period.

#### *The usage of "scavenger" additives*

The word "scavenger" is sometimes used to denote various high-charge cationic polyelectrolytes, as well as soluble aluminum-based products, that can be used to neutralize excess negative colloidal charges in paper machine systems. Other common terms include "anionic trash collectors," "fixatives," and "sacrificial" additives. The idea is to neutralize DCS by using something relatively inexpensive, on a mass basis. Benefits to the performance of retention aids following the use of scavengers to at least partly neutralize the DCS have been reported (Auhorn and Melzer 1979; Chung *et al.* 1993; Glittenberg *et al.* 1994; Näsman *et al.* 1998; Zhang *et al.* 2007, 2009; Liu *et al.* 2010; Ni *et al.* 2011). Similarly, significant improvements in drainage rates (Auhorn and Melzer 1979; Linhart *et al.* 1987; Miao *et al.* 2006; Liu *et al.* 2010), and sizing performance (Li *et al.* 2002b; Hu *et al.* 2004; Chen *et al.* 2012a,b) have been reported following the use of high-charge cationic additives. Furthermore, scavenger chemicals have been shown to be effective in destabilizing at least part of the DCS so that it can be retained in the paper web (Wågberg and Ödberg 1991; Neimo 1993; Sundberg *et al.* 1993, 1994a; Kunzel and Prinz 2006; Belosinschi and Bobu 2008).

A study by Tijero *et al.* (2012) showed that talc, a hydrophobic, platy mineral product, can be used to remove at least some of the colloiddally charged material from the papermaking process water. The mechanism by which this happens involves deposition of such whitewater components as wood pitch onto the talc surfaces. Due to their platy shape and larger size (*e.g.* several  $\mu\text{m}$ ), the pitch particles are more readily retained during the paper forming process. As the white water passes multiple times through the forming zone, the concentration of pitch-like materials in the water becomes reduced. Tijero *et al.* (2012) observed a 25% to 50% drop in the cationic demand of process water during different paper machine trials in which talc treatment of the furnish was compared to a control condition with no talc addition.

#### *Better washing of the incoming pulp*

Since scavenger chemicals cost money and also due to the possibility that precipitation of DCS may result in deposits, reduced paper brightness, or other problems, it makes sense to consider ways to remove DCS before it enters the papermaking process. It has been suggested that "improved washing" is one of the most important strategies that can be employed (Sundberg *et al.* 1993; Bräuer *et al.* 2001). The lack of a washing stage following the peroxide bleaching of mechanical fibers in many paper machines systems has been blamed for many problems related to DCS (Thornton 1994). However, before implementing such a strategy, one would need to consider the capacity of the wastewater treatment system, as well as the increased costs of water-treating additives in order to accommodate the filtrate from washing. The use of press filters between the

peroxide bleaching stage and the papermachine can keep most of the DCS on the pulp mill side and thus facilitate a cleaner white water system at the paper machine. Another important issue that needs to be considered is what substances are removed in the press. Usually the hydrophilic, dissolved substances are the easiest to remove in a press, *i.e.* hemicelluloses and pectins and other low-molecular-mass substances, while the hydrophobic, colloidal substances are more prone to be retained in the pulp, *i.e.* wood pitch. As dissolved hemicelluloses, which stabilizes wood pitch, tend to be removed to a higher degree than the more detrimental pitch, washing may in some cases even cause a more problematic situation at the paper machine. The conditions used during washing, especially the pH, are very important.

## COMPONENTS OF DISSOLVED AND COLLOIDAL SUBSTANCES

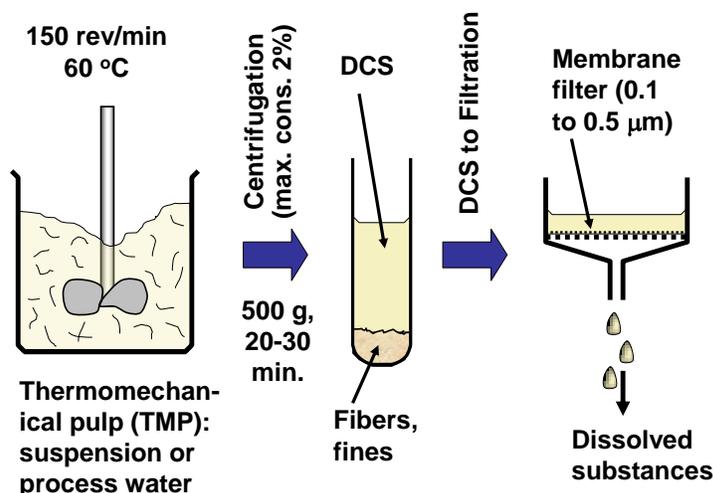
Different components of DCS are found in paper machine process waters, either dissolved in the water or dispersed as colloidal particles. The dissolved substances typically consist of ions and molecules having dimensions less than 0.1  $\mu\text{m}$ , *e.g.* soluble polyelectrolytes such as hemicelluloses, pectins, and lignin fragments. The colloidal substances consist of dispersed particles about 0.1 to 1  $\mu\text{m}$ , *e.g.* wood pitch, latex (from coated broke), and microfines. Though the strategies of scavenger use and improvements in pulp washing have served the paper industry well in many instances, some writers have suggested that more effective control of DCS might be achieved by focusing attention on its different components (Linhart *et al.* 1987; Sjöström *et al.* 2006; Ni *et al.* 2011). For instance, if enzymatic approaches are under consideration, then it is clear that different kinds of enzymes will be needed to break down or modify different components of the DCS (Thornton 1994; Lindberg *et al.* 2001; Zhang *et al.* 2002). Therefore, this section will consider some of the major DCS components that have been described.

The amount of DCS is usually measured without adjusting the pH, by titrating to find the cationic demand of the dissolved and colloidal substances (DCS). The negative charges of DCS generally originate from the dissociation of the carboxylic groups of pectic acids, oxidized lignin, resin acids, and fatty acids. Contributions to titratable charge can be differentiated into two classes by determining the cationic demand of DCS at both pH 4.5 and pH 7.0 due to the difference of  $\text{pK}_a$  of their carboxylic groups (He *et al.* 2004). At pH 4.5, only the uronic type of carboxylic groups in anionic hemicelluloses, such as polygalacturonic acid, can effectively dissociate into anionic groups. By contrast at pH 7.0, all the four types of carboxylic groups (uronic acids, lignin carboxylic species, resin acids, and fatty acids) can dissociate into anionic groups. Therefore, the cationic demand determined at pH 4.5 is mainly due to anionic hemicelluloses. The difference of the cationic demand between pH 7.0 and pH 4.5 can be attributed to oxidized lignin and resin and fatty acids.

### Fractionation Schemes for Analysis of DCS

One of the first steps to consider, with respect to identifying the components of DCS in different paper machine systems, involves the option of fractionating the sample. Several fractionation schemes have been proposed (Örså and Holmbom 1994; Neto *et al.* 1999; Holmbom and Sundberg 2003; Pranovich *et al.* 2005; Toledano *et al.*

2010). Centrifugation is a very reliable method to separate DCS from a fiber suspension (Örså and Holmbom 1994; Holmbom and Sundberg 2003; Sundberg *et al.* 2000a) (see Fig. 4). This approach avoids the formation of a fiber mat during filtration that would change the pore size. The consistency of the fiber suspension should not exceed 2%, and the suspension should not be allowed to cool down before centrifugation in order to avoid sorption. The dissolved fraction can then be separated from the DCS by filtration in small portions on a membrane filter having a 0.1 to 0.5  $\mu\text{m}$  pore size.



**Fig. 4.** Separation of DCS and DS (dissolved substances) from a fiber suspension

After separation, the different components of the DCS can be analysed. For instance, Holmbom and Sundberg (2003) determined the amount of hemicelluloses and pectins, wood pitch components, lignans, and lignin fragments by gas chromatographic methods and UV measurements. Differences in solubility of various components of DCS can also be used as a promising means of fractionation. Thus, Neto *et al.* (1999) were able to identify more than 60 compounds in samples of black liquor from kraft pulping by a comprehensive fractional solubilization scheme employing ether and water. Since the solubility of lignin components in water tends to drop with decreasing pH, stagewise reduction of pH can be used as an effective means of fractionation of such compounds (Toledano *et al.* 2010). Nuopponen *et al.* (2004) used UV resonance Raman spectroscopy to identify unsaturated components in extractives.

Chromatographic separations can be used effectively in order to facilitate more detailed analysis of the complex mixtures of species likely to be found in a paper mill system. Bikova *et al.* (2000) employed high performance size-exclusion chromatography (HPSEC) to separate different hemicelluloses and different lignin components, making it possible to obtain information about the molecular mass of the separated species. Likewise, Valto *et al.* (2011) used high performance liquid chromatography (HPLC) to fractionate the extractives obtained from papermaking process waters, allowing definitive analysis of their chemical composition. Duarte *et al.* (2003), Yuan *et al.* (2009), and Toledano *et al.* (2010) employed ultrafiltration to separate lignin-related fractions from the effluent from bleached kraft pulp mills.

For completeness it should be mentioned that there are alternative approaches involving multivariate analysis of mixtures. The idea is that, instead of fractionating the sample, one instead employs computer power to interpret complex mixtures. Louhelainen and Alén (2009) demonstrated such an approach for FTIR analysis of black liquor composition.

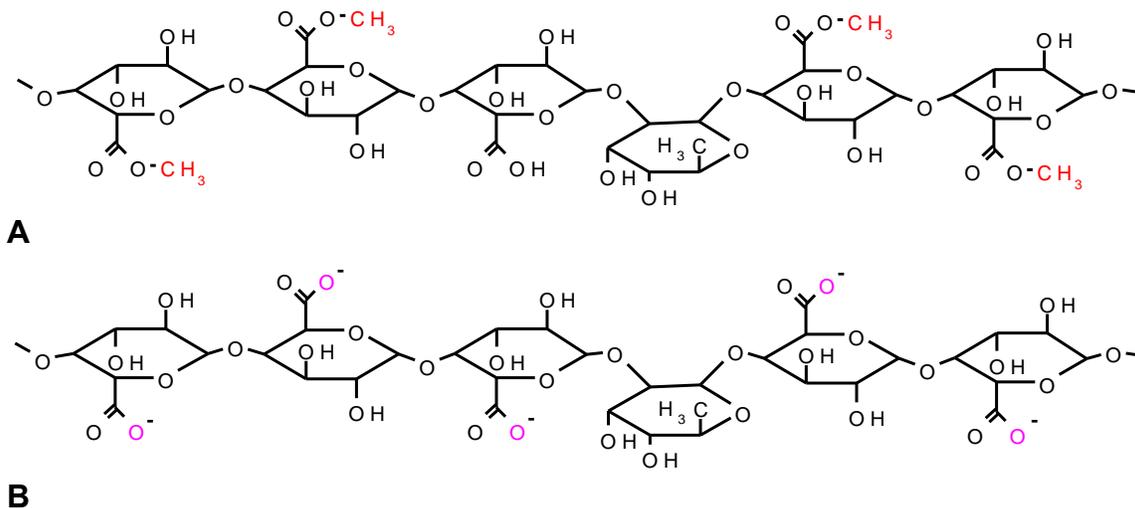
### Dissolved Hemicelluloses and Pectins

The major components of DCS are usually hemicelluloses and pectins, especially in the case of mechanical pulps. Wågberg and Ödberg (1991) analyzed DCS obtained from thermomechanical pulp and found that 60% of it was hemicelluloses and pectins, which also can be called polysaccharides or carbohydrates, whereas just 30% of it appeared to be lignin-derived, and about 10% consisted of extractives. The main contributors to the cationic demand in unbleached mechanical pulp suspensions are the arabinogalactans, which are very water-soluble and contain glucuronic acid units (Thornton *et al.* 1994a, Willför *et al.* 2002). The arabinogalactans are present especially in the heartwood of spruce and pine. Heartwood of larch species contains extra-ordinarily high amounts of arabinogalactans, typically 15 to 20%. In the case of peroxide-bleached spruce thermomechanical pulp (TMP), He *et al.* (2004) estimated that 45% of the cationic demand was associated with lignin byproducts, 40% with uronic acids (from the carbohydrates), and 15% from fatty and resin acids. It should be noted that not all of the hemicelluloses are anionic.

In particular, many authors have written about the nature and effects of hemicellulose decomposition products resulting from alkaline peroxide bleaching of mechanical pulps (Thornton *et al.* 1993; Sundberg *et al.* 1994a; 1998; 2000a,b; He *et al.* 2004; Hafrén and Daniel 2005; Saarimaa and Pranovich 2007). In addition, hemicellulose-related DCS has been characterized in bleached kraft pulps (Bhardwaj *et al.* 2006). In the case of softwood mechanical pulp, polygalacturonic acids or pectic acids contribute to a large proportion of the cationic demand (Thornton *et al.* 1993; Sundberg *et al.* 1998; Mosbye and Moe 2002). Figure 5 shows a typical structure of pectins and pectic acids. Though this component comprised about 5% of the dry mass of the DCS (Sundberg *et al.* 1994a), it accounted for about 40% of the total cationic demand in the system (Sundberg *et al.* 2000a; Pranovich *et al.* 2003).

The reason that peroxide bleaching of mechanical pulp furnish can more than double the cationic demand of both the DCS and the fibers has been traced to de-esterification or demethylation of the pectin fraction (Sundberg *et al.* 2000a; Hafrén and Daniel 2005). Peroxide bleaching further induces a cleavage of the pectin chain so that more pectins are released from the fibers to the water phase. It has been shown that the alkaline condition during peroxide bleaching is the main reason for these reactions (Örså *et al.* 1997; Sundberg *et al.* 2000a; Pranovich *et al.* 2003). He *et al.* (2004) showed that the increase in cationic demand is a rapid reaction, with most of the charge increase occurring early in the bleaching process. Interestingly, it was possible to suppress most of the increase in cationic demand by using a modified bleaching procedure in which the pulps was first treated with NaOH, Epsom salt, and sodium silicate for a few minutes before the addition of hydrogen peroxide. The likely mechanism is that in the modified peroxide bleaching process (the P<sub>M</sub> process) the *in situ* formation of peracetic acid is

prevented due to the removal of the acetyl groups from hemicellulose in the alkaline pre-treatment step, prior to hydrogen peroxide addition.



**Fig. 5.** Partial structures of wood pectins. A: Pectins naturally occurring in wood where the carboxylic group is methylated, B: Pectins after alkaline treatments or alkaline peroxide bleaching, with demethylated anionic galacturonic acid units.

In the conventional peroxide bleaching process, peracetic acid is formed rapidly after the alkaline hydrogen peroxide liquor is mixed with pulp, due to the reaction of hydroperoxyl anions with the acetyl groups on hemicellulose. Since peracetic acid is a much stronger oxidant than hydrogen peroxide, its formation in the peroxide bleaching process will lead to more oxidation reactions to form more carboxylic groups, which contribute to the increase in the cationic demand. Addition of calcium may also decrease the release of pectic acids (Saarimaa and Pranovich 2007). Recently it was found that treatment with alkali at a low temperature prior to the actual peroxide bleaching decreases the release of pectins from mechanical pulps (Pranovich *et al.* 2009). When adding alkali at a low temperature in a first stage, the pectins will be demethylated fast, and thereafter the alkali-induced depolymerization of pectins leading to pectin dissolution is suppressed in the peroxide stage. This results in much less DCS in the process waters and also preserves about 2% ISO brightness.

The cationic demand contribution of the hemicellulose-related fraction of DCS appears to be highly dependent on molecular mass. Jacobs and Dahlman (2001) employed size-exclusion chromatography and a mass spectroscopic method to characterize the molecular masses of different hemicellulose samples. Hemicellulose samples obtained from mechanical pulp were found to have higher mass than those obtained from kraft pulp samples. Sjöström *et al.* (2006) compared different process water samples and found that the most “problematic” samples, in terms of high cationic demand and associated problems, happened to be those in which the molecular mass of hemicellulose products was relatively high. Jansson and Brännvall (2011) found that the molecular mass of dissolved xylans from kraft cooking of spruce was in the range of 6000 to 11,000 g/mole. Lisboa *et al.* (2005) and Magaton *et al.* (2011) reported molecular masses in the range of 15,000 to 19,000 g/mole for xylans released during kraft pulping

of *Eucalyptus* species. Jacobs and Dahlman (2001) showed that various pulping processes tend to lower the molecular mass of hemicelluloses originally present in the wood.

Some of the strongest evidence supporting the molecular mass dependency of cationic demand related to hemicellulosic materials comes from studies in which enzymes were used to cleave the macromolecules (Thornton *et al.* 1993; Sundberg *et al.* 1993; Mou *et al.* 2008; Zhang *et al.* 2008; Liu *et al.* 2010). The cited studies show that the cationic demand contribution can fall dramatically as a result of the enzymatic treatment. The enzymatic treatment has the effect of reducing the molecular mass of galacturonic acid oligomers. Thornton (1994) found that a degree of polymerization (DP) of 6 or greater was needed before such oligomers made a substantial contribution to charge demand.

A process that tends to complicate consideration of released hemicellulose components involves the tendency of at least some of them to become redeposited onto the fibers (Johnsen and Stenius 2007; Ribe *et al.* 2010). Such redeposition appears to be favored by decreasing pH and increasing ionic strength. Johnsen and Stenius (2007) reported that hemicelluloses have a greater tendency to reprecipitate onto cellulose-rich fibrils, rather than onto lignin rich flake-like fines; this tendency is presumably due to chemical similarity. Galactoglucomannans (GGMs), both in native acetylated form and in deacetylated form, are sorbed strongly and irreversibly to both unbleached and bleached chemical pulp fibers, such as in the mixing chest where mechanical and chemical pulps are mixed (Hannuksela *et al.* 2002, 2003). Neither TMP nor CTMP from spruce sorb any acetylated galactoglucomannans. The sorption of mannans is only little affected by external conditions such as temperature, pH, and salt addition (Hannuksela 2002).

#### *Hemicellulose byproducts in other pulp types*

Since kraft pulping is carried out under highly alkaline conditions and high temperature, it is not surprising that substantial amounts of hemicelluloses and pectins are degraded in the process and removed by washing (Feng *et al.* 2001; Vu *et al.* 2003). Furthermore, kraft pulping conditions are sufficiently intense that much of the released hemicelluloses and pectins may be broken down into monomeric species (Vu *et al.* 2003; Rautianen and Alén 2010). Hemicelluloses and pectins also tend to get released during bleaching of kraft pulps (Ristolainen and Alén 1998; Kukkola *et al.* 2011). Work reported by Silvestre *et al.* (2000) and Feng *et al.* 2002; showed that although there are many carboxylated species present among the carbohydrate byproducts in black liquor samples, most such species are monomeric, and only a few have as many as two carboxyl groups per molecules; thus, such species would not be expected to contribute significantly to cationic demand. Hemicellulose components contributing to DCS are also released from recycled pulp fibers (Johnsen *et al.* 2004). In the cited study, xylans and pectic acids were the main components found to be contributing to cationic demand.

#### *Silicates*

Because papermakers often add silicates to mechanical pulp furnish to improve the effectiveness of peroxide bleaching, it is worth noting here that silicates also can contribute to cationic demand (Saastamoinen *et al.* 1996; Larnicol *et al.* 2001). Saastamoinen *et al.* (1996) showed that both the colloidal and soluble oligomeric portions of silicates can exhibit substantial cationic demand.

### Lignin-Related Contributors to Cationic Demand

Though lignin byproducts can contribute a great deal to the cationic demand in certain types of pulp, the relationships between solubilized lignin and cationic demand clearly require further study. According to Sjöström (1989), native lignin in wood does not have a significant amount of carboxylic acid groups and essentially no sulfur-related acidic groups; it follows that lignin's possible contribution to cationic demand in papermaking situations would have to be a consequence of changes during pulping or bleaching.

Several authors have reported the presence of substantial amounts of lignin-related materials colloidally dispersed or dissolved in paper machine process waters (Örså *et al.* 1997; Pranovich *et al.* 2005; Li *et al.* 2008). In the case of lignin released during peroxide bleaching of spruce thermomechanical pulp, the mean molecular mass of the released material was 1770 g/mole, but none of the identified lignin-related compounds contained carboxylic acids (Pranovich *et al.* 2005).

In the case of kraft pulps, though lignin is clearly released from the fiber (Alber *et al.* 1998; Bikova *et al.* 2000; Duarte *et al.* 2003; Rautiainen and Alén 2010), the relationship of such lignin to cationic demand is not well known. Alber *et al.* 1998 found that a totally chlorine free (TCF) bleaching cycle was particularly prone to releasing a lot of lignin into the water phase. Much of the lignin that is released from fibers during kraft pulping would tend to be removed from the pulp during brown-stock washing (Lappan *et al.* 1996; Pacheco *et al.* 2006; Lind 2011). In addition, studies have shown that released lignin has a great tendency to deposit back onto fibers surfaces, especially if the pH is adjusted from an initial high value (> 10) to a range suitable for papermaking (Alber *et al.* 1998; Koljonen *et al.* 2004). As shown by Alén and Vikkula (1989) and Rautiainen and Alén (2010), the most prominent lignin-derived species in black liquor tend to be uncharged or have just one carboxylate group and of very low mass, thus not likely to be important contributors to cationic demand. Detailed structural analyses of dissolved pine and eucalyptus kraft lignins revealed the presence of several carboxylated species (Neto *et al.* 1999; Silvestre *et al.* 2000; Balakshin *et al.* 2003), but there has been no demonstration as to whether such species contribute significantly to cationic demand. Structures of the alpha-hydroxyacid type or "aliphatic acid" types were reported to be important degradation products, but there was no test to find out whether these species had sufficient molecular mass and charge density to form a complex with a cationic polyelectrolyte.

Duarte *et al.* (2003), Tolenado *et al.* (2010), and Jansson and Brännvall (2011) found that much of the lignin content present in the black liquor from the kraft cooking of spruce was bound to xylan moieties. In particular, lignin-derived species of higher molecular mass tended to be more associated with carbohydrate structures, *i.e.* hemicellulose-related oligomers. Yuan *et al.* (2009) found that lignin fractions having higher amounts of associated polysaccharides (and hence a greater likelihood of contributing to cationic demand) could be obtained by solubilization in organic solvents having higher Hildebrand parameters, which often implies a greater hydrophilic character. Such hydrophilic moieties bound to the lignin may at least partly explain observations that kraft lignin from black liquor can exist as colloidally stable particles in aqueous suspension (Nyman and Rose 1986; Zhang 2000). Thus, it may be the carboxyl

groups on polysaccharides associated with colloidal lignin particles, rather than the lignin itself, that has potential to contribute significantly to cationic demand.

Some limited work has been carried out to demonstrate the negative colloidal charge of isolated kraft lignins. Thus, Rowan and Scott (1992) titrated kraft lignin suspensions with cationic polyelectrolyte, demonstrating its negatively charged character. Sjöholm *et al.* (2000) measured the electrophoretic mobility of lignin particles that had been precipitated from black liquor by reduction of pH, and they found a broad distribution of negative zeta potential. Further evidence of the negative character of lignin particles consists of the ability to precipitate such material from aqueous suspension by use of cationic polyelectrolytes (Belosinschi and Bobu 2008). To explain their data, especially the fact that the lignin particles remained negative in charge when the pH was reduced far below 10, it was proposed that lignin can be associated with polysaccharide species in the black liquor. Carboxylated species related to lignin were found to have a mean molecular mass of *ca.* 800 g/mole. To put this into perspective, the authors stated that the amount of carboxyl groups was low relative to the phenolic group content of the lignin. Phenolic groups are not expected to contribute to cationic demand in papermaking applications, since the  $pK_a$  of such groups is about 10, well above the pH range used in paper formation.

Kukkola *et al.* (2011) considered the release of lignin-related materials from softwood kraft pulps subjected to various different bleaching sequences. It was found that the highest molecular mass material tended to be solubilized by peroxide and chelating stages, whereas the lowest molecular mass materials were solubilized in the presence of strong oxidants such as chlorine dioxide and ozone. Ristolainen and Alén (1998) found that carboxylated species in solution after TCF bleaching of pine kraft pulp were low molecular mass compounds such as formic, acetic, glyconic, and 3-hydroxypropanoic acids. In another study these authors determined lignin species in TCF effluents to have molecular masses within the range of 700 to 5350 g/mole, depending on the bleaching stage (Ristolainen *et al.* 1996).

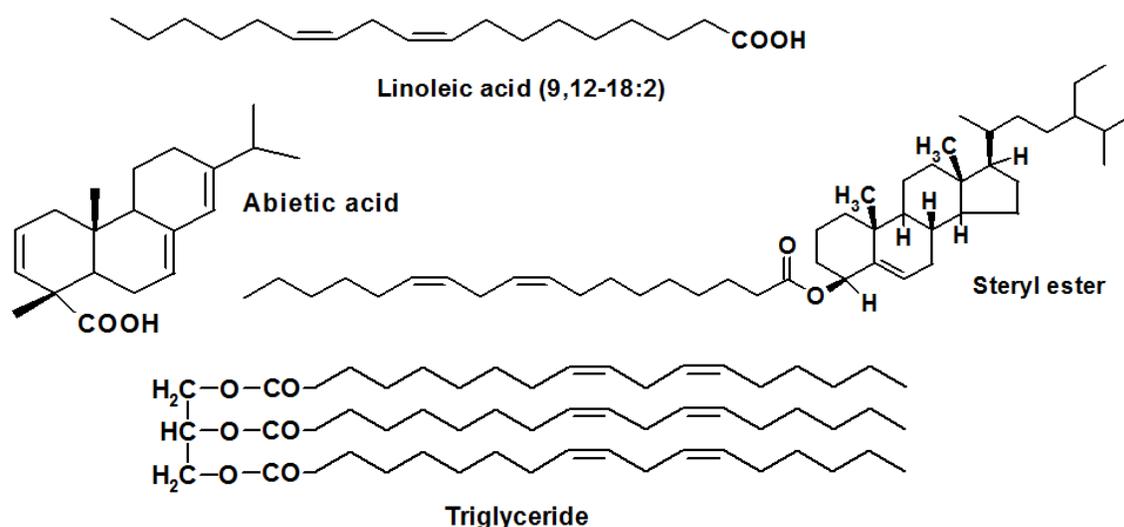
Sulfonated lignin species have been found to interact strongly with cationic polyelectrolytes. This tendency has been noted especially in the case of high molecular mass lignosulphonates resulting from sulfite pulping. Willis *et al.* (1987) reported molecular mass values for lignosulfonates in the range 11,000 to 61,000 g/mole. Vanerek and van de Ven (2006) found that such complexation led to coacervate formation, *i.e.* phase separation between polyelectrolyte-rich and poor phases. The interaction between the lignin species and cationic polyelectrolytes followed a stoichiometric relationship. Higher-mass cationic PAM showed increased ability to interact with the lignin in aqueous suspension.

Pranovich *et al.* (2003) and He *et al.* (2004) reported a substantial contribution to cationic demand due to the presence of oxidized, solubilized lignin species, following peroxide bleaching of spruce TMP. Pranovich *et al.* (2005) also found that the lignin released from TMP fibers after peroxide bleaching is extensively oxidized and has a slightly higher average molecular mass than lignin released from unbleached TMP. In peroxide bleaching of mechanical pulp, lignin oxidation occurs, which removes chromophores from lignin structures, and as a result increases the pulp brightness. These oxidation reactions lead to formation of carboxylic groups in lignin. An example of lignin oxidation is the formation of muconic acid structures in lignin with two carboxylic

groups that can be dissolved from fibers into the water phase as DCS. The phenolic group of lignin has a  $pK_a$  of about 10, and therefore its contribution to cationic demand is small in an acidic to neutral pH range. On the other hand, the carboxylic groups of oxidized lignin have a  $pK_a$  of about 4 to 5, so that they can be dissociated into anionic groups at neutral pH.

### Extractives-Related Contributors to Cationic Demand

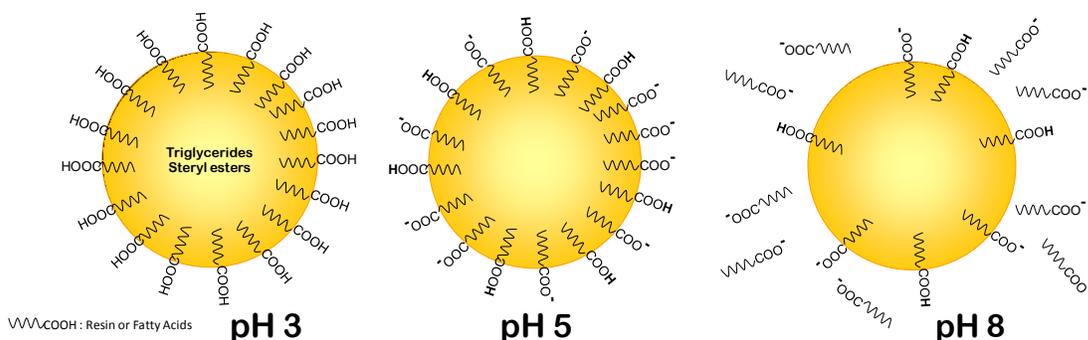
Though the component of wood known as “extractives” makes up only about 1 to 5% of the wood’s dry mass, depending on the species (Back and Allen 2000; Freire *et al.* 2006), such materials can have a large impact on the papermaking process and the quality of the product. The extractives in wood mainly comprise esters of fatty acids, free (non-esterified) fatty acids, resin acids (found only in softwood species), and unsaponifiable hydrophobic compounds such as  $\beta$ -sitosterol (Örså *et al.* 1997). Examples are shown in Fig. 6.



**Fig. 6.** Examples of extractive components in wood – fatty acids represented by linoleic acid, resin acids represented by abietic acid, and the esterified compounds steryl esters and triglycerides

The hydrophobic components of the lipophilic extractives will form colloidal droplets in the process waters, with a size in the range 0.1 to 2  $\mu\text{m}$  (average about 0.5  $\mu\text{m}$ ). The core of the droplets consists of the most hydrophobic components, which are the esterified triglycerides and the steryl esters. The resin and the fatty acids contain a lipophilic part (the hydrocarbon chain) and a hydrophilic part (the carboxylic group). These will be concentrated at the surface of the droplets with the lipophilic part generally oriented towards the centre of the droplets and the carboxylic groups towards the water phase (Fig. 7). The carboxylic groups are in protonated form at low pH, which means that the droplets are uncharged at pH below 3 (Nylund *et al.* 2007). At increasing pH, the carboxylic groups are increasingly dissociated, and the colloidal droplets are anionically charged. When further increasing the pH, some of the resin and fatty acids are released from the colloidal droplets and are dissolved in the water phase (Sundberg *et al.* 2010;

Strand *et al.* 2011). This especially will affect washing and filtration processes. The resin and fatty acids (free or associated with the colloidal droplets) will interact with divalent ions, especially calcium (Back and Allen 2000). The dissolved fatty and resin acids can also form micelles if their concentration is high enough.



**Fig. 7.** The different extractive components form colloidal droplets. The resin and fatty acids at the surface will dissociate and also be released from the colloidal droplets, depending on pH.

Substantial amounts of extractives can be expected to be present in mechanical pulp systems, and also in high-yield kraft pulp waters. According to Sundberg *et al.* (1993) the lipophilic extractives are the main part of the colloidal substances in mechanical pulp suspensions. Their chemical composition, after 3 to 6 h pulp agitation in water at 90 °C and pH 5.1 to 6.3, is similar to that of the extractives in the wood, and the amount of them dispersed in water depends on several factors such as the age of the wood raw material, the pH, and the amount of added electrolyte (Örså *et al.* 1997). Alkaline peroxide bleaching significantly increases the DCS of the pulp suspension (Thornton *et al.* 1993), but it is principally due to the release of hemicelluloses containing uronic acid units under alkaline conditions (Sundberg *et al.* 1993). The amount of colloidal extractives remains constant, although they can be more oxidized (Sundberg *et al.* 1993).

On the other hand, various analyses of black liquor from kraft pulping have shown the presence of substantial amounts of palmitic acid and related species (McMahon 1980; Neto *et al.* 1999; Silvestre 2000). Freire *et al.* (2006) found that, due to their chemical stability and compatibility with the fibers, long-chain aliphatic acids tended to be retained within the fibers throughout not only the kraft pulping, but also, to a large extent, through the various bleaching stages employed. Fatty and resin acids, including palmitic, stearic, oleic, linoleic, and dehydroabiestic acids, have been found in paper machine process waters (Valto *et al.* 2011).

Numerous authors have reported undesirable effects of extractives on wet-end operations or product quality (Allen 1980; Hassler 1988; Dunlop-Jones and Allen 1989; Otero *et al.* 2000; Sundberg *et al.* 2000b; Blazey *et al.* 2002; Vercoe *et al.* 2005). Observed decreases in paper's dry-strength due to the presence of extractives (Sundberg *et al.* 2000b; Johnsen and Stenius 2007) have been attributed to interruption of hydrogen bonding opportunities between adjacent fiber surfaces. In other words, the particles, films, or aggregates of lipophilic matter at the fiber surface get in the way of hydrogen bonding.

Contributions of extractive materials to cationic demand also have been documented (He *et al.* 2004). The previous subsection, concerning lignin, mentioned that

a single carboxyl group on an organic compound is usually insufficient to give rise to significant cationic demand effects. However, an important point to keep in mind regarding the extractives in paper machine systems is that the amphiphilic nature of some of the molecules, each having both a water-loving and an oil-loving end, favors the formation of stabilized colloids such as pitch emulsion droplets in aqueous systems. Recalling the images in Fig. 7, the hydrophilic groups at the surface of a pitch emulsion droplet tend to be relatively close together, facing outwards to the bulk aqueous solution. It has been reported that most of the extractives present in process water from a paper machine system can be expected to exist either adsorbed onto colloidal matter or as micelles (Ekman *et al.* 1990; Zhang 2000). In cases where the amphiphilic species are negatively charged, *e.g.* with carboxylate or sulfonate groups, relatively strong interactions with cationic polyelectrolytes have been documented (Dubin and Davis 1985; Leung and Goddard 1985; Naderi *et al.* 2005). Without calling into question the foregoing evidence of cationic demand of various extractive materials, it also has been reported that non-charged, unsaponifiable compounds may make up the majority of extractives from some species, including eucalyptus (Prinsen *et al.* 2012).

The colloidal stability of colloidal wood extractive particles (or “pitch”) has been shown to depend critically on pH and the ratio of free to esterified fatty acids (Blazey *et al.* 2002; Strand *et al.* 2011). Koljonen *et al.* (2004) showed that although a reduction of pH tended to precipitate extractive particles out of suspension, such particles did not adhere tightly to the fibers. Furthermore, pitch particles can be stabilized by the presence of hemicelluloses such as galactoglucomannans (Sundberg *et al.* 1995; Otero *et al.* 2000; Johnsen *et al.* 2004; Strand *et al.* 2011). Galactomannans as well as xylans are also good stabilizers of wood resin emulsions (Hannuksela and Holmbom 2004). On the other hand, pitch particles have an increased tendency to agglomerate and precipitate out of solution in the presence of divalent cations (Sihvonen *et al.* 1998). Finally, and of particular relevance to us here, pitch particles can form colloiddally unstable complexes with cationic retention aid polymers and other cationic additives (Wågberg and Ödberg 1991; Sundberg *et al.* 1993, 1994a; Nylund *et al.* 1995; Nurmi *et al.* 2004; Belosinschi and Bobu 2008; Leiviskä and Rämö 2008; Tanase *et al.* 2010). The molecular mass and charge density of the polyelectrolytes used for flocculation define the mode of interaction with the DCS. Using low dosages of a high charge density poly-DADMAC (Mw 47 kDa), Sundberg *et al.* (1993) showed that the dominating mechanism for destabilization of DCS from TMP suspensions is patch flocculation. On the other hand, when using cationic polyacrylamides (Mv  $5 \times 10^6$  Da) having different charged densities, Nylund *et al.* (1995) showed that the mechanism is bridging flocculation.

### **The Fiber Component and its Contribution to Cationic Demand**

While “fibers” cannot be considered as part of the “dissolved and colloidal” fractions of a pulp furnish, there is no denying that they have the ability to take up cationic polyelectrolytes from solution. This ability has been demonstrated, for instance, by charge-related tests repeated either in the presence or absence of the fiber component (Ström and Stenius 1987). Indeed, in optimizing the usage of various chemical additives during papermaking it is reasonable to consider, for instance, how large is the adsorption capacity of the fibers in comparison to the cationic demand due to DCS and fines. Since adsorption of polyelectrolytes onto fibers is not a main focus of this article, readers who

want additional information are recommended to consult the following sources (van de Steeg *et al.* 1992; van de Ven 2000; Wågberg 2000; Horvath *et al.* 2008).

Cellulosic fiber surfaces typically contribute to the anionic colloidal charge of papermaking systems due to their content of carboxylic acid groups, and in some cases also to the presence of sulfonic acid groups (Sjöström 1989; Zhang *et al.* 1994). The carboxylic acid groups can be quantified by potentiometric or conductometric titrations (Katz *et al.* 1984; Bhardwaj *et al.* 2006; Fardim *et al.* 2002). Fardim *et al.* (2002) showed that similar information could be obtained more conveniently, and with high reliability, by a dye adsorption assay. These types of tests essentially measure the “total charge,” including all carboxyl groups in contact with liquid water. From the standpoint of optimizing papermaking processes, it may be more important to just estimate the net amount of charged groups accessible on the outer surfaces of fibers. Fardim *et al.* (2005) demonstrated precise quantification of anionic charges near to fiber surfaces by use of a two-step analysis. In the first step the cellulosic materials were exposed to an excess of methylene blue, a cationic dye having strong affinity for anionic groups on fiber surfaces. In the second step, the cellulosic materials were dried and then subjected to X-ray photoelectron spectroscopy, a highly surface-specific method.

#### *Fiber mesoporosity and its effects on polyelectrolyte permeation and surface charge*

The effects of very small pores in the cell walls of water-swollen cellulosic fibers, especially in the case of kraft pulp fibers, have become increasingly well known (Stone and Scallan 1968; Li *et al.* 1993; Berthold and Salmén 1997; Alince and van de Ven 1997; Alince 2002; Hubbe 2006; Hubbe *et al.* 2007b). One of the consequences of fibers' mesoporous nature is that low-mass cationic polymers tend to adsorb in greater amounts compared to their higher-mass analogues (Hostetler and Swanson 1974; Lindström and Söremark 1976; Petlicki and van de Ven 1994; Farley 1997; Horvath *et al.* 2008; Taipale *et al.* 2011).

Studies have shown that, following treatment with low levels of cationic polyelectrolyte, the zeta potentials of cellulosic fiber surfaces tend to revert back in the direction of their initial value prior to treatment (Strazdins 1977; Koethe and Scott 1993; Farley 1977; Wang and Hubbe 2002). Effects of time on polyelectrolyte complexation have also been reported (Dautzenberg and Karibyants 1999; Phipps 1999; Naderi *et al.* 2005; Hubbe 2006; Vanerek and van de Ven 2006). In practical terms this means that if one wants to achieve a certain state of cationic demand at the forming zone of a paper machine, then the amount of highly charged additive will have to be increased, in accordance with how far back in the system it has been added to the furnish (Strazdins 1972; Goossens and Luner 1976). Fatehi *et al.* (2011) observed differences in the ability of low-charge and high-charge cationic polyelectrolytes of similar molecular mass and structure. Surprisingly, the low-charge macromolecules showed greater tendency to diffuse into the mesopore structure of the cell walls. The effect was attributed to charge-charge repulsion between already-adsorbed high-charge macromolecules and similar molecules approaching from the solution phase.

### *Surface charge*

A number of authors have compared adsorption capacities of highly cationic polyelectrolytes of very high vs. very low molecular mass to estimate the ratio of surface carboxyl groups to total carboxyl groups in typical pulp samples. In particular, an effective “surface charge” can be estimated by tests involving the adsorption of high-mass cationic polyelectrolytes (Wågberg *et al.* 1989; Horvath *et al.* 2006; Horvath and Lindström 2007). The principle of such analyses was pioneered by Hostetler and Swanson (1974), who used silica gel as a model mesoporous substrate. The validity of such an approach rests upon a number of assumptions, including (a) there is a 1:1 stoichiometry of interactions between the test polymer and the surface groups, and (b) the selected polyelectrolyte does not permeate into the cell wall to a significant extent during the time of testing. The first assumption seems to be valid as long as the polyelectrolyte has sufficient charge density, has a linear structure, and as long as the electrical conductivity of the system is very low (Horvath *et al.* 2006). The low conductivity rule is because salt-free conditions allow individual charged groups on the solid surface and on the polyelectrolyte to sense each other’s presence over long distances, such that the oppositely charged ions form pairs in an efficient manner. The second assumption also appears to be valid as long as the selected polyelectrolyte has a molecular mass of about a million g/mole or larger and the test is carried out within a matter of minutes (Wågberg *et al.* 1989; Wu *et al.* 2009).

More recently, the same approach was used to estimate ratios of surface to total charge for various types of pulp; results were reported in the range of 0.03 to 0.14 (Horvath and Lindström 2007). The lowest of these reported values corresponded to bleached softwood kraft fibers, a type of fiber that is known to have abundant mesopores when in its swollen state (Stone and Scallan 1966, 1968; Berthold and Salmén 1997). The highest of these values corresponded to TMP fibers, which tend to be substantially less porous than kraft fibers. However, lower surface charge densities were found when using the method that combines methylene blue sorption and XPS measurements, as proposed by Fardim *et al.* (2005).

Because the carboxylic acid groups on a fiber surface are fixed in location, and presumably some of them are close together, dissociation of one group can influence the dissociation of the next (Jano and Hardcastle 1999; Petrov *et al.* 2003). Annenkov *et al.* (1998) used a randomized simulation study to demonstrate the concept in an analogous case of adjacent carboxyl groups on acrylic acid copolymers and their complexes.

The proportion of different gross classes of carboxylic acid groups in pulps can be discerned by studying the detailed shapes of potentiometric titration curves. As noted by Laine *et al.* (1996), the  $pK_a$  value for uronic acid groups in xylans and pectic acids is about 3.3, whereas the  $pK_a$  value for carboxylic acid groups associated with lignin is about 5.5. Theoretical fits of potentiometric titration data indicated that the uronic acid groups accounted for about 80% and 90% of the totals, respectively, for unbleached hardwood and softwood kraft pulps.

### *Characteristic differences among types of cellulosic fibers*

Different classes of typical cellulosic fibers have different densities of anionic charge at their surfaces. Classic work carried out by Herrington and Petzold (1992) showed that the density of carboxylic acid groups varied greatly depending on the origin

and treatments of the fibers. The lowest values were obtained in the case of cotton. Related work has been applied to a variety of pulp samples (Lloyd and Horne 1993; Lindgren *et al.* 2002). Fiber surface charge was found to increase according to the following sequence: bleached softwood kraft < bleached hardwood kraft < unbleached kraft < mechanical pulps < peroxide-bleached mechanical pulps. Likewise, Horvath and Lindström (2007) found the lowest charge density in the case of bleached softwood kraft fibers and the highest charge density in the case of certain TMP fibers. This can be attributed to the demethylation of pectins to pectic acid during peroxide bleaching of TMP fibers and degradation and removal of hemicelluloses and pectins from the fibers during kraft pulping.

In the case of mechanical pulps, Koljonen *et al.* (2004) carried out polyelectrolyte adsorption and dye adsorption experiments, in addition to potentiometric and conductimetric titration of carboxyl groups, to compare different types of mechanical pulps prepared from spruce wood. Alkaline treatments greatly increased the observed negative charge density, and oxidative bleaching treatment with peroxide or ozone made the surfaces yet more negative. Between 30 and 90% of the observed charge could be attributed to just two kinds of groups: galacturonic acid and sulfonic acid.

During the kraft cooking and bleaching of wood chips, there is a competition between two processes that affect the surface charge of the resulting fibers in different ways (Fras *et al.* 2005). On the one hand, some of the more easily solubilized material tends to be released from the fiber into the aqueous solution, thus tending to decrease the surface charge of the fibers. On the other hand, oxidizing treatments have the potential to create additional carboxylic acid groups on the fiber surface. However, as a complicating factor, such carboxylic acid groups contribute to making the treated material yet more soluble and more likely to be incorporated into the DCS fraction. Thus, kraft cooking appears to have the net effect of solubilizing negatively charged species, especially if the process is carried out to sufficiently low yield (Bhardwaj *et al.* 2006). In the cited work the anionic hexenuronic acid (HexA) groups of pine appeared to be liberated more easily than lignin compounds. Laine *et al.* (1996) used an innovative enzymatic approach, together with polyelectrolyte adsorption and potentiometric titration to confirm that HexA groups were responsible for a substantial portion of the fiber surface charge. Following treatment with a hemicellulose-specific enzyme, the surface charge density was found to have been decreased.

Peroxide bleaching is associated with observed increases in the amount of negatively charged groups detected at fibers surfaces (Laine 1997; Sundberg *et al.* 2000a). However, no such relationship was found by Bhardwaj and Nguyen (2005) in a study of bleached de-inked pulps; apparently under the conditions of testing there was a sufficient release of oxidized species into the dissolved and colloidal phase such that the apparent negative charge density of the fiber surfaces remained almost constant. Furthermore, most of the fibers in de-inked pulp have already been subjected to sufficient peroxide bleaching (mechanical pulp) or high alkaline conditions (kraft pulp) so that further demethylation of pectins to pectic acids is not significant.

Sundberg *et al.* (2000a) observed that extraction of spruce TMP with hexane before separating the fractions resulted in a higher surface charge on the fiber surface, as determined by titration. Presumably this observation implies that the polysaccharide component of the fibers had a higher effective charge density than that of the extractives.

### *Refining and the effect of surface area*

The amount of cationic polymer adsorbing onto fiber surfaces has been found to increase with increased refining (Strazdins 1972, 1980; Carrasco *et al.* 1996; Mutje *et al.* 2001; Bhardwaj *et al.* 2007a,b; Konn *et al.* 2007). A number of such studies were able to correlate cationic demand of the furnish to some measure of the effective surfaces area (Strazdins 1980; Mutje *et al.* 2001; Bhardwaj *et al.* 2007b; Konn *et al.* 2007; Lin *et al.* 2010). Konn *et al.* (2007) found that sulphonic groups in lignin components and demethylation of uronic acids groups in pectins to free carboxyl groups accounted for most of the newly-available surface charge resulting from refining of CTMP.

### **Charge Demand Contribution of the Fines Fraction**

The “fines” fraction of papermaking furnish can be technically defined as being any solid particles small enough to pass through a 72  $\mu\text{m}$  opening, according to a standard test (TAPPI T261 cm-94). In practical terms, fines are solid particles small enough to pass through the openings in the forming fabric of a paper machine.

### *Cellulosic fines*

To a first approximation it may be useful to think of the cellulosic “fines” portion of a pulp suspension as being just like fibers, but much smaller in size. It follows that the ratio of external surface area to mass will be much larger. Because the surfaces of various fine matter can adsorb polyelectrolytes, they can have a large impact of the measured charge demand of process water in a paper mill. In fact, large differences have been found in the values of cationic demand obtained when different filtration procedures are used to collect samples of process water from a paper mill (Hubbe 2005a). A classic series of studies by Marton (1980a,b, 1991) showed that the fines fraction in typical papermaking furnish usually takes up 2 to 10 times as much of various cationic additives per unit mass, compared to the fibers. Results published by Mutje *et al.* (2001) tend to confirm those findings.

Due to the fact that typical fines are much thinner than the fibers, much less time may be required to saturate the pore structure of fines with the cationic additive, compared to the fibers. This concept was demonstrated most dramatically by Strazdins (1977), who added a cationic polyelectrolyte to a suspension of fibers and fines and then promptly filtered a portion of the mixture, obtaining a suspension with only fines and no fibers. Microelectrophoresis test results showed a very large change in the zeta potential with time, going from positive back toward their original negative conditions, in the case of the fines that had been kept stirring gently in the presence of fibers. By contrast, very little decay of the positive zeta potential of treated fines was observed in the suspension from which fibers had been removed. The results show that, in a sense, the fibers continue to act as sponges for various multivalent cationic additives, whereas the fines quickly get saturated throughout their accessible structure with whatever is present in the solution.

Chemical and structural differences among fines from different sources also can lead to differences in their capacities to adsorb polyelectrolytes (Taipale *et al.* 2011). Koljonen *et al.* (2001) showed distinct differences between stone groundwood, TMP, and CTMP pulp fines all derived from the same softwood source. Because of fibers' layered

structure, as well as the non-uniform distribution of extractives within wood structures, one can expect large differences in chemical composition, depending on shape (Koljonen *et al.* 2001; Mosbye and Moe 2002; Sundberg *et al.* 2003). Fibrillar fines in mechanical pulps are more likely to have large proportions of cellulose and hemicelluloses on their surfaces, whereas flake-like fines are more likely to be encrusted with pectic acids, lignin, and extractives, giving them a more negative charge density. Ray cells, which already are in the size range of fines, can be expected to be rich in pectic acids and extractives, which tend to be highly anionic due to the presence of dissociated fatty acid and resin acid groups (Sundberg *et al.* 2003).

#### *Other kinds of fine solids in papermaking systems*

The mineral fillers most often used in papermaking have a relatively high ratio of surface area to mass (Marton 1980a,b). However, they are different from cellulosic fines in an important respect: they generally are not porous. Thus, whatever contribution they make to sorption of polyelectrolytes tends to be immediate, not requiring many minutes for the polyelectrolytes to permeate into a fine pore structure. There can be important differences in the charge characteristics of mineral products used in papermaking, depending on how they are prepared. Suspensions of relatively pure calcium carbonate (calcite mineral) tend to have a weakly positive zeta potential, dependent on the concentrations of  $\text{Ca}^{2+}$ , bicarbonate ions, and other charged species in the solution (Pierre *et al.* 1990; Madsen 2002). But most filler products that need to be shipped any significant distance are prepared with anionic dispersants, such as phosphates or acrylates (Järnström 1993; Rantala *et al.* 1999), and these can contribute a lot to the cationic demand of the system to which such fillers are added.

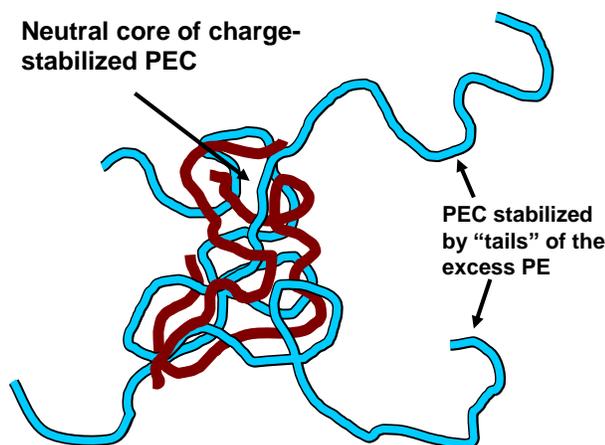
#### *Polyelectrolyte complexes acting as fines*

Because of the likelihood of formation of polyelectrolyte complexes (PECs), the dividing line between “dissolved” versus “colloidal” materials in papermaking systems can become blurred. Studies have shown that PECs can be used as dry-strength-enhancing systems for paper (Sato and Nakajima 1975; Kramer *et al.* 1997a,b; Buchhammer *et al.* 2003; Gernandt *et al.* 2003; Hubbe 2005b; Hubbe *et al.* 2005; Lofton *et al.* 2005; Heermann *et al.* 2006; Feng *et al.* 2007b; Fatehi *et al.* 2009).

It has been shown that PEC particles can exist in stable suspension due to an outer layer that is enriched in whichever polyelectrolyte is present in excess (Chen *et al.* 2003). The mechanism is illustrated schematically in Fig. 8. In cases where Fig. 8 can be used to represent the PEC component, one can expect there to also be some free polyelectrolyte present in solution corresponding to excess charge. In other cases, especially when titrating large polyelectrolyte molecules against smaller ones, it is possible for the complex to remain completely soluble (Kabanov and Zezin 1984; Dautzenberg and Karibyants 1999; Vanerek and van de Ven 2006). It has also been shown that the tendency of PECs to precipitate onto fiber surfaces can be controlled by adjusting the ratio between the oppositely charged polyelectrolytes (Kekkonen *et al.* 2001).

Vanerek and van de Ven (2006) showed that the concept of *complex coacervation* can be applied to systems of sulfonated kraft lignin and cationic polyelectrolytes. The properties of such systems were shown to be highly dependent on the molecular mass of the cationic polymer. The PECs were found to initially contain a lot of water, but the

water tended to be expelled over the course of time as the macromolecules gradually rearranged themselves in order to achieve a more efficient pairing of oppositely charged groups.



**Fig. 8.** Schematic illustration of a charge-stabilized polyelectrolyte complex (PEC) in which the core is a neutralized “ladder” or “scrambled” structure of approximately 1:1 pairing of ionic groups, whereas the stabilizing layer is formed by whichever poly-ion is in excess

#### *Steric stabilization of fine matter*

The fate of colloidal materials in paper machine systems tends to be critically dependent on their colloidal stability. Colloidal materials are called “stable” if they can remain for an extended time as a finely dispersed suspension. By contrast, “unstable” colloidal mixtures will tend to deposit on surfaces or form agglomerates. The hemicellulose component of DCS appears to be particularly effective in stabilizing colloidal materials in certain papermaking systems (Sundberg *et al.* 1994b; Rundlöf *et al.* 2002; Johnsen *et al.* 2004; Saarimaa *et al.* 2006b; Johnsen and Stenius 2007). Such effects are often attributed to “steric stabilization,” a term referring to the action of an adsorbed long-chain surfactant or soluble polymer that essentially coats the suspended particles and keeps the solids from getting close enough together to adhere (Hesselink 1977). A requirement for effective steric stabilization is that the macromolecule needs to contain extended solvent-loving segments that can extend outwards from the solid surfaces. The first mention of steric stabilization in the context of papermaking applications may have been in an article by Allen (1979). Shortly thereafter, one of the present authors took part in a study in which a polystyrene latex suspension was treated with filtrate from newsprint furnish (Pelton *et al.* 1980b). The adsorbed DCS had little effect on zeta potential of the latex but increased the critical coagulation concentration (CCC) enormously, indicating steric stabilization.

Steric stabilization also has been shown to be important as a factor resisting the deposition of wood pitch and other tacky materials in certain papermaking systems (Clas *et al.* 1993; Sundberg *et al.* 1994a). Monte *et al.* (2010) used the concept of steric stabilization to explain why, for instance, a mixture of thermomechanical pulp and deinked pulp led to greater deposition of pitch than would have been predicted from a linear interpolation between results for two component pulps. It was proposed that the

polysaccharides tending to stabilize the tacky materials became spread out over a larger area of fiber, thus lowering the colloidal stability of the tacky materials in the system. Notably, the observed enhancement of deposition in the mixed pulp systems was not correlated with trends in cationic demand.

In the case of hemicelluloses, the stabilizing effects sometimes can be overcome, at least in part, by the presence or increased concentration of divalent ions such as  $\text{Ca}^{2+}$ , *i.e.* water hardness. The high-mass fraction of pectic acids can be precipitated out of solution by calcium ions, whereas the shorter-chain pectic acids tend to remain in solution (Saarimaa and Pranovich 2007). Nyman and Rose (1986) reported that kraft lignin and lignosulfonates tended to be present as sterically stable colloidal particles in pulp suspensions. Sundberg *et al.* (1993) showed that stabilization effects also can be achieved if a high-charge cationic polyelectrolyte is added as an overdose to papermaking systems that contain lipophilic colloids.

Salt can play a multifaceted role with respect to the stability of colloidal particles. In the case of PECs, increased salt concentrations can cause the material to swell more with water, due to weaker interactions between the oppositely charged polymers. But on the other hand, salt tends to promote coagulation between like-charged particles. Also, a certain level of salt is needed to promote PEC formation (Schindler and Nordmeier 1994). In papermaking applications the typical salt levels are either sufficient or too high to maximize polyelectrolyte adsorption and PEC formation.

The optimum retention aid strategy to retain colloidal materials during papermaking may be different from that which is optimal for cellulosic fines. Neimo (1993) observed that the colloidal fraction could not be efficiently removed from the suspended phase without use of a high-charge cationic additive. By contrast, high-mass polyelectrolytes, such as cPAM, either alone or together with high-charge additives, tend to be effective for retention of cellulosic fines (Hubbe *et al.* 2009).

### Charge Demand of Common Pulp

Table 3 presents a summary of typical data for the charge demand corresponding to the solid components in common types of papermaking pulps. The fact that the ranges of values given in Table 3 are quite broad can be understood based on differences in chemical treatments during pulping and bleaching, differences in refining, differences in washing, different titration methods, and even differences in the species of wood used in different studies (Herrington and Petzold 1992; Lloyd and Horne 1993; Lindgren *et al.* 2002; Fardim and Holmbom 2005).

One of the important implications of the data in Table 3 is that different types of pulp solids will tend to sorb different amounts of cationic additives. Thus, when adding a cationic agent to a blended furnish, one has reason to expect that a disproportionate amount of the agent to adsorb onto the most anionic of the furnish components. Though it is possible to overcome such effects, at least in part, by adding cationic agents earlier in the process, before different types of pulp have been blended together (Bley and Winter 1997; Nikkinen *et al.* 2001; Gruber *et al.* 2003), there has been insufficient study of whether such strategies are advantageous in practice.

**Table 3.** Adsorption onto Pulp Solids as a Contribution to Cationic Demand of a Pulp Suspension

Pulp Type	Specific Charge Content ( $\mu\text{eq/g}$ )	(notes)	Citations
Cotton linters	5	a, b	Herrington & Petzold 1992
Bleached softwood kraft	24 3-45 6-16 (surface) 35-85 (total) 31-67 35	a, b b a, d a, d a, c a, e	Lloyd & Horne 1993 Laine 1997 Laine & Stenius 1997 " " " Fardim <i>et al.</i> 2002 Fardim & Holmbom 2005
Unbleached softwood kraft	83 48-89 37 88-113 53-87 75	a, b a, b b b a, c a, e	Herrington & Petzold 1992 Lloyd & Horne 1993 Laine 1997 Lindgren <i>et al.</i> 2002 Fardim <i>et al.</i> 2002 Fardim & Holmbom 2005
Bleached hardwood kraft	27-87 10-27 (surface) 47-129 (total) 45-110 60-75	a, b a, d a, d a, c a, e	Herrington & Petzold 1992 Laine & Stenius 1997 " " " Fardim <i>et al.</i> 2002 Fardim & Holmbom 2005
Unbleached hardwood kraft	100-187 87-141 115-130	b a, c a, e	Lindgren <i>et al.</i> 2002 Fardim <i>et al.</i> 2002 Fardim & Holmbom 2005
Pine or spruce groundwood	59 35-150 (surface) 95-220 (total,bleach)	a, b a, d a, d	Lloyd & Horne 1993 Koljonen <i>et al.</i> 2004 " " "
Thermomechanical (TMP)	57 65-187 50-202 32-50 (surface) 88-140 (total) 85	a, b a, c b a, d a, d a, e	Lloyd & Horne 1993 Fardim <i>et al.</i> 2002 Lindgren <i>et al.</i> 2002 Koljonen <i>et al.</i> 2004 " " " Fardim & Holmbom 2005
Peroxide-bleached chemi-TMP	95-109 234 (total) 132-249 37-90 (surface) 110-250 (total) 175-200	a, b a, f a, c a, d a, d a, e	Lloyd & Horne 1993 Li & Ni 2001 Fardim <i>et al.</i> 2002 Koljonen <i>et al.</i> 2004 " " " Fardim & Holmbom 2005

Notes: a: Thoroughly washed pulps (acid treatment, followed by multiple rinsing with de-ionized water); b: potentiometric titrations; c: range shown includes tests with conductimetric endpoint, methylene blue adsorption, potentiometric titrations, and polyelectrolyte titrations; d: adsorption of poly(l,5-dimethyl-l,5-diazaundecamethylene) bromide, 8000 g/mole; e: methylene blue adsorption; f: conductometric titration

The contributions of soluble polyelectrolytes also need to be considered. The amount of soluble or colloidal polyelectrolytes in a given pulp suspension will be highly dependent on whether the pulp has been washed, and if so, the extent of such washing. On the other hand, the charge demand contributions of key soluble macromolecules present in different kinds of pulp furnish can be calculated from the corresponding chemical formulas. This is what has been done in Table 4. As shown, a typical polygalacturonic acid molecule or pectic acid (see. Fig. 5B), when fully dissociated (for

instance at neutral or alkaline pH) is expected to have a charge density of about 5 meq/g. This value of charge is more than 20 times greater than the positive charge density of typical cationic starches, and also higher than the charge density of typical acrylamide copolymers used as retention aids. By contrast, typical scavenger chemicals such as polyamines, poly-DADMAC, and PEI may have positive charge densities even higher than the negative charge density of the pectic acid example listed.

**Table 4.** Charge Demand of Soluble Components in Pulp Suspensions

Component	Specific Charge Content (meq/dry g) *	Reference
Fully deacetylated pectic acids	- 5.0	Fig. 5B, calculated
Xylans (Xyl:meGlcA:Ara ratio 10:2:1.3)	- 1.1	Calculated
Cationic Starch (DS = 0.024 to 4 typical)	+ 0.14 to + 0.24	Calculated
CPAM (5-10 mole % cationic)	+ 2 to + 4	Moormann-Schmitz <i>et al.</i> 1994
Poly-DADMAC (independent of pH)	+ 6.19	Calc'd; Koljonen <i>et al.</i> 2004
Polybrene	+ 5.34	Koljonen <i>et al.</i> 2004
Poly-ethylenimine (PEI, at pH = 4)	+ 20	Moormann-Schmitz <i>et al.</i> 1994
Polyvinylsulfate, potassium salt (PVSK)	- 6.17	Calculated
Polyethenesulphonate (PES-Na)	- 7.69	Koljonen <i>et al.</i> 2004

\* The values shown are based on calculations from the corresponding chemical structures, assuming 1:1 stoichiometric interactions

### Papermaking Additives' Contributions to Cationic Demand

Many of the additives in frequent use for wet-end, size press, or coating addition fall into the categories of either “dissolved polyelectrolytes,” or “colloids”, as just discussed. Furthermore, many of them have a significant net ionic charge. Therefore, such additives need to be included among the factors affecting the overall charge demand. Some discussion of how certain wet-end additives affect charge balance – potentially affecting both the process and product – have been provided in some earlier articles (Medvecz 1993; Sanders and Schaefer 1995; Hubbe 1999). The highly anionic silicates often used to protect hydrogen peroxide against decomposition have already been mentioned (Linhart *et al.* 1987; Nyström 1993; Saastamoinen *et al.* 1996; Bräuer *et al.* 2001; Larnicol *et al.* 2001; He *et al.* 2004), as have the mineral fillers, along with the dispersing agents that often accompany their use (Huang *et al.* 1991; Sanders 1992; Bown 1996; Sondi *et al.* 1997). In addition, significant cationic demand contributions, depending on usage levels, can be expected from the additives listed in Table 5.

**Table 5.** Additives that Can Contribute Significant Charge Demand

Charge	Item	References
-	Direct dyes (anionic type)	Lips 1981
-	Fluorescent whiteners (OBAs)	Roltsch & Lloyd 1987; Bobu <i>et al.</i> 2002
-	Microparticles (silica, bentonite)	Swerin & Ödberg 1993; Andersson & Lindgren 1996
-	Some dry-strength additives	Reynolds & Wasser 1980; Linke 1968
-	Clays, ground carbonate fillers	Bown 1996; Sondi <i>et al.</i> 1977
-	Coating latex, dispersants	Huang <i>et al.</i> 1991; Järnström 1993; Rantala&L.1999
+	Pure CaCO <sub>3</sub> , fresh PCC	Pierre <i>et al.</i> 1990; Madsen 2002
+	Cationic polymers	Howard & Jowsey 1999; Shirazi <i>et al.</i> 2003
+	Aluminum products, alum	Strazdins 1989; Exall & van Loon 2003

Two items in Table 5 merit particular attention due to the fact that their mechanisms of action are closely associated with their colloidal charge: the “microparticle” products and the “soluble aluminum” products (see the two subsections that follow). The microparticles, including colloidal silica and montmorillonite (bentonite) products typically have a negative charge. By contrast the aluminum products have a strong positive colloidal charge, at least under acidic papermaking conditions.

#### *Charge demand characteristics of microparticles*

Colloidal silica and bentonite microparticle (or “nanoparticle”) products are widely used, in combination with cationic polymers such as cationic acrylamide copolymers (cationic PAM retention aids) and cationic starch, to promote retention and dewatering (Andersson and Lindgren 1996; Hubbe 2005c; Wågberg *et al.* 1996; Liu *et al.* 2003). The microparticle products in the most common usage all have a strong negative surface charge (Andersson and Lindgren 1996; Asselman and Garnier 2000; Lee and Hubbe 2008).

Past studies have shown that microparticle programs often show their most promising effects, especially with respect to dewatering rates, after a sufficient amount of cationic additives have been added to shift the net colloidal charge of the system to positive (Penniman and Makhonin 1993). Such adjustment of the system charge facilitates a rapid and thorough complexation reaction between the microparticles and the loops of cationic polymer, which has the effect of allowing water to flow more easily from the solids. By contrast, an excess of DCS has been shown to adversely affect the performance of microparticle additive programs (Wackerberg *et al.* 1994).

#### *Soluble aluminum species*

Aluminum can exist in a number of different ionic forms, or as an uncharged  $\text{Al}(\text{OH})_3$  “floc,” depending on the extent of interaction between the trivalent Al and different numbers of  $\text{OH}^-$  ligands. In particular, a number of studies have highlighted the existence of some rather large ionic species, such as  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ , which have a high positive valence (Akitt *et al.* 1972; Hayden and Rubin 1974; Bottero *et al.* 1980; Bottero and Fiessinger 1989; Crawford and Flood 1989; Bi *et al.* 2004). Conditions conducive to the presence of oligomeric forms of aluminum tend to maximize the coagulation and deposition of suspensions of negatively charged particles (Bottéro *et al.* 1980; Arnson 1982; Lartiges *et al.* 1997; Exall and van Loon 2003). In addition, the oligomeric form of aluminum has been shown to be effective in giving a positive charge to the treated surfaces of cellulosic fibers (Arnson and Stratton 1983). Such effects depend strongly on such factors as pH and time (Arnson and Stratton 1983; Strazdins 1989; Kitaoka and Tanaka 2002; Chen *et al.* 2004). Charge titrations carried out with negatively charged polyelectrolytes such as polyvinyl sulfate (PVSK) reveal remarkably strong complexation with oligomeric aluminum cationic species (Chen *et al.* 2004; Novakov *et al.* 2011). By contrast, Chen *et al.* (2004) found little effect on charge titrations when the pH was low enough for the aluminum ions to be mainly present in their  $\text{Al}^{3+}$  form or high enough that it was mainly present as neutral  $\text{Al}(\text{OH})_3$  floc. Trksak (1990) observed large differences in the amount of anionic titrant (PVSK) consumed by aluminum-containing solutions of different pH that had been prepared with aluminum sulfate, aluminum chloride, and poly-aluminum chloride (PAC); the observed differences

were consistent with strong interaction between aluminum oligomers and PVSK. Time may be required for aluminum species and a polyelectrolyte to reach equilibrium (Ringenbach *et al.* 1995); the observed sluggishness of aluminum ion-polyelectrolyte interactions is consistent with the large ionic forms of the aluminum, in addition to the high molecular mass of the polyelectrolytes.

Though the species and equilibria are shifted in the presence of sulfate ions, many of the phenomena are similar to those observed in the absence of sulfate (Matijević and Stryker 1966). In particular, in systems based on aluminum sulfate addition to paper machine it is generally not possible to achieve strong charge reversal to highly positive positive zeta potential (Strazdins 1989; Kitaoka and Tanaka 2002).

Due to their opposite charges, multivalent aluminum oligomers can be expected to interact strongly with colloidal silica and bentonite, *i.e.* with microparticles that are used in various retention and drainage aid programs. In principle, the two classes of additive may simply neutralize each other upon contact when they are added sequentially to a paper machine system. A study by Lartiges *et al.* (1997) showed that adsorption of cationic Al oligomers onto colloidal silica, beyond a certain level, caused charge neutralization. Such a mechanism might account for the rather slow progress of implementation of microparticle programs in the case of paper machine systems where the pH is in the acidic range and where the use of aluminum products is common. Because the aluminum oligomers have lower molecular mass than the starch or acrylamide-based retention polymers, they can diffuse to the microparticle surfaces more quickly than the cationic starch or acrylamide macromolecules. In this way the aluminum ionic species can be expected to interfere with the intended promotion of dewatering rates and retention (Andersson and Lindgren 1996; Hubbe 2005c; Wågberg *et al.* 1996). The intended effects of microparticles require their surfaces to have a strong negative charge density, enabling their strong interaction with the cationic polymers.

## METHODS FOR DETERMINING CHARGE DEMAND

Several methods have been described for the quantification of colloidal charge of water samples and/or fiber suspensions obtained from paper machine systems. The main features of the topic have been covered in previous articles (Springer and Taggart 1986; Kirbawy 1992; Penniman 1992; Lorz and Linhart 1993; Patton and Lee 1993; Gratton and Pruszynski 1995; Reiter *et al.* 1998; Kam and Gregory 1999; Hubbe 2000; Lindgren *et al.* 2002; Bhardwaj *et al.* 2004; Koljonen *et al.* 2004). The emphasis in this section will be on how these various methods work and what they can teach us about interactions between strongly charged polyelectrolytes and various components of DCS. In addition, a comparison of the different approaches is intended to help in the selection of a test procedure or procedures for a given application.

In general terms, the colloidal charge, “cationic demand”, or “anionic demand” of a given volume of an aqueous sample or suspension can be determined by a titration, answering the question: “How much of a standard high-charge-density polyelectrolyte does it take to neutralize the DCS in the system?” Alternatively, one may ask how much of a cationic additive is needed to neutralize the surfaces of particulate matter in the suspension, in addition to the DCS. The condition of “net neutral surfaces” is equivalent

to saying that the zeta potential should be zero at the titration endpoint (Hiemenz and Rajagopalan 1997). It is important to point out that charge demand and zeta potential are very different quantities (Schemp 1988; Penniman 1992). As noted by Kirbawy (1992), though both quantities are related to the charge of DCS or fibers in an aqueous suspension, they are as unrelated to each other as a speedometer and a gas gauge on your automobile. Zeta potential can be defined as the electrical potential (usually measured in millivolts) at a hydrodynamic slip plane very close to the surface of the material under study (Stratton and Swanson 1981; Hiemenz and Rajagopalan 1997). Sample size does not have to be taken into consideration when evaluating zeta potential. By contrast, the colloidal charge demand can be defined by how much of a standard polyelectrolyte titrant it takes to neutralize (make the zeta potential go to zero) the charge of a given amount of sample.

Studies have demonstrated maximum levels of fine particle retention, the best performance of dry-strength additives, and/or the fastest dewatering rates when enough of a high-charged cationic additive was added to adjust the zeta potential close to zero (Strazdins 1977; Lindström *et al.* 1974; Horn and Melzer 1975; Stratton and Swanson 1981; Bhardwaj *et al.* 2005; Hubbe *et al.* 2007b). Such observations provide evidence that, at least in those cases, charge interactions can play a dominant role. The governing mechanisms may include charge neutralization and interaction between charged patches (Horn and Linhart 1996). An exception to this rule is when retention efficiency is dominated by the action of very-high-mass retention aids; in such cases the correlation between retention efficiency and zeta potential may be poor (Linhart *et al.* 1987). Brouwer (1991) recommended, at least in one case, that a paper machine additive system could be optimized by selecting additive levels that achieved a charge demand of zero as well as a zeta potential of zero.

### Cationic Demand Titrations

A titration can be defined as a procedure in which one gradually adds a metered amount of probe material, having a known concentration, to a known quantity (usually volume) of the sample to be tested and determines how much of the titrant is needed to reach an endpoint. The charge demand tests to be discussed in this section mostly conform to this definition, and the titrants can be polyelectrolytes, dyes, or strong acids or bases.

#### *Polyelectrolyte titrants*

The mostly widely used titrants for purposes of charge demand determinations have been linear polyelectrolytes having high charge density. When the sign of net charge of the colloidal material in the sample is negative, the most popular titrants are polydiallyldimethylammonium chloride (poly-DADMAC) (Nicke *et al.* 1992; Swerin and Wågberg 1994; Fang and Ming 2006; Mocchiutti and Zanuttini 2007) and poly-3,6-ionene (commonly known by its brand name Polybrene) (Wågberg *et al.* 1989). In the less common situation that a sample to be tested happens to have a net positive charge, the most popular titrants are the potassium salt of polyvinylsulfate (PVSK, Bley 1992; Mocchiutti and Zanuttini 2007) and polyethylenesulphonate (Pes-Na) (Bley 1992).

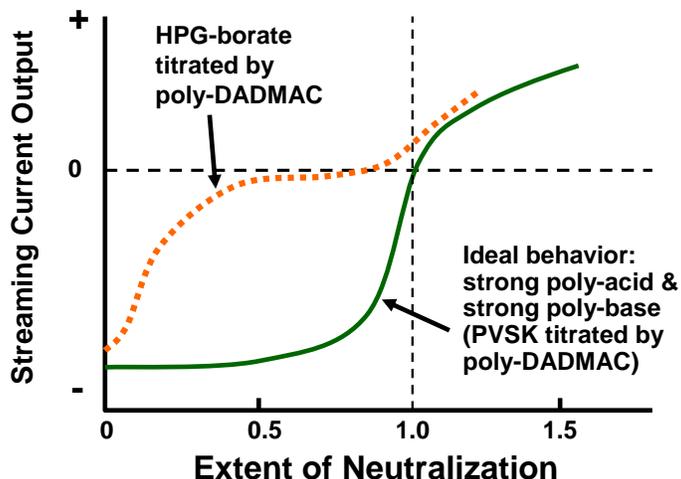
*Streaming current meter endpoint*

Presently the most frequently used method to detect the endpoint of charge demand titrations of aqueous samples or filtered fiber suspensions from paper machine systems is the streaming current (SC) method (Gerdes 1966; Ojala 1993; Barron *et al.* 1994; Gratton and Pruszyński 1995; Kam and Gregory 1999). The apparatus, at its core, is remarkably simple. A loosely-fitted plastic piston moves up and down with a frequency of about 4 Hz within a dead-ended plastic cylinder or “boot”. The method rests upon the assumption that colloidal material in the aqueous sample adsorbs onto and completely covers the plastic surfaces (Cardwell 1966; Barron *et al.* 1994; Jaycock 1995). Though the validity of the assumption is somewhat doubtful in the case of samples containing highly hydrophilic polyelectrolytes such as oxidized starch (Chen *et al.* 2001), usually there is sufficient precipitation of neutralized PECs as the titration endpoint is approached so that the meter reading will reach zero (Kenaga *et al.* 1967; Böckenhoff and Fischer 2001). Though Phipps (1999) reported deviations from an expected stoichiometric relationship when evaluating certain samples of interest to papermakers, most users generally report success in routine use of the equipment for evaluation of paper machine process waters.

The presence of salt can have significant effects on the results of SC titrations. Chen *et al.* (2003) found that titrations carried out between the two standard titrants poly-DADMAC and PVSJ were in good agreement when carried out in deionized water, but that the results deviated from 1:1 charge stoichiometry to a greater extent as the concentration of sodium sulfate in the solution was increased. In fact, the results depended on the direction of the titration as the salt level was increased. To explain such observations, it was proposed that the presence of salt favored the existence of charge-stabilized PECs suspended in the solution, wherein each particle was neutral in its interior, but there was an outer layer enriched with segments of whichever polyelectrolyte was in excess (see Fig. 8). Depending on the details of experimentation, sometimes it was not possible to reach an endpoint of zero signal if the electrical conductivity was above a threshold level lying somewhere between 1000 and 5000  $\mu\text{S}/\text{cm}$  (Chen *et al.* 2001; 2003). This absence of an endpoint has been attributed to inhibition of polyelectrolyte adsorption in the presence of sufficiently high salt concentration (van de Steeg *et al.* 1993; Chen *et al.* 2003). Fortunately, the problem can be overcome by a revised procedure: Each sample to be evaluated is diluted by a factor of ten; the amount of titrant needed to reach the endpoint is then multiplied by a factor of ten (Hubbe and Chen 2004; Hubbe 2008). Alternatively, indistinct or shifted endpoints of polyelectrolyte titrations may be due to the presence of divalent cations; in such cases Tanaka (1983) showed that clearer, more reliable endpoints can be achieved by removing the offending ions with the use of ion exchange resins.

Cui *et al.* (2008) showed that there can be differences in the shapes of titration curves, depending on the nature of the aqueous sample. It was shown that the neutral water-soluble polymer hydroxypropyl guar (HPG) behaved as an anionic polyelectrolyte upon addition of borate or boronate ions, causing the SC signal to become strongly negative. Whereas titration of a strongly anionic polyelectrolyte such as PVSJ can be expected to yield a clear, sharp endpoint, upon titration with poly-DADMAC (Pelton *et al.* 2007), the authors found that in the case of HPG-borate, the signal approached zero with just a minor addition of the cationic titrant and then remained at that level until

sufficient poly-DADMAC had been added to tie up all of the boron-related ions (Cui *et al.* 2008; Pelton 2010). It was proposed that the HPG-borate system represents a previously unrecognized class of “labile polyelectrolytes”. Figure 9 illustrates the difference in appearance of the titration curves for either an ideal strong poly-acid (e.g. PVSK) or a labile poly-acid (such as the HPG-borate system) vs. the strong poly-based poly-DADMAC. Based on such findings, future research is recommended in which the shapes of titration curves are included as key output information, with a focus on SC titrations of samples related to papermaking applications.



**Fig. 9.** Forms of typical curves for two streaming current titrations, both employing a strong poly-base as the titrant. Upper (dotted) curve: Sample is a labile complex of borate and hydroxypropyl guar (HPG); lower (solid) curve: Sample is a strong poly-acid, e.g. PVSK.

Bockenhoff and Fisher (2001) compared endpoints of SC titrations with results of ion exchange capacity determinations. As might be expected, the two types of analysis yielded different results. In general the SC endpoints were lower in absolute value. It was proposed that the difference could be explained by immobilization of counter-ions.

Online versions of SC titration equipment operate in essentially the same fashion as their lab-based counterparts, except that the batch-wise operation is automated and carried out repeatedly (Kaunonen 1989; Veal 1997; Bley 1998; Rantala *et al.* 1999; Nikkinen *et al.* 2001; Gruber *et al.* 2003). Another key difference is that online tests facilitate a much higher frequency of testing – always with a very fresh sample – so that it may be possible to detect the onset of upset conditions in a papermaking process.

Though most users of SC equipment in papermaking applications prefer to focus on the titration of screened or filtered process water, it is possible to carry out tests in the presence of suspended fibers. This is most often achieved by a back-titration approach in which a known amount of usually cationic titrant, above the amount needed to neutralize the colloidal charge of the system, is added to the suspension (Kenaga *et al.* 1967; Spence *et al.* 1997). Then, after mixing, the suspended matter is removed by filtration and the filtrate is back-titrated with the anionic titrant, e.g. PVSK.

*Polyelectrolyte titrations with color endpoint*

Excellent reviews of the colorimetric method to determine the endpoint of polyelectrolyte titrations have appeared in conference publications (St. John and Gallagher 1992; Laine and Lindström 2000). The key to the method is a strong shift in the hue of certain dyes when they form a reversible complex with certain polyelectrolytes of sufficiently high charge density (Terayama 1952). One takes advantage of the fact that the mutual interactions between the oppositely polyelectrolytes are generally much stronger than the dye-polyelectrolyte interaction. Thus, the color shift is observed only when the polyelectrolyte opposite in charge to the dye is present in excess. The method has become widely used within the paper industry (Kam and Gregory 1999; Koljonen *et al.* 2004; Mocchiutti and Zanuttini 2007). Though the method has been applied successfully in paper mills, the presence of multivalent ions has been found to sometimes interfere with the color endpoint of charge titrations (Hubbe 1979; Sjödin and Ödberg 1996; Mocchiutti and Zanuttini 2007).

As in the case of the SC method, an online system has been developed based on the colorimetric determination of charge demand (Rice and Roeraade 2003). The online method employs automated filtration of pulp slurry, followed by back-titration tests to separately evaluate the charge associated with the solids and the filtrate. The automated procedure makes use of a colorimetric analysis (Horn 1978).

When the paper industry first began to use the colorimetric method, a procedure was developed whereby it was possible to obtain results that correlated well to zeta potential tests, for which the equipment was more expensive and the procedures more tedious (Halabisky 1977). It was shown that the logarithm of the ratio between the adsorbed amounts of cationic and anionic polyelectrolytes (log CTR), based on the color endpoints from a pair of titrations, gave an excellent correlation with zeta potentials obtained from microelectrophoresis tests (Halabisky 1977; Wallace 1992; Carrasco *et al.* 1998). The CTR method was criticized (Hubbe 1979), since the calculation of CTR converts an extensive measurement (related to charge demand) to an intensive measurement (analogous to zeta potential). It was proposed instead to rely upon the titration results directly, without taking the ratio. By such an approach, the colorimetric method can estimate how much of a charge-control chemical would be needed to completely neutralize a given sample of fiber suspension, using a back-titration approach.

*Streaming potential or microelectrophoretic endpoints*

Though the approach is much less common than the SC and colorimetric methods just described, it also is possible to use electrokinetic measurements to detect the endpoints of polyelectrolyte titrations. For many years the capillary microelectrophoresis technique was considered to be the most convenient and reliable means of determining when enough titrant had been added to neutralize fine particles in paper machine process water (Strazdins 1972, 1994; Jaycock 1995). Such measurements are conducted by observing the movement of fiber fines or filler particles in the process water as they are placed in an electrical field within a glass or quartz capillary tube between two chambers.

More recently, the streaming potential (SP), based on the electrical potential developed when an aqueous fluid is forced through a pad of fibers, has been used to estimate the charge demand (Koethe and Scott 1993; Gratton and Pruszyński 1995; Wang and Hubbe 2001; Hubbe 2001, 2006). The word “estimate” is used here, since it has been

shown that SP tests carried out under typical conditions of electrical conductivity do not give a true measure of the potential at the outer surface of cellulosic fibers; rather the observed signal appears to be influenced by the mesoporous spaces inside of the fiber wall (Hubbe 2006; Hubbe *et al.* 2007a,b). Such mesopores are too small to allow full access to most polyelectrolytes within the available time of testing or of papermaking. To overcome this problem, a procedure has been developed so that only the potential of the outer surface of the fibers is detected. This is achieved by quickly dewatering the fiber slurry just before the SP titration and replacing the filtrate with deionized water (Hubbe 2006, 2008; Hubbe *et al.* 2007).

#### *Dye adsorption*

In principle, the amount of colloidal and surface charges in an aqueous suspension can be measured by dye adsorption. After addition of a selected amount of dye to a fixed volume of sample, the solids are removed by centrifugation or filtration, and the color of the filtrate is compared to that of a blank experiment, in which no solids or colloidal materials are present (Fardim *et al.* 2002). Koljonen *et al.* (2004) found that results of such tests correlated well with those of more sophisticated tests of colloidal charge. Fardim *et al.* (2005) extended the approach by using adsorption isotherms, in addition to analysis of the dyed cellulosic surfaces by means of X-ray photoelectron spectroscopy (XPS) and infra-red spectroscopy. It was shown that methylene blue dye has a stronger association with surface-bound anionic groups in comparison to cationic polyelectrolytes and that the dye adsorbs according to the Langmuir model (Adamson and Gast 1997). Precise quantification of the number of charged groups within a set distance from the surface of cellulosic fines was obtained by XPS analysis, sensing the amount of methylene blue molecules relative to other components.

Tanaka and Ichiura (1999) pioneered a related method in which chromophoric groups were polymerized with diallyldimethylammonium chloride (DADMAC), forming a copolymer very similar to that used routinely in charge titrations.

#### *Potentiometric and conductometric titrations*

Because the two methods sense the same phenomena by different approaches, it makes sense to group potentiometric and conductometric methods together. Both procedures are designed to quantify the amounts of carboxylic acid groups that are accessible to water (Herrington and Petzold 1992; Laine *et al.* 1996, 1997; Fardim *et al.* 2002; Fras *et al.* 2005). In both cases one is titrating to find out how much base (or acid) it takes to dissociate (or protonate) all of the carboxylic acid groups in the sample. Blank titrations are carried out to account for the amount of acid or base needed to change the pH of an equivalent amount of pure water, and that amount is subtracted from the results obtained with the sample present. The endpoint of the titration is determined either by use of a pH meter (*i.e.* a potentiometer device) or by continuously measuring the electrical conductivity. Results are expected to differ from those based on polyelectrolyte complexation because (a) potentiometric or conductometric tests do not sense the presence of strong acids, for instance when sulfonic acid groups are present, and (b) some of the carboxylic acid groups sensed by the potentiometric or conductometric tests are inaccessible to cationic polyelectrolytes, especially those having high molecular mass.

## Other Methods

### *Methanolysis and gas chromatography for uronic acid content*

A more specific way to estimate the charge of DCS and fibers is to determine the total carboxylic groups in the uronic acid components by acid methanolysis and gas chromatography (Sundberg *et al.* 1996; Willför *et al.* 2009) and in the fatty and resin acids by extraction, silylation, and gas chromatography (Örså and Holmbom 1994). This estimation was found to be quite accurate for mechanical pulps when compared to polyelectrolyte titration with SC endpoint detection (Sundberg *et al.* 2000a). In unbleached mechanical pulp much of the galacturonic acid groups are methylesterified, which needs to be taken into account when calculating the total amount of carboxylic groups. Furthermore, it has been found that the polyelectrolytes used for titration (polybrene and poly-DADMAC) might also interact with other dissolved substances than anionic carbohydrates and extractives, since only about half of the titrable charge in the dissolved substances can be attributed to carboxylic groups in uronic acids, fatty acids, and resin acids (Sundberg *et al.* 2000a). Such species may include oxidized lignin fragments (Pranovich *et al.* 2003), but it is also possible that the polyelectrolyte interacts with neutral dissolved substances such as mannans. It also has been shown that the fatty and resin acids give a substantial contribution to charge only when present in the colloidal fraction. In chemical pulp, where a lot of the charged groups are found in oxidized cellulose, lignin fragments, and as hexenuronic acid, determinations of the carboxylic acid groups other than those described above might be needed.

### *Total Organic Carbon (TOC), Chemical Oxygen Demand (COD)*

If one makes the assumption that the components of DCS in a given system have a relatively steady proportional composition, then it follows that there might be a correlation between the amount of organic materials in a filtrate sample and the cationic demand. In fact, such correlations have been observed in several studies (Springer and Taggart 1986; Lorz and Linhart 1993; Reiter *et al.* 1998; Zhao *et al.* 2002; He *et al.* 2004). However, it should be kept in mind that many of the substances included in TOC do not contribute to charge demand, and there is usually no reason to assume that the ratio between charged and uncharged materials will remain fixed, especially when comparing different types of pulp.

### *UV absorbance as a measure of solubilized lignin*

For the estimation of lignin-related species in water, ultraviolet light absorption tests have been widely used (Alén and Hartus 1988; Sjöström 1990; Rowan and Scott 1992; Nyström *et al.* 1993; Örså and Holmbom 1994; Sundberg *et al.* 1994; Örså *et al.* 1997; Zhao *et al.* 2002; Duarte *et al.* 2003; Bhardwaj *et al.* 2006; Li *et al.* 2008; Kukkola *et al.* 2011; Liang *et al.* 2011). The 280 nm wavelength is often used in order to avoid an absorbance from certain hemicellulose-related species (Alén and Hartus 1988). However, due to differences in the UV light absorbing ability of different lignin-related species, relative to their charge characteristics (Alén and Hartus 1988), such measurements must be regarded as estimates. In mechanical pulp waters there usually is more of lignans than of lignins. To get a specific value for polymeric lignin, which potentially can form polyelectrolyte complexes, lignans should be removed by liquid-liquid extraction before the UV determination (Örså and Holmbom 1994). Also, it is

difficult to find and isolate suitable standards in order to calibrate such results based on UV absorbance.

### Stoichiometry of Polyelectrolyte Complexation

Although most analyses of colloidal charge demand by means of polyelectrolyte titrations assume a nearly 1:1 stoichiometry of interaction between charged groups at the endpoint of a charge titration, many examples already have been given in which deviations from such a relationship were observed. Because the stoichiometry of interaction between a standard polyelectrolyte and the DCS-containing sample is so critically important, the topic will be considered here in more detail. Only the endpoint condition will be considered, since it is to be understood that various charge-imbalanced PECs may exist in a colloidal suspension or solution when there is a stoichiometric excess of one of the charges (Feng *et al.* 2007a). The cited article shows examples of precipitate formation in a narrow zone, defined by a certain ratio between a polyacid and polybase. Outside of that zone, however, there was a colloidal suspension, which is an indication of complexation having taken place. Whether such colloidal matter is charge-imbalanced, charge stabilized, or represents a mixture of nearly stoichiometric PECs with excess polyelectrolytes in solution is beyond the scope of the present article.

Several different factors have been found to lead to deviations from 1:1 stoichiometry of interaction of charged groups on the titrant polyelectrolyte and the DCS components – either associated with a titration endpoint or when precipitated PECs are analyzed. These are summarized in Table 6, along with key citations from the literature.

Caution should be exercised by readers so that the large number of items in Table 6 does not obscure an important point: the rule of 1:1 stoichiometry at titration endpoints and in precipitated PECs has been found to be valid, at least as an approximation, in a great many practical cases involving strongly dissociating polyelectrolytes of relatively high charge density and mass (Webster *et al.* 1997; Mende *et al.* 2002).

#### *Effects of salt concentration*

Different theories have been developed to explain the effects of electrolyte concentration on polyelectrolyte adsorption on non-porous surfaces (van de Steeg *et al.* 1992; Fleer *et al.* 1993). In particular, van de Steeg *et al.* (1992) proposed two regimes for polyelectrolyte adsorption: If only electrostatic attraction exists between polyelectrolyte and surface, then the increase in ionic strength always decreases the amount of polyelectrolyte adsorbed (pure electrosorption), while if nonelectrostatic attraction also exists, the increase in ionic strength increases the amount of polyelectrolyte adsorbed. In the latter case, a maximum can be established if the counterions also have a specific interaction with the surface, and polyelectrolyte desorption can also occur.

In agreement with the theories proposed, experimental results obtained by Ödberg *et al.* (1995) using an ellipsometric technique showed that the thickness of an adsorbed layer of high-molecular-mass cationic polyacrylamides ( $M_w$   $5 \times 10^6$  and different charge densities) on a non-porous negatively charged silica surface increased when the electrolyte concentration was increased up to 0.5 N NaCl. Similar experimental results were later obtained by Samoshina *et al.* (2005). These results can be interpreted in terms of a three-dimensional conformation of the adsorbed polyelectrolyte, *i.e.* an expansion of

the polymer layer, and a deviation from the 1:1 stoichiometry between the polyelectrolyte and the surface when the ionic strength of the liquid medium is high (Fig. 10A).

**Table 6.** Published Explanations for Agreement or Deviations from 1:1 Stoichiometry of Polyelectrolyte Titration Endpoints

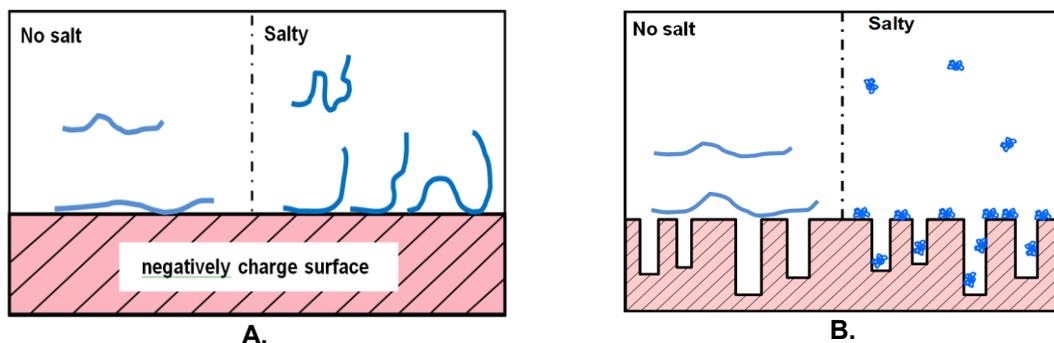
Category	Brief Explanation	Key Citations
Yes 1:1	Release of counter-ions increases the system's entropy and provides a strong driving force for 1:1 stoichiometry of complexation.	Michaels <i>et al.</i> 1965; Cundall <i>et al.</i> 1979; Argüelles-Monal <i>et al.</i> 1990
	Cooperativity of interaction between adjacent charged groups along the chains of oppositely charged PEs favors completion of PEC process.	Michaels <i>et al.</i> 1965; Petrov <i>et al.</i> 2003; Kiseleva <i>et al.</i> 2011
	A 1:1 stoichiometry was observed despite contrasting DP, charge density, <i>etc.</i>	Webster <i>et al.</i> 1997; Mende <i>et al.</i> 2002
	Polyelectrolyte titration endpoints often show good agreement with turbidity maxima and other indications of charge neutrality.	Chen <i>et al.</i> 2003; Lofton <i>et al.</i> 2005
Salt	Charge-stabilized PECs in suspension have increased thickness of stabilizing layer with increasing salt.	Kötz <i>et al.</i> 1986; Dautzenberg <i>et al.</i> 1996; Dautzenberg & K. 1999; Chen <i>et al.</i> 2003
	Surface-charge overcompensation takes place on colloidal particles and surfaces in the sample due to the 3-dimensional nature of an adsorbed layer at high salt levels or high polyelectrolyte bulk concentrations.	van de Steeg <i>et al.</i> 1992; Laine & Lindström 2000; Horvath <i>et al.</i> 2006; Mocchiutti & Zanuttini 2005
	The Debye length becomes less than the distance between charged groups in the PEs.	Laine & Lindström 2000; Horvath <i>et al.</i> 2006
	Aggregation takes place between adjacent PECs when a critical salt level is reached.	Schindler and Nordmeier 1994
	The tendency of certain PEs to adsorb onto a probe surface will decrease with increasing salt (SC method)	Kaunonen 1989; van de Steeg <i>et al.</i> 1993; Jaycock 1995
	The complexation between the titrant and DCS becomes weak at high salt levels.	Kötz <i>et al.</i> 1992; Dragan and Cristea 2001; Dautzenberg & K. 1999
	The SC signal gets close to zero at very high salt level, regardless of what else is in the system.	Chen <i>et al.</i> 2001, 2003
	High salt levels can interfere with interactions of PEs during papermaking; such effects might not be sensed to the same extent during charge titrations.	Beaudoin <i>et al.</i> 1995; Buontempo <i>et al.</i> 1996
DCS	A DCS component (PE) of low charge density may incompletely interact due to too large a contrast in charge density relative to that of the titrant.	Haronska <i>et al.</i> 1989
	The charge density is too low to achieve a strong complex with the titrant.	Haronska <i>et al.</i> 1989; Koetz <i>et al.</i> 1996; Laine & Lindström 2000
	The degree of polymerization is too low to achieve a strong complex with the titrant.	Thornton 1994
	A branched molecular structure may interfere with 1:1 complex formation with the titrant.	Polderman 1975
	The solubility of the DCS component is so low that some charges remain inaccessible to the titrant.	Koetz <i>et al.</i> 1996; Borukhov <i>et al.</i> 2000

Table 6. Continued

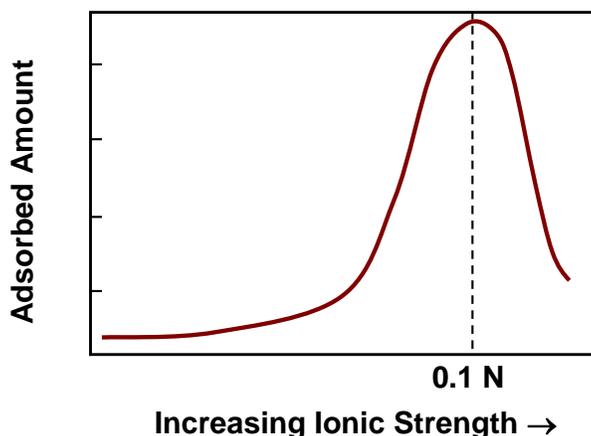
	Labile PEs in the sample change their degree of association in the course of the charge titration.	Pelton <i>et al.</i> 2007; Cui <i>et al.</i> 2008; Feng <i>et al.</i> 2008; Pelton 2010
	A “guest-host” interaction between large titrant molecules and tiny DCS molecules favors soluble PECs that don’t give a clear endpoint.	Kabanov & Zezin 1984; Ström and Stenius 1987
	The structure of DCS leads to slow kinetics, so that the system does not approach equilibrium within the time allowed for titration.	Ström and Stenius 1987; Phipps 1992; Dautzenberg & K. 1999; Naderi <i>et al.</i> 2005; Vanerek & van de Ven 2006
	Weak PEs (especially with carboxyl groups and non-quaternary amine groups) may be uncharged, dependent on the pH.	Hattori <i>et al.</i> 1994
	Weak PEs (especially with carboxyl groups and non-quaternary amine groups) may form ion pairs during complexation.	Horn 1980; Haronska <i>et al.</i> 1989; Thornton 1994; Horvath <i>et al.</i> 2006;
	There are non-charge-related interactions between the DCS and the PE.	Phipps 1992
	Depending on the nature of the DCS & other details, the PECs have widely diverse forms: a colloid, a bulk precipitate, or soluble.	Ström <i>et al.</i> 1979, 1982; Vanerek & van de Ven 2006
Other	Counter-ion shielding prevents some groups from participating in the interaction.	Fardim <i>et al.</i> 2002
	Shrinkage of PECs with time and salinity conditions implies a complicated interpretation of turbidimetric endpoints.	Wang <i>et al.</i> 2011
	Interference by relatively weak interactions of multivalent inorganic ions obscures endpoints.	Michaels <i>et al.</i> 1965; Kekkonen <i>et al.</i> 2001
	Participation of surface-active species in the complexation complicates endpoints.	Dubin & Davis 1985; Leung & Goddard 1985; Naderi <i>et al.</i> 2005
	The inflexibility of polyelectrolyte chains is predicted to prevent 1:1 pairing in some cases, according to molecular dynamics simulations.	Ullner & Jonsson 1996
	Certain polyelectrolyte titrants may interact with DCS even more strongly than poly-DADMAC.	Nicu <i>et al.</i> 2011

Figure 10B shows an alternative model, in which the increased adsorption with increasing salinity is attributed to greater permeation of the polyelectrolyte into the fine pores of cellulosic material. It is possible that both mechanisms could operate simultaneously, especially if polyelectrolytes of widely different chain length are present.

Horvath *et al.* (2006) studied the effects of electrolyte concentration on the adsorption of a high-molecular-mass poly-DADMAC ( $9.2 \times 10^5$  Da) on porous surfaces, such as cellulosic fibers. They found an initial increase in the amount of the polyelectrolyte adsorbed when the ionic strength of the solution was increased up to 0.1N  $\text{NaHCO}_3$ , after which the adsorption decreased to zero (Fig. 11). Similar results were previously shown by other authors (van de Ven 2000; Wågberg *et al.* 2000).



**Fig. 10.** Two models to account for increased adsorption of cationic polymer with increasing ionic strength of the medium. A: Salinity decreases the effective range of electrostatic forces, resulting in an extended conformation in which fewer segments of each polyelectrolyte molecule interact with the substrate. B: Salinity results in a more condensed conformation of the polyelectrolyte such that it can permeate into smaller pores and more macromolecules can fit per unit area of substrate.



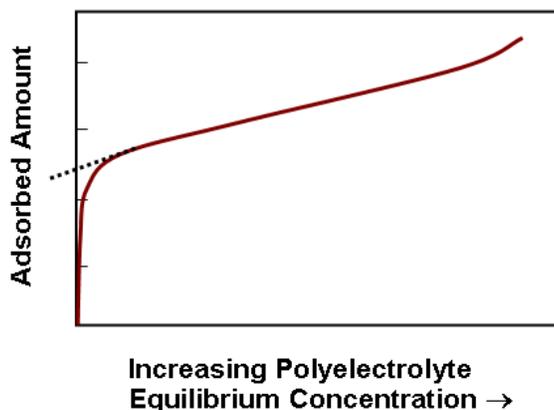
**Fig. 11.** Schematic relation between the amount of a high charge density and high-molecular-mass linear polyelectrolyte adsorbed on porous cellulosic fibers at a given equilibrium concentration and ionic strength

As proposed by Horvath *et al.* (2006), the initial increase can be caused by both: a) the swelling of the adsorbed layer, which means transformation from a flat polymer conformation on the surface to loops and tails (Laine and Lindström 2000), and b) the penetration of the coiled polyelectrolyte into the swollen fiber cell wall (Fig. 10B). In both cases, surface charge overcompensation can be established. They also suggested that the sharp decrease sometimes observed in the amount adsorbed when the electrolyte concentration is higher than 0.1N NaHCO<sub>3</sub> because only electrostatic interactions exist in such cases between the polyelectrolyte and the surface (*i.e.* pure electrosorption).

Laine and Lindström (2000) and Horvath *et al.* (2006) ascribed the deviation from stoichiometry to the fact that when the ionic strength of the solution is high, the thickness of the electrical double (Debye length) layer decreases, and eventually the distance between the polyelectrolyte charges exceeds the thickness of the double layer. In that case, the ionized groups appear as discrete charges instead of as a large multivalent charge, causing the adsorption to deviate from stoichiometry.

### Effects of polyelectrolyte bulk concentration

A simple model with a fixed number of adsorbable sites at solid surfaces in a papermaking suspension might lead one to expect that the amount of a highly charged cationic polyelectrolyte adsorbing onto cellulosic fibers would reach a plateau and then not increase further as the bulk concentration of the polyelectrolyte is further increased. Nevertheless, when the adsorption capacity of the surface becomes saturated by the polyelectrolyte, a three-dimensional adsorbed layer has been suggested (Hesselink 1977) and the isotherm never becomes completely horizontal (Fig. 12).



**Fig. 12.** Schematic relation between the amount of polyelectrolyte adsorbed as a function of the polyelectrolyte equilibrium concentration

Experimental adsorption isotherms of high-molecular-mass and high-charge-density linear polyelectrolytes on fibers at a constant and low ionic strength of the liquid medium (different to zero) showed behavior similar to Fig. 12 (Wågberg *et al.* 1989, Mocchiutti and Zanuttini 2005; Lingström *et al.* 2006, Horvath *et al.* 2006). At zero ionic strength of the liquid medium, an apparent plateau level can be reached (Lingström *et al.* 2006), probably because only in that case the polyelectrolyte is stoichiometrically adsorbed (Laine and Lindström 2000) in a flat form.

Three likely contributing mechanisms have been proposed to explain the phenomenon:

(1) One well-established explanation is based on the fact that most commercially available polymer samples have relatively broad distributions of molecular mass (see, for instance, Swerin and Wågberg 1994). For nonionic polymer samples, theoretical and experimental investigations of Cohen Stuart *et al.* (1980) showed that lower molecular mass polymers have higher rates of diffusion, so they tend to reach surface sites sooner. But they later tend to be replaced by higher molecular mass chains. If the adsorption is at least somewhat three-dimensional, then a higher molecular mass adsorbed polymer implies a higher adsorbed amount per unit of external surface area. Furthermore, if the bulk concentration is higher, then there is a larger pool of relatively high-mass macromolecules capable of replacing the early-arriving adsorbate molecules. Nevertheless, for polyelectrolyte samples, Tanaka *et al.* (1997) showed that the effects of molecular mass on the adsorption onto anionic non-porous surfaces can be small.

(2) A second explanation assumes that the process has substantial irreversible character (Claesson *et al.* 2005; Wen *et al.* 2012). In other words, one makes the assumption that the polyelectrolytes are sufficiently large and interactive so that they become trapped into non-equilibrium conformations, depending on the details of the adsorption process. If the bulk concentration of polyelectrolyte is sufficiently low, then an adsorbing polymer has the opportunity to spread to a preferred, relatively flat conformation. By contrast, when the bulk concentration is higher, the opportunities of each adsorbed macromolecule to spread out are more limited, due to the competition between adjacent adsorbed macromolecules. As a consequence, each polymer, on average, gets trapped into a more extended adsorbed conformation with a larger proportion not in contact with the surface.

(3) Mocchiutti and Zanuttini (2005) proposed that the behavior shown in Fig. 12 can arise from equilibrium considerations when a variable excess of polyelectrolytes in solution are competing for a fixed number of adsorption sites at the surface. As the polyelectrolyte bulk concentration increases, the amount of free adsorption sites decreases, and the fraction of the polymer adsorbed in the form of loops and tails increases. Since this explanation is relatively new, further research may be encouraged to determine its range of utility. The proposed approach makes it possible to determine the accessible surface charges, which is normally estimated by the extrapolation of the linear-like portion of the isotherm to zero polyelectrolyte concentration (Wågberg *et al.* 1989).

Polyelectrolyte additives used routinely in papermaking processes often have relatively high charge density and high molecular mass. Thus they would appear well designed for analysis by charge titration. However, this is not true universally; the presence of various low-charge-density materials, such as some starch products in paper machine systems can be expected to make charge analysis more challenging to carry out and interpret in such cases. Wet-end chemical system involving relatively weak complexation interactions have been considered by several authors (Kam and Gregory 1999; Laine and Lindström 2000; Vanerek and van de Ven 2006; Feng *et al.* 2008).

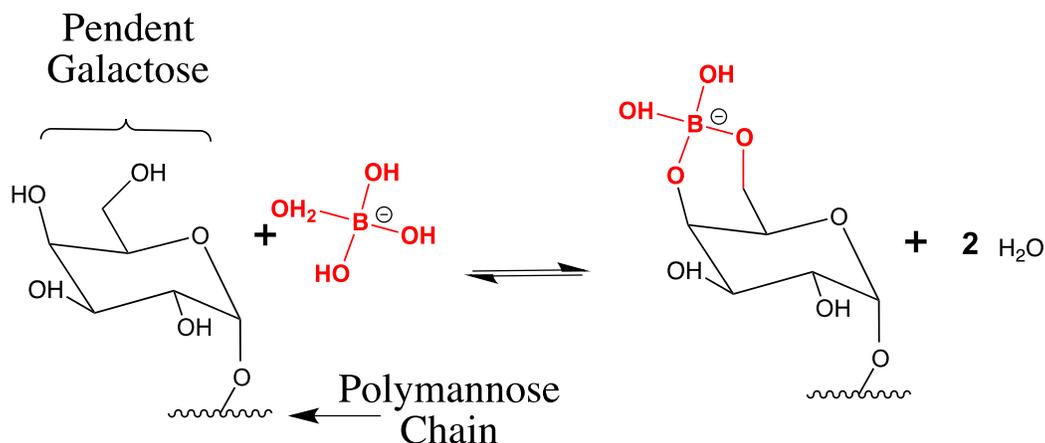
#### *Weak complexation of a different type*

A situation involving weak complexation was revealed recently, with a labile polyelectrolyte, the hydroxypropylguar (HPG)-borate system (Pelton *et al.* 2007; Cui *et al.* 2008; Feng *et al.* 2008). Guar and hydroxypropyl guar are nonionic water-soluble polymers. However, in the presence of borate ions, guar becomes an anionic polyelectrolyte because borate ions condense onto the galactose sugars (see Fig. 13).

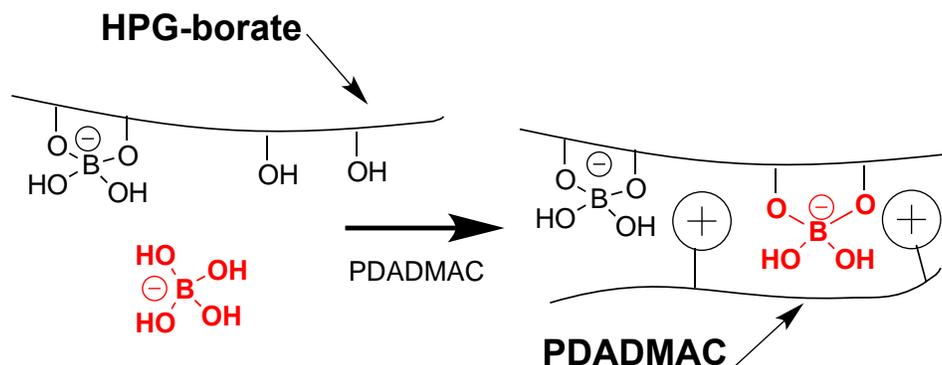
Because the binding energy of borate to HPG is low, the fraction of occupied borate binding sites is sensitive to the local environment. For example, upon adding polyDADMAC to HPG-borate, a polyelectrolyte complex forms. Since the complex is nearer to zero net charge density than HPG-borate alone, more borate groups condense onto HPG until it is saturated with bound borate (see Fig. 14). This complexation-induced binding of the labile borate groups can account for the unusual shape of the polyelectrolyte titration curve shown earlier in Fig. 9.

Guar with borate is generally not used in papermaking. However, the above example illustrates the complexities introduced by weak ion/polymer interactions. Aluminum species and other complex cations may be expected to show similar behaviors that are difficult to identify in complex papermaking suspensions, particularly in highly

closed systems. Another situation that has been found to give rise to streaming current titration curves resembling that shown in Fig. 9 is when the sample is a low-charge, hydrophilic polymer solution, *i.e.* oxidized starch (Chen *et al.* 2001); in such a case the interaction between the cationic titrant and the anionic polyelectrolytes in the sample are relatively weak.



**Fig. 13.** Borate anion condenses onto galactose units of guar or HPG converting a nonionic polymer to an anionic polyelectrolyte

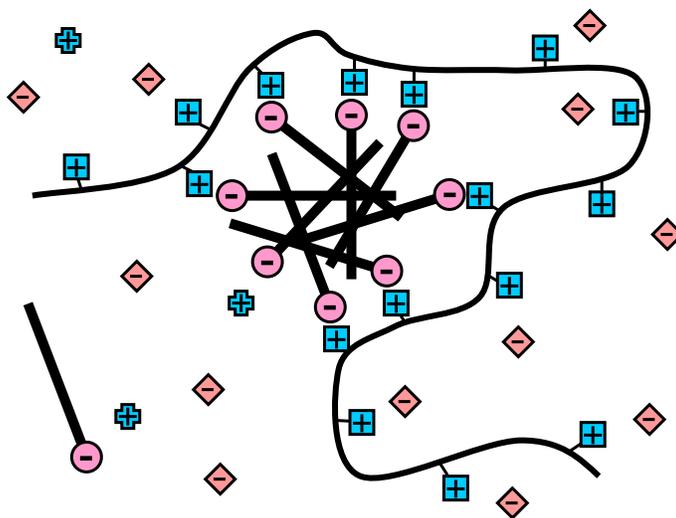


**Fig. 14.** The density bound borate ions on HPG increases with poly-DADMAC complex formation because the cationic groups facilitate borate ion approach and condensation

#### *Concern about a possible role of surfactants*

As was noted in Table 6, some researchers have reported that the presence of surfactants can interfere with the endpoints of polyelectrolyte titrations (Dubin and Davis 1985; Leung and Goddard 1985; Naderi *et al.* 2005). Figure 15 represents a situation in which an anionic surfactant molecule, *e.g.* fatty acid soap, would be expected to interact with a cationic titrant molecule or perhaps with a cationic polymer additive to the paper machine system. As noted by Goddard (1986), anionic surfactants can cause major changes in the conformation and other properties of a cationic polyelectrolyte. Again, factors that favor such complexation include (a) the multi-charged nature of a micelle or surfactant-stabilized colloidal particle formed with the charged surface-active molecules,

and (b) the greater degrees of freedom experienced by the counter-ions that can be freed up upon interaction between the polyelectrolyte and the micelle. Work by Zheng and Cao (2001) showed that some such interactions can be highly stoichiometric and involve cooperative interactions in the case of sodium dodecyl sulfate (SDS) micelles interacting with ionene polycations. Further research will be needed in order to understand whether and to what extent such surfactant interactions tend to interfere with or shift the results of polyelectrolyte titrations in papermaking systems.



**Fig. 15.** Schematic diagram representing the interaction between a cationic polyelectrolyte and anionic surfactant molecules, e.g. fatty acid soap. Squares with “+” sign represent charges along the polymer chain. Diamonds with “-” sign represent counter-ions originally or still associated with the polyelectrolyte. Circles with a “-” sign represent the carboxylate or other negative ionic group of the surfactant, the hydrophobic part of which is represented by a heavy line. Counter-ions originally associated with the surfactant molecules are represented by a “+” inside a similar shape.

## ASPECTS DESERVING FURTHER RESEARCH

### Strategies for Dealing with DCS

#### *What’s next in scavenger use?*

Since the 1970s there have been numerous articles recommending the use of inexpensive, high-charge cationic additives to at least partly neutralize the excess DCS in paper machine systems, thereby achieving more rapid drainage and better efficiency of high-mass acrylamide-type retention aids (Auhorn and Melzer 1979; Linhart *et al.* 1987; Patton and Lee 1993; Neimo 1993; Glittenbert *et al.* 1994; Näsman *et al.* 1998; Kunzel and Prinz 2006; Belosinschi and Bobu 2008; Chen *et al.* 2010). In principle, the idea is to employ a high-charge cationic additive to bind colloidal materials to larger cellulosic fines or fibers, taking advantage of either a charge-patch mechanism or charge neutralization (Chung *et al.* 1993; Sundberg *et al.* 1993). However, overdosing should be avoided. Though the use of scavenger chemicals has become common, the industry still has a long way to go with respect to automatic control the charge demand. Many paper

machines either lack such equipment or have not yet implemented automatic control of the flow of a scavenger chemical.

Poly-DADMAC, polyethyleneimine (PEI), and polydimethylamine-epichlorohydrin (PAE) are commonly used as scavengers to overcome the problems associated with the use of BCTMP and other high-yield pulp (HYP) types. Li *et al.* (2001 and 2002a) reported that the negative effect of the DCS of BCTMP/HYP on internal alkylketene dimeter (AKD) or rosin ester sizing could be eliminated by the addition of the high-charge cationic polymers polyDADMAC, PEI, or PAE. Although HYP contains much more fines and DCS than bleached kraft pulp (BKP), a partial substitution of BKP with HYP can actually improve AKD sizing, provided that a charge scavenger is used properly. Recently, Chen *et al.* (2012a,b) reported that using cationic polymers, such as PAC, PEI, cPAM, Poly-DADMAC, can significantly improve the alkenyl succinic anhydride (AKD) sizing efficiency in high-yield pulp containing furnish.

The next generation of charge scavengers could be starch-based cationic polymers, which are greener and more cost-effective. Such additives have the potential to be sustainable, renewable, and biodegradable. Zhang *et al.* (2007 and 2009) found that the addition of a highly substituted cationic starch (HS-CS) could essentially eliminate the negative effect of the DCS of BCTMP/HYP on the performance of a dual-component retention system. Studies using optical and atomic force microscopy (AFM) indicated that the addition of HS-CS caused the DCS to aggregate and deposit on the surface of pulp fibers, most likely by a charge neutralization mechanism.

Another option for scavenging DCS is to pre-adsorb a high-charge cationic agent onto very fine solid material. As an example, Guyard *et al.* (2006) described the modification of silica particles with a high-charge cationic polymer. The pretreated mineral was found to be effective for adsorbing polygalacturonic acids and retaining the precipitated material in the paper sheet.

#### *Points of addition*

The next question that is often asked, after it has been decided to modulate cationic demand levels on a paper machine by adding a high-charge cationic agent, is where to add it. One reasonable strategy is to add the high-charge agent relatively near to the end of the process so that only a few seconds of time need to pass before the affected furnish has been made into paper (Kaunonen 1989; Veal 1997; Bley 1998; Rantala *et al.* 1999). By this approach one stands to minimize the permeation of the scavenger molecules into the mesopore spaces of the fiber (Wu *et al.* 2009), a process that essentially inactivates some of the additive, reducing its efficiency as a charge-control agent. However, many papermakers believe that it is more prudent to make sure that the excess DCS levels are moderated and under steady control *before* the stock is diluted at the fan pump of a paper machine. Thus it has been suggested to add a scavenger chemical to whichever of the thick-stock streams that contains either the highest level of DCS or the greatest variability of DCS (Nikkinen *et al.* 2001; Gruber *et al.* 2003). Such strategies can be paired with online charge titration equipment that is capable of automatically sampling filtrate from a fiber suspension (Nikkinen *et al.* 2001; Rice and Roeraade 2003).

### *Management of colloidal materials*

As has been shown, precipitation of solids from solution may occur when high-charge cationic additives are used to neutralize the charge of DCS in paper machine process water (Sundberg *et al.* 1994a; Leiviskä and Rämö 2008). Studies are needed in order to better predict whether the consequence of such precipitation will be beneficial or not in a given case. Under favorable circumstances the precipitation of DCS may result in more rapid dewatering, more efficient retention, reduction in deposits on papermaking equipment, and better sheet properties (Ström and Stenius 1987; Kaunonen 1989; Bley 1992; Stetter and Eisenschmid 1993; Stitt 1998; Gliese 2000; Zhang *et al.* 2007, 2009; Mocchiutti *et al.* 2011). Ideally one can expect the precipitated material in a paper machine system to either adhere to fiber surfaces or to form sufficiently large agglomerates to allow efficient retention by a filtration mechanism when the paper is being formed (Wågberg and Ödberg 1991). But under unfavorable conditions the precipitated material may cause deposits and papermaking equipment, the filling of press-felts, and spots in the product (Gill 1996). For instance, a study by Miranda *et al.* (2008) analyzed the different components of tacky deposits in a newsprint mill used 100% recovered fibers; wood pitch components, as well as various other materials falling into the category of DCS were found to be major contributors to deposits in that system.

### *When to incorporate polyelectrolyte complexes (PECs) into the paper*

Before considering strategies for possible removal of DCS materials, or of complexes formed by their neutralization, from the paper machine system, it is worth noting that PECs often can play positive roles in papermaking. For instance, Petzold *et al.* (1997) used precipitation of PECs as a means of modifying fibers surfaces. *In-situ* formation of PECs by sequential addition of oppositely charged polyelectrolytes to an agitated fiber suspension can be used as a means to achieve unusually high dry-strength levels (Lofton *et al.* 2005; Hubbe 2005b; Hubbe *et al.* 2005). In the cited studies both the retention of the PECs and their beneficial effects on strength tended to be maximized when the PECs had a slight excess of charge, opposite to that of the fibers. Heermann *et al.* (2006) showed that by the *in-situ* addition strategy it was possible to use very high chemical addition levels and surprisingly high strength levels; by contrast, sticky precipitates resulted if the polyelectrolytes were allowed to mix with each other before their addition to the furnish.

Another approach to increasing dry strength is based on the use of a highly branched or cross-linked anionic polyelectrolyte (*i.e.* a “gel”), the charge properties and other attributes of which can be modified by treatment with a lesser amount of high-charge cationic polyelectrolyte (Wen *et al.* 2012). Such structures were shown to provide substantial adhesion in papermaking applications, even in the wet state (Wen and Pelton 2012a,b). The effectiveness of the gel structures in achieving adhesion was attributed, in part, to the relatively large size of the water-swollen structures, as well as the positive charge of their surfaces, factors that tend to hold the macromolecular material at the outside surfaces of a cellulosic substrate.

### *When to break down DCS to render it harmless*

When pectinase enzymes are used to break down polygalacturonic acids (pectic acids) and related materials, there is no denying that the cationic demand and its

consequences can be sharply reduced (Thornton 1994; Thornton *et al.* 1996; Bobu *et al.* 1999; Reid and Ricard 2000; Ricard and Reid 2004; Ricard and Orcotoma 2005; Ricard *et al.* 2005; Li *et al.* 2006; Mou *et al.* 2008; Zhang *et al.* 2008; Liu *et al.* 2010a,b; Miao *et al.* 2010; Yang *et al.* 2010; Zhang *et al.* 2010; Pruszyński *et al.* 2011). Despite such demonstrations of effectiveness, greater consideration of pectinase treatment may be discouraged by the relatively high pH conditions prevailing in many modern paper machine systems. Whereas pectinase has been found to work well in a pH range of about 5.0 to 5.5, which can easily be achieved in systems where SO<sub>2</sub> is being used to control pH, it has become more common to maintain the pH in a weakly alkaline range for a wide range of printing grades of paper (Pruszyński 2012). Pectinase treatments are also sensitive to temperature conditions, and a provision must be made for about 20 to 30 minutes of contact time between the enzyme and the furnish. Another inherent consequence of treatments with pectinase, however, is the release of low-mass saccharide oligomers (Thornton 1994). A question that does not appear to have been adequately addressed in the scientific literature is whether such low-mass sugar-like material is likely to favor the proliferation of slime bacteria (Hoekstra 1991). Industrial-scale trials with pectinase have not shown increased microbiological problems, pitch problems, or increased effluent treatment costs (Pruszyński *et al.* 2011).

Lipase treatment has been proposed as a way to overcome adverse consequences of esterified components in wood resin (pitch), which can be key contributors to pitch deposit problems on paper machines (Lindberg *et al.* 2001; Mustranta *et al.* 2001; Rundlöf *et al.* 2002). Blanco *et al.* (2009) demonstrated the use of thermostable lipases in reducing the levels of triglyceride fats present in a suspension of thermomechanical pulp. Lindberg *et al.* (2001) showed that unsaturated fatty acids can be further broken down by enzymes exuded from suitable bacteria. Because fatty acids, when acting as stabilizers for colloidal particles, can contribute to cationic demand, such lipase treatments have particular relevance; rather than being a strategy to help overcome problems with cationic demand, they have potential to increase the cationic demand. This example helps to illustrate the importance that papermakers place on solving their most serious seasonal pitch problems.

Laccases are another enzyme system that has potential to be used with certain DCS components. Zhang *et al.* (2002, 2005) showed that certain extractives could be broken down by laccase.

### Strategies to Remove DCS

The option to “remove” DCS from a paper machine system is left almost to the end of this discussion due to the presumption that anything requiring a new unit operation – and most likely an additional piece of equipment – may be expensive. Other options, some not requiring a capital investment, should be considered first. Alternatively, even if a capital investment is justified in order to reduce consequences of DCS in a paper machine system, sometimes the solution may involve an upgrade or replacement of existing pulp-washing equipment (Pacheco *et al.* 2006; Lind 2011).

Tanase *et al.* (2010) studied the use of a filter press as a means of removing extractives after thermomechanical pulping of spruce. They showed that cationic polymers could be used to precipitate hydrophobic components, though the removal

efficiency varied between DCS component and wood species. The authors attributed some of the differences to morphological features of the fibers.

Dissolved air flotation (DAF) technologies are widely used for contaminant removal during deinking (Ajersch and Pelton 1999; Mehta *et al.* 2004). Ben *et al.* (2003) found that the efficiency of a DAF unit to remove DCS components was very low. Monte *et al.* (2009a,b, 2011) reported low, but at least stable performance of a DAF unit in removing DCS components. Notably, the most effective removal of pitch-like substances was observed following pretreatment of the water with soluble aluminum compounds and their mixtures with high-charge cationic polyelectrolytes (Monte *et al.* 2009a, Miranda *et al.* 2009b,c). Saarimaa *et al.* (2006a) showed that a DAF unit could remove 90% of pitch from TMP water in the presence of an inorganic coagulant and an organic flocculant. Opedal *et al.* (2011) showed that DAF, plus the use of poly-DADMAC and cationic acrylamide retention aid, could be quite effective in removing extractives from pretreated wood chips. Leviska and Ramo (2008) also showed that chemical treatments were able to remove 92% of the wood extractives.

Ultrafiltration (UF) membrane units have been used to purify paper machine process water. Nuortila-Jokinen *et al.* (1994) found that such equipment could increase the brightness of the resulting paper by removing various chromophores that were believed to come from the lignin and carbohydrate fractions. Monte *et al.* (2011) found that UF equipment was very effective, at least initially, in removing DCS from process water. However, the performance of the UF membranes in removing the dissolved and colloidal fractions fell by 75% and 30%, respectively, during a week of continuous operation.

Thickening of pulp by pressing is commonly practiced at bleached chemi-thermo-mechanical pulp (BCTMP) mills. This approach has proved to be cost-effective in removing DCS from bleached mechanical pulp. Babineau *et al.* (2003) found that when the consistency of a mill-produced BCTMP was increased from 13% to 30% by pressing, its DCS content decreased by 70%. They also found that acidification after alkaline peroxide bleaching could reduce DCS content significantly, due to the re-deposition of the oxidized lignin dissolved in the liquid phase onto the surface of pulp fibers. A flash-drying process can further decrease the amount of DCS in the commercial BCTMP due to the irreversible adsorption of some of the dissolved and colloidal substances (DCS) onto fibers. However, in comparison to bleached kraft pulp, commercial BCTMP still contains more DCS, which may lead to changes of the wet-end chemistry of the papermaking process when BCTMP is substituted for bleached hardwood.

### **Option to Leave Some or All DCS in the Furnish**

One issue that merits more research attention is the question of whether some or all of the DCS provides sufficient benefit to either the papermaking process or to the paper product so that it is better to leave some or all of it in the furnish. For instance, hemicelluloses are known to contribute to the dry strength of paper (Hannuksela *et al.* 2004; Helmerius *et al.* 2010; Bai *et al.* 2012). Also, various hemicellulose-related components can inhibit the undesirable deposition of pitch particles under some conditions (Sundberg *et al.* 1993; Johnsen *et al.* 2004). Future studies might consider, for instance, the feasibility of removing “bad DCS” from the furnish, while allowing “good DCS” to remain. The definition of the terms good and bad could be part of such studies.

Alternatively, a partial washing approach might be used, so that a balance can be achieved between paper machine runnability, product quality, and operational costs.

## CONCLUDING REMARKS

The interactions of conventional papermaking polymeric additives with fillers, fibers, and DCS are dominated by electrostatic interactions. Thus, most polyelectrolytes used as scavengers for DCS removal are cationic. So are many of the retention aids, strength-enhancing polymers, and polymers used to stabilize emulsions of hydrophobic sizing agents. There are no silver bullets; a DCS-rich stock requires more chemicals compared to cleaner stocks.

Speculating about future trends is always fun, but suspect. From an industry perspective we can anticipate cleaner stocks in the future because of increasing recycling, with its necessary de-inking and washing steps. In the somewhat longer term, biorefinery activities can be expected to remove some of the DCS components for other potential uses and chemical transformations. On the other hand, as papermaking expands in drier parts of the world, we should expect much more closure of paper machine water circuits, resulting in great increases in the ionic strength of papermaking stocks. High electrolyte contents attenuate electrostatic interactions, perhaps requiring new papermaking chemicals.

For the chemical suppliers, the challenge is to move away from our dependency on simple electrostatic interactions. Biology offers much inspiration. Biochemical systems depend upon very specific polymer/polymer (mainly protein) interactions in very salty media. Perhaps the earliest example of bio-inspired paper chemicals is the use of cellulose-binding domains (modules) to promote specific adhesion to cellulose (Kitaoka *et al.* 2001; Levy *et al.* 2002; Yokota *et al.* 2008). Cellulose binding domains are the part of cellulase enzyme protein that specifically adheres to cellulose.

More recently, DNA aptamers that specifically bind to cellulose have been reported (Boese and Breaker 2007). These are short, synthetic single strands of DNA that, in the presence of metal ions, fold into a specific shape. Recently, these cellulose aptamers have been grafted onto polyacrylamide giving a new type of polymer that strongly adsorbs onto cellulose particularly in the presence of high calcium ion concentrations (Sato *et al.* 2012).

When one considers the large extent and quality of research that went into the studies cited in this review article, it is tempting to conclude that the physical chemistry of papermaking is pretty well understood. However, much of our current understanding comes from experiments with model systems that are much cleaner than papermaking furnishes. The work cited in the present article shows clearly that the DCS in a typical pulp suspension, *i.e.* the dirty components, can have profound and complex effects. Clearly not all interactions within such systems can be understood just based on models related to polyelectrolyte complexes. Rather, the charge demand interactions within paper machine systems need to be placed within a broader context, taking advantage of improvements in sensing devices, computational approaches, and a fuller range of molecular interactions besides just charge-based interactions.

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## ABBREVIATIONS AND ACRONYMS

AFM: Atomic force microscopy (an imaging method)  
AKD: Alkylketene dimer (hydrophobic sizing agent)  
CCC: Critical coagulation concentration  
COD: Chemical oxygen demand  
cPAM: Cationic copolymer for acrylamide (retention aid)  
CTMP: Chemi-thermomechanical pulp  
DAF: Dissolved air flotation (a water-treatment system)  
DCS: Dissolved and colloidal substances  
HexA: Hexenuronic acid  
HPG: Hydroxypropyl guar  
HS-CS: Highly substituted cationic starch  
HYP: High-yield pulp, *i.e.* mechanical pulp  
PAC: Polyaluminum chloride  
PE: Polyelectrolyte  
PEC: Polyelectrolyte complex  
PEI: Polyethyleneimine (high-charge cationic polymer)  
Poly-DADMAC: poly-diallyldimethylammonium chloride (*e.g.* cationic titrant)  
PVSK: Polyvinylsulfate, potassium salt (anionic titrant)  
SC: Streaming current (endpoint detection method)  
TCF: Totally chlorine free (bleaching sequences)  
TMP: Thermomechanical pulp  
TOC: Total organic carbon  
UF: Ultrafiltration (a water treatment system)  
UV: Ultraviolet  
XPS: X-ray photoelectron spectroscopy

## KEY TERMS

**Cationic demand:** The amount of standard cationic titrant required to reach a neutral point when titrating an aqueous sample (often expressed as milliequivalents per unit mass or volume of sample)

**Charge demand:** The amount of a standard high-charge polyelectrolyte required to neutralize the net ionic charge of DCS. This is a more general term used when one wants to recognize the possibility of a process water sample with a

net-positive charge due to an overdose of cationic additives (*i.e.* anionic demand)

**Dissolved and colloidal substances (DCS):** The sum of polyelectrolytes, other dissolved substances, and very small suspended particles (at least one dimension smaller than 1  $\mu\text{m}$ ) present in an aqueous suspension

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