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ADSORPTION OF LIGNIN AND LIGNIN/CATIONIC POLYMER COMPLEXES ON CELLULOSE FIBRES AND THEIR EFFECT ON SHEET PROPERTIES

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ABSTRACT OF DOCTORAL DISSERTATION

Author Natalia Maximova

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Supervisor	Professor Janne Laine
(Instructor)	Emeritus professor Per Stenius

Abstract

The objective of this dissertation was to deepen the understanding of lignin uptake by cellulose fibres by systematic studies under well-controlled conditions, and to clarify its effect on the papermaking properties of the fibres. It was possible to gain some direct insight into lignin sorption mechanisms by a comprehensive approach including studies of lignin behaviour in the solution, adsorption measurements and surface chemistry examination, studies of lignin distribution in the fibres, as well as analysis of sheet technical properties. It was found that van der Waals' interactions between lignin and fibres in aqueous dispersion are very weak and do not overcome the mutual electrostatic repulsion. No lignin is adsorbed from aqueous lignin solutions onto pure cellulose fibres: lignin loosely attaches to bleached fibres by imbibition with solution and filtration effect, and can be washed away with water. However, in sheets lignin binds to the fibres: some lignin is distributed throughout the cell wall, but the major part is located in the layers formed between the fibres. Restrained drying is responsible for binding of trapped lignin to the fibrous mat.

Irreversible adsorption may occur in the presence of cationic polymers. The course of adsorption depended on the sequence of polymer addition. Kraft lignin is adsorbed as a monolayer onto cationised surfaces. In the aqueous solutions lignin and cationic polymers (PDADMAC and cationic starch (CS)) form both soluble and insoluble complexes, which are cationic or anionic, depending on the lignin/cationic polymer charge ratio. The complexes adsorb on kraft pulp fibres (and mica), especially at low lignin/polyelectrolyte ratios, when the complexes are cationic, covering the surface with patches, films or blobs. The driving force for adsorption of lignin/cationic polymer complexes on chemical pulp fibres is primarily electrostatic: adsorption takes place as long as the fibre surface and the lignin are oppositely charged. Adsorption of complexes is highly dependent on the sequence of addition of lignin and cationic polymer. If the complexes are formed in solution prior to adsorption on the fibres there is a relatively sharp maximum in adsorption at cationic polymer/lignin ratios below the isoelectric point. If complexes are formed directly on the fibre surface (adsorption of lignin on fibres treated with cationic polymer) the isotherm reaches a plateau value. Adsorbed complexes are located on the outermost surface of the fibres, which leads to brightness losses. Papers made from fibers with adsorbed lignin complexes exhibit improved strength and water resistance. This could be utilized in the manufacture of packaging grades of paper. Lignin particles in the solution are elongated and are about 1 nm thick and 2.5 nm wide. They adsorb onto cationised substrates in the form of individual granules, consisting of about 20 primary lignin particles that are held together by strong cohesive forces.

Keywords Lignin, fibres, cationic polymers, complexes, adsorption, paper properties, wetting, interfacial behaviour

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Лучшей из матерей,
тебе, моя родная,
с благодарностью и любовью

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Espoo, May 31, 2004
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LIST OF PUBLICATIONS

This dissertation is based on the following papers (Appendices I–V), which are referred to in the text by their Roman numerals.

I. *Maximova, N., Stenius, P., Salmi, J.:* Lignin uptake by cellulose fibres from aqueous solutions. Nord. Pulp Pap. Res. J. 2 (2004), 135-145.

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II. *Maximova, N., Österberg, M., Koljonen, K., Stenius, P.:* Lignin adsorption on cellulose fibre surfaces: Effect on surface chemistry, surface morphology and paper strength. Cellulose 8(2001), 113–125.

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III. *Maximova, N., Stenius, P., Laine, J.* Adsorption of Lignin-Cationic Starch Complexes on Cellulose Fibres and their Effect on Sheet Properties. Peer-reviewed and accepted to Paperi ja Puu. May 2004.

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IV. *Maximova, N., Österberg, M., Laine, J., Stenius, P.:* The wetting properties and morphology of lignin adsorbed on cellulose fibres and mica. Colloids Surf.A. 239 (2004), 65-75.

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V. *Vainio, U., Maximova, N., Hortling, B., Laine, J., Stenius, P., Simola, L.K., Gravitis, J., Serimaa, R.:* Morphology of dry lignins and size and shape of dissolved lignin particles by x-ray scattering. Langmuir 20 (2004), 9736–9744.

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AUTHOR'S CONTRIBUTION

I. Planning, experiments (main part), interpretation of the results, writing and publishing work under supervision of Per Stenius (co-author). Surface force measurements by J. Salmi (co-author). CLSM imaging performed by Patricia Moss as indicated in Acknowledgements. Basic laboratory analyses performed with the help of laboratory assistants indicated in Acknowledgements.

II. Planning, electrophoretic mobilities and adsorption experiments, samples design, interpretation of the results, and main writing under supervision of Per Stenius (co-author), AFM part and publishing work by M. Österberg (co-author), paper strength part by K. Koljonen (co-author). ESCA measurements performed by Leena-Sisko Johansson and Joseph Campbell as indicated in Acknowledgements. Basic laboratory analyses were performed with the help of laboratory assistants indicated in Acknowledgements.

III. Planning, experiments, interpretation of the results, writing and publishing work under supervision of Janne Laine and Per Stenius (co-authors). CLSM imaging performed by Patricia Moss as indicated in Acknowledgements. ESCA measurements performed by Leena-Sisko Johansson as indicated in Acknowledgements. Basic laboratory analyses were performed with the help of laboratory assistance indicated in Acknowledgements.

IV. Planning, samples design, adsorption and contact angle measurements, data analysis, writing and publishing work under supervision of Janne Laine and Per Stenius (co-authors). AFM part by M. Österberg (co-author). Basic laboratory routine (kappa measurements and handsheet formation) performed with the help of laboratory assistants indicated in Acknowledgements.

V. Carrying out dissolved lignin sampling and electrophoretic mobilities experiments, assisting with USAXS measurements, and contributing to writing under supervision of Janne Laine and Per Stenius (section 3.3, "Dissolved kraft lignin" and Table 1, "Previous Studies Concerning the size and shape of lignin particles in solution"). The first author (Ulla Vainio) carried out SAXS/USAXS measurements, their interpretation and main writing.

SYNOPSES OF THE ARTICLES

I. Van der Waals' interactions between lignin and fibres in aqueous dispersion are very weak and do not overcome the mutual electrostatic repulsion. Adding calcium and aluminium to the solutions induces precipitation of lignin flocs onto the fibres as long as the negative charge on lignin is neutralized. Lignin loosely attaches to bleached fibres by imbibition with solution and filtration effect, forming layers between the fibres upon drying.

II. Irreversible adsorption of lignin on cellulose fibres is achieved only in the presence of cationic polymer. Adsorption depends on the sequence of polymers addition. Lignin irreversibly adsorbs as a granular monolayer onto PDADMAC-treated fibres, whereas cationic lignin/PDADMAC complexes formed in the solution adsorb as unevenly distributed blobs. Anionic complexes are not adsorbed by anionic fibres. Together PDADMAC and lignin increased the bonding between fibres.

III. Lignin is irreversibly adsorbed onto CS-treated fibres. Complexes formed between kraft lignin and cationic starch (CS) in aqueous solutions adsorb on kraft pulp fibres, especially when the complexes are cationic. The presented adsorption isotherms give indications of acceptable levels of dissolved lignin e.g. under conditions of water circulation closure. Paper properties are significantly affected by the adsorption of lignin/CS complexes. Sheet brightness decreases but different strength properties of paper generally increase when lignin/CS complexes are adsorbed. Moreover, the increase brought by the lignin/CS complex is greater than the increase due to the addition of CS alone. Papers made from fibres with adsorbed lignin/CS complexes exhibit lower brightness, but improved strength and water resistance. This could be utilized in the manufacture of packaging grades of paper.

IV. Lignin was adsorbed from aqueous solution on the surfaces of mica and cellulose fibres in the presence of cationic polyelectrolytes (PDADMAC and CS). The wetting behaviour and the morphology of lignin adsorbed on cellulose fibres and mica have been studied. Both the structure of the adsorbed layer as well as the hydrophobicity depended on the polymer addition strategy. Lignin, that adsorbed as granules on cationised surfaces of mica and cellulose fibres, was capable of weakening the adhesion of water to both hydrophilic substrates. In contrast, polymer/lignin complexes that were formed in solution and then adsorbed on mica or cellulose were not as effective in lowering the adhesion of water. They adsorbed on mica and pulp fibres as either a thin film or as larger blobs, depending on the properties of the cationic polymer.

V. The morphology of several lignins was studied using small-angle and ultra-small angle x-ray scattering. The radius of gyration of dissolved kraft lignin particles was determined. The shape of the particles in NaCI and NaOH solutions was found to be elongated. Particles were about 2 nm thick while the length depended greatly on the solvent and slightly on the lignin concentration. The size of these primary particles was consistent with the size of the pores or particles in the fractal aggregates of the dry kraft lignin, which was determined to be about 3.5 nm in size.

CONTENTS

APPENDICES

1 INTRODUCTION

Tens of millions tons of dissolved lignin are annually produced in the kraft pulping process. Control of the redeposition of lignin onto cellulose fibres during cooking, washing, and bleaching has become an important issue for the overall pulping process control, in particular, with the introduction of displacement batch cooking procedures and increased water circulation closure. Lignin can precipitate on fibres during different process stages such as at the end of kraft cook (Surewich 1962) or pulp washing (Sundin and Hartler 2000a), impairing the wanted pulp properties (e.g. brightness). Especially as the result of closure of the water circulation, the white waters of paper machines may contain significant amounts of dissolved and colloidal lignin that may have an effect on the paper properties (Lindström et al. 1977; Springer et al. 1986; Springer and Pires 1988; Springer et al. 1985). Previous studies of the lignin uptake by cellulose fibres have largely taken a technical approach; specifically referring to alkaline cooking conditions (Surewich 1962; Janson et al. 1975; Kleinert 1966; Moskovtsev et al. 1976a,b), papermaking conditions (Lindström et al. 1977; Springer et al. 1985, 1986), lignin precipitation induced by acidification (Hartler 1978, Brattberg 1977, Corneer and Olausson 1977), and pulp washing (Sundin and Hartler 2000b). Mechanisms of lignin uptake by cellulose fibres discussed in literature mainly refer to alkaline cooking conditions (Kleinert 1965; Moskovtsev et al. 1976 a.b) and in some cases to pulp washing conditions (Sundin and Hartler 2000b). It is difficult to compare the studies referred to above to each other because of the very variable conditions used. In my study I have tried to simplify conditions by keeping the temperature constant (room temperature) and investigating just the effects of pH, ionic strength and counter ion valency.

In this work an attempt is made to evaluate in a more general way the conditions for attachment and sorption of lignin on cellulose fibres under alkaline or neutral conditions when lignin is present either in soluble or colloidal form. Thus, the results should be of relevance to the behaviour of lignin during pulp washing and in neutral papermaking.

A second aspect, which interested me, was formation and adsorption of lignin/polymeric complexes. Polymers are largely used in papermaking mainly for tensile strength improvement, filler and pigment retention, fibres recovery, drainage aids and as flocculants in effluent water treatment. Most of the polymers used in papermaking nowadays are cationic polyelectrolytes. Cationic starches (CS) which usually are starch ethers containing a quaternary ammonium group, are widely used for improving e.g. dry strength and retention. Lignin can associate with both non-ionic polymers, such as polyethylenoxide (PEO), via a bridging flocculation mechanism (Lindström 1979a) and with highly charged cationic polymers, such as PDADMAC, via ionic bonding and forming colloidal and macroscopic complexes (Li and Pelton 1992).

The universality of electrostatic interactions between cationic and anionic polyelectrolytes suggests that under conditions of water circle closure the formation of lignin/CS (and lignin complexes with synthetic cationic polymers) could occur in paper machine white waters and that the complexes could adsorb on cellulose fibres.

From a practical point of view, the goals of this part of work were to elucidate the critical properties of lignin/PDADMAC and lignin/CS complexes that influence the adsorption of such complexes on pulp and to clarify the effect of adsorbed lignin on paper properties, of which brightness, strength, and wetting behaviour are some of the most important.

A third aspect of my interest was the interfacial properties of lignin, which determine its adsorptive behaviour. In this study, the sensitivity of contact angles of water to the state of the solid substrate was exploited to investigate the effect of adsorption of lignin and lignin/polyelectrolyte complexes. Two quite different surfaces were investigated: cellulose and mica. My particular interest lays in direct comparison of lignin morphology in the aqueous solution, and on the surface of cellulose fibres modified with adsorbed lignin (papers II and IV) in order to evaluate the correlation between them. This should shed light on the formation of the adsorbed lignin layers and on fundamentals of interactions between lignin and cellulose. It was especially interesting to compare morphologies of lignin in the solution revealed by USAXS (paper V) and morphologies of lignin in the adsorbed layers on the solid substrates revealed by AFM (papers II and IV).

In this part of work my first task was to ascertain the wetting properties of adsorbed lignin layers as such, undistorted by roughness and porosity of a fibrous substrate, and to find the correlation between the wetting properties and the morphology of adsorbed lignin. For this purpose, lignin was adsorbed on cleaved mica, which is a smooth, non-porous, hydrophilic surface. Obviously, any increase in contact angle and any new structures found on mica surface would be due to adsorption. My second task was to ascertain the wetting properties of cellulose fibres modified by adsorbed lignin, and to evaluate the correlation between them and morphology of adsorbed lignin. My third and main task was to find out the specific interfacial behaviour of lignin by comparison of its behaviour on chemically and morphologically different substrates and in the solution.

I explored how the lignin is sorbed by cellulose fibres and tried to answer the following questions: What is the mechanism of lignin sorption? Is it adsorbed on the fibre surface or only imbibed into pores? Is it retained on the surface after washing? Under which conditions is lignin retained on the fibre surface?

The main goal of this work was to deepen the understanding of lignin uptake by cellulose fibres by systematic studies under well-controlled conditions, and to clarify its effect on the paper properties, of which brightness, strength and wetting behaviour are some of the most important ones.

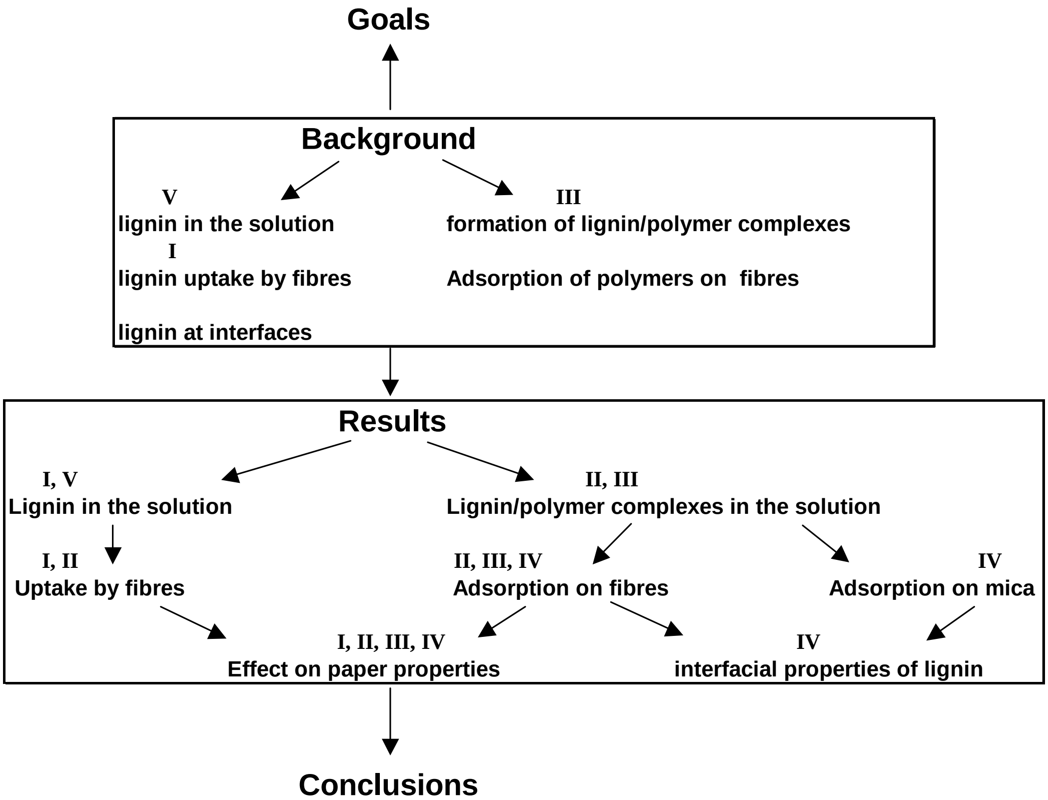


Diagram 1. Structure of the dissertation. Roman numerals refer to papers.

]

2 BACKGROUND

Lignin is a biopolymer consisting of phenylpropane units with an oxygen atom in the p-position (as OH or O-C) and with no, one or two methoxyl groups in the o-positions to this oxygen atom (guaiacylpropane, syringylpropane, and p-hydroxyphenylpropane). The phenylpropane units are attached to one another by a series of characteristic linkages (β-O-4, β-5, β-β, etc.). The polymer is branched and cross-linking occurs (Sarkanen and Ludvig 1971). The lignin content in wood species ranges from 20–40 % of the dry weight of wood (Fengel and Wegener 1989). In order to produce high quality paper with good strength properties it is necessary to remove the lignin from the wood matrix, since it hinders the formation of hydrogen bonds between fibres, restricts the swelling of fibres and makes them stiff. Furthermore, the light absorption (colour) of pulp is mainly associated with its lignin content.

During chemical pulping, lignin undergoes more or less drastic degradation reactions depending on the pulping conditions. Kraft lignin refers to the alkali soluble lignin degradation products in spent liquors after pulping. The physicochemical properties of lignin are of great importance for example in lignin recovery from cooking liquors, in pulp and paper mill effluents and during pulp washing.

This literature survey is aimed to review those properties of lignin in the solution and at the interfaces that could be relevant to the adsorptive behaviour of lignin towards cellulose fibres, in particular, regarding kraft pulping and papermaking conditions.

2.1 Lignin in the solution

Lignin is somewhat soluble in many solvents, among which are aliphatic alcohols and acids, methyl and ethyl acetate, acetone, clorophorm, dioxane, pyridine, DMS, THF. Lignin that is air-dried after precipitation in water is insoluble in water, ether, benzene, or carbon tetrachloride (Loughborough and Stamm 1936). Dry kraft lignin (in H-form) is insoluble in water and can only be dissolved in alkaline solution. However, there is a hysteresis of lignin solubility; once it has been dissolved in alkali, that is, transferred into Na-form, the lignin solution remains stable at lower pH levels upon the addition of acid (Nyman and Rose 1986).

The polyelctrolytic behaviour is established for lignosulfonates (Gardon and Mason 1958), which were found to be flexible polyelectrolytes. Kraft lignin is not a polyelectrolyte, but can acquire a polyelectrolytic properties in the alkaline medium (e.g. Chupka et al. 1970).

The associative behaviour of lignin molecules in the solution has been investigated rather extensively. Association upon decrease of pH has been reported by e.g. Sarkanen et al. (1984), Woerner and McCarthy (1988), Lindström (1979b), Rudatin et al. (1989), Gilardi and Cass (1993). Lignin exhibits different degrees of association in different solvents (Gross et al. 1958; Yaropolov and Tishchenko 1970a,b; Brown 1967), which leads to different molecular weight distributions. Increased lignin concentration (Sarkanen et al. 1984; Rudatin et al. 1989), increased salinity (e.g. Rudatin et al. 1989) have been found to favour the association of lignin sol particles. The association behaviour was ascribed to secondary valence forces/long-range van der Waals forces (Lindström 1979b; Gilardi and Cass 1993). Increase in lignin size with increase of pH was also reported and ascribed to polyelectrolyte swelling (Chupka et al. 1970; Garver and Callaghan 1991).

Size and shape of lignin particles in the solution

Despite the extensive literature reports on lignin's structure, physicochemical and hydrodynamic properties, it is rather difficult to assess what is the exact shape and the actual size of isolated lignin particle. Table 1 summarizes shape interpretation and size assessment of lignin particle as found in different studies.

Table 1. Studies concerning the size and shape of lignin particles in solution.

Lignin	Medium	Size assessment	Analytical method
maple lignin isolated by methanol-HCl and by NaOH-ethanol	different organic solvents	3 x 16 x 100 a.u., elliptical particle, shape factor 7.5 *Loughborough and Stamm (1936)*	viscosity, spreading and trough technique
milled-wood, dioxane, kraft lignins	spread on water	film thickness 1.7 nm, area per kraft lignin molecule 2.1–2.4 nm^2 *Luner and Kempf (1970)*	spreading and trough

alkali lignin solubilized by a mild procedure	$NaHCO_3$-NaOH buffer pH 9.5	R_g 44–170 nm. Microgel particles surrounded by a layer of loosely coiling chains. Hydrodynamically between random a random coil and a rigid sphere. *Gupta and Goring (1960)*	sedimentation, viscosity
spruce Bjorkman lignin	pyridine	R_h 2 nm for *Mw 7150* *Alekseev et al. (1971)*	viscosity, sedimentation
dioxane lignin	aqueous NaOH, 0.2–4 N	effective R_h 22–32 Å, globular particles *Chupka et al. (1970)*	intrinsic viscosity, potentiometric back titration
thyoglycolic acid lignin	pyridine-DMS-H_2O	apparent R_h 0.97–2.09 nm and 0.78–2.09 nm, assuming Einstein spheres with strongly immobilized tight network core and a more loose surface region *Törmälä et al. (1975)*	spin labelling and viscosity
kraft lignin	aqueous solutions	R_g 15–750 Å *Lindström (1979)*	gel permeation chromatography in DMF, viscosity
kraft lignin	aqueous alkali 0.1 M	for discrete components expansion factor 2.5–3.7, expanded random coil conformation without effects of long chain branching, for associated lignin complexes flexible lamellar configuration *Sarkanen et al. (1982)*	size exclusion chromatography, ultracentrifuge
kraft lignin	1.0 M NaOD aqueous buffer	R_h 2.05–2.28 nm basic particle, 38 nm as agglomerate (D_20 pH 6.5). Oblate ellipsoid with an axial ratio of 18. *Garver and Callaghan (1991)*	self-diffusion, PGSE-NMR[1]
acetylated kraft lignin	1.0 M $CHCl_3$	R_h 0.5–1.31 nm. Oblate ellipsoid with axial ratio < 18. *Garver and Callaghan (1991)*	self-diffusion, PGSE-NMR
kraft lignin	0.1 M NaOH/NaOD	R_h 1.0–2.2 nm (M_w 1600–12100) *Norgren and Lindström (2000)*	self-diffusion, PGSE-NMR

kraft lignin (hardwood)	DMSO, DMF, methyl-cellulose, pyridine	2.4–2.7 nm or 120–350 nm depending on molecular weight *Maier et al. (1997)*	photon correlation spectroscopy
organosolv lignin	aqueous solution pH 10–3	40 nm pH 10, 150 nm pH 3, 70 % of particles 2–50 nm, primary particles in nm range, agglomerates 65 nm *Richter et al. (1998)*	filtration, photon correlation spectroscopy
dioxane lignin (pine)	diluted organic solvents: DMSO, DMF, dioxane, pyridine	110–157 nm, 9–23 nm depending on solvent and M_w *Bogolitsyn et al. (1995)*	viscometry, photon correlation spectroscopy

1) Pulse Field Gradient Spin Echo-NMR

Colloidal properties

The colloidal properties of kraft lignin have been quite extensively studied (e.g. Lindström 1979b; Lindström 1980a,b; Lindström and Westman 1982; Nyman and Rose 1986). Depending on the interaction with solute species, lignin sometimes behaves as a lyophobic colloid (i.e. it forms colloidal particles) and sometimes as a lyophilic colloid (i.e. a soluble macromolecule) (Lindström 1980a). Marton (1964) stated that lignin behaves like a hydrocolloid: the lignin precipitates with decrease of pH with simultaneous protonation of the acidic groups in the lignin. The pH at which lignin starts to precipitate increases with increasing salinity (NaCl).

Charged anionic lignin colloids were found to agglomerate and precipitate in the presence of simple monovalent or divalent cations provided the concentration of the added ions was above the critical coagulation concentration for the system (Lindström 1980a; Sundin and Hartler 2000a). The pH, temperature and concentration of added polymers affect the behaviour of the lignin sol (Lindström 1979b; Lindström 1979a; Rowan and Scott 1986).

Dong et al. (1996) reported monotonic decrease of zeta potential of kraft lignin as the pH decreased from 10 to 1.0, which indicates that the charge density of lignin surface decreases gradually with reduced pH. The strong dependence of the zeta potential on pH suggests that H^+ and OH^- are the potential determining ions of lignin, and, thus, the ionisation is the principle mechanism for the origination of surface charges on the kraft lignins. When the concentration of H^+ increases further to a point neutralizing all negative charges at the shearing surface, the lignin particle with the attached materials becomes electrically balanced. This pH corresponds to the IEP. The isoelectric point for kraft lignins was determined to be at pH 1.0 (Dong et al. 1996). Klason lignin from eucalyptus showed zeta potential of about -30 mV, and kraft lignin at pH 4.5 of -40 mV.

Al^{3+} binds specifically to lignin at low pH and shift its IEP to a higher pH. Al^{3+} and Zn^{2+} caused charge reversals and three IEP values. The first IEP at low pH is the intrinsic IEP of kraft lignin, the second IEP at medium pH is due to specific adsorption of the hydrolysed species of Al and Zn, and the third IEP at high pH is a dual lignin surface coated and uncoated with neutral metal hydroxide (Dong 1996).

Rowan and Scott (1992) determined that at pH 11, the charge of dissolved kraft lignin was 2.5 mmol/g lignin while it was 1 mmol/g at pH 7 and 0.4 mmol/g at pH 4.

Lignin sols are easily destabilized by simple and complex electrolytes in a manner typical for lyophobic colloids, although the steric and cohesive interactions originating from the molecular chains in the surface layer are considered to be of importance (e.g. Lindström 1979, 1980; Nyman 1986).

Lindström (1980 a) determined the critical coagulation concentrations (c.c.c.) of kraft lignin sols for different electrolytes. The c.c.c. for LiCl was 0.4 M (lignin sol concentration 0.1 g/l), and similarly for all the monovalent salts, indicating that the c.c.c. was not specific for monovalent counterions. The extent of coagulation was 85 %. The temperature had no effect on the value of c.c.c. with monovalent electrolytes for pH exceeding 5. For divalent electrolytes, the c.c.c. was dependent on temperature: when the temperature was elevated from 25 °C to 60 °C the c.c.c. for $MgCl_2$ decreased from 0.02 M to 0.003 M. The c.c.c. for pH 6.2 at 25 C was 0.006 M for $CaCl_2$ and 0.008 for $BaCl_2$. Thus, the c.c.c. increases in the order $Ca^{2+} < Ba^{2+} < Mg^{2+}$. The lignin sol was stable at all pH values exceeding pH 2.7 at 25 °C, and at pH over 3.4 at 60 °C. The c.c.c. increased with increasing pH for all electrolytes. For monovalent and divalent counterions, the c.c.c. was independent on sol concentration within the range 0.02–0.5 mg/l. The c.c.c. of $LaCl_3$ and aluminium salts increased with increasing salt concentration. With aluminium salts the c.c.c. increased from pH 3 to 10. No typical restabilisation for lyophobic colloids occurred. The electrophoretic mobility measurements revealed that no charge reversal could be obtained either. The tetravalent thorium ions could restabilise the lignin sol and the amount of thorium salt needed to recharge the lignin sol was linearly dependent on the sol concentration. At pH 4.8 and lignin concentration 0.5 g/l, the recharging occurred at 0.00015 mol/l $Th(NO_3)_4$. It was assumed that the thorium ions are totally adsorbed as tetravalent species. In a qualitative sense the stability behaviour of kraft lignin sol resembles that of lyophobic colloids. The effect of pH on the variation of the c.c.c. was explained by the increase in the number of ionised groups on the lignin sol particle with increased pH, the association between sol particles resulting in partial flocculation even before the salt is added, and the simultaneous increase of the intramolecular association of the macromolecular chains in the surface region of the microgel particle at low pH with a consequent decrease in chain mobility. The decreased electrostatic repulsive forces between the chain segments and the decrease in chain mobility compress the loose surface layer. Steric stabilization is significant in alkaline solutions $pH > 9$ where the sensitivity against e.g. NaCl is lost. The c.c.c. dependence on temperature might indicate the capability of divalent ions to induce the intramolecular bonding between chain segments in the surface layer of the microgel particles. The effects of sol concentration are linked to differences in adsorbability of different ions. The adsorbability of ions increases with charge. The lyophobic behaviour of the kraft lignin sols suggested that the long-range van der Waal’s forces play and important role in the stability at $pH < 9$. If a kraft lignin sol is dried in the hydrogen form and then mechanically dispersed, turbid sols with coarser particles are formed (Lindström 1980a).

Sundin and Hartler (2000a) studied coagulation of alkaline solutions of kraft lignin with Na^+, Mg^{2+} Ca^{2+} and Al^{3+} ions and came to the very same conclusions as Lindström (1980). All salts were able to precipitate lignin. Above pH 9 sodium and aluminium showed minor effects. The c.c.c. increased in most cases with increasing pH and lignin concentration, but decreased with increasing temperature and valency of the metal cation. More than 60% of the lignin in black liquor was precipitated by calcium at pH 13–9. The lignin precipitated by calcium ions has a lower content of ionisable groups than the part of the supernatant lignin. Sundin and Hartler (2000a) ascribed it to the differences in molecular mass between the two types of lignin. I think that calcium will bind primarily to ionisable groups, and at a given calcium concentration the lignin with the lowest number of ionisable groups would be first precipitated. It is conceivable that there is a correlation between the charge density and lignin degradation (i.e. the lower the molecular weight, the higher the charge): molecular weight of lignin decreases and charge density of lignin increases during the cook (Obiaga and Wayman 1973, Sjöholm and Norman 2000).

The extent of coagulation was found to be dependent on the molecular mass of the lignin. High molecular weight fraction (above 5000 g/mol) precipitates almost completely, fraction of medium molecular mass (1000–5000) precipitates partly while low molecular mass lignin (<1000) remains in supernatant (Sundin and Hartler 2000a).

Studies of the coagulation of kraft lignin in the presence of salts reported by Nyman and Rose (1986) revealed that the lignin behaves as a sterically stabilized colloid, particularly at high pH. Lignin specifically adsorbs onto solid calcium hydroxide at pH 12.2 and reverses the sign of the zeta potential. The results of the potentiometric titration of kraft lignin in aqueous media showed a variation of the apparent dissociation constant with degree of dissociation, which makes lignin markedly different from a classic polyelcetrolyte. The apparent dissociation constant decreases with dissociation at low degree of dissociation, increases with the decrease of dissociation up to degree of dissociation up to 0.9 and then decreases again. This behaviour was attributed to aggregation effects at low degree of dissociation, classic polyelectrolytic behaviour at higher dissociation and to surface chain ionization and extension at full dissociation. These results were consistent with the resistance of lignin to coagulation with NaCl and supported the steric stabilization of lignin at neutral to alkaline pH. The intrinsic dissociation constant of kraft lignin was equivalent to that of a carboxyl group, and it was essentially constant at ionic strength above 0.06 M. The free energy consisting of electrostatic and conformational terms decreased as the ionic strength increased (Nyman and Rose 1986).

Norgren et al. (2001a) studied the aggregation of kraft lignin in diluted aqueous alkaline solutions as a function of temperature, salt concentration, pOH and divalent counterion by means of turbidity measurements. Temperature induced aggregation of lignin sols with high salinity (NaCl) was found to be of coagulative nature and irreversible with respect to temperature changes. Phase separation was detected at pOH 2 and 175 °C. Additions of $CaCl_2$ in the millimolar regime resulted in dramatic coagulation already at pOH of 1–2 (Norgren et al. 2001a).

Lignin forms coloured complexes with transition metal ions (Fe^{3+}, Fe^{2+}, Cu^{2+}, Mn^{2+}, and Al^{3+}), exhibiting ultraviolet shielding properties. Fe^{3+} showed the strongest effect. Addition of chelant to solutions containing transition ions and lignin blocked the coupling reactions (Peart and Ni 2001). Also, the surfactants, most effectively the sodium salts of bile acids were found to be efficient stabilizers of lignin dispersion against coagulation (Norgren et al. 2001b).

Torre et al. (1992) discussed calcium bonding to the lignin and cellulose in the fibre. The influence of calcium concentration in the solution on bonding by lignin and cellulose when pH and fibre concentration was constant showed that lignin exhibited a higher capacity for calcium retention than cellulose. Binding by lignin increased at higher initial metal ion concentration. The relationship was linear over the concentration range 0–1 μeq/ml, and then levelled off when initial concentration of calcium was increased to 4.5 μeq/ml, which means that lignin became saturated with calcium at a fibre to metal ion ratio of 100:0.5 (milligrams of fibre to milligram of calcium). Thus, calcium interactions with cellulose are weak. Lignin can strongly interact with calcium through formation of stoichiometric bonds involving dissociating groups (carboxyl, methoxyl, hydroxyl) of its structure. Whether the bond is electrostatic or chelate, and what is contribution of adsorption or ion exchange is an open question (Torre et al. 1992).

The general conclusion can be drawn that kraft lignin is coagulated by the addition of the counterions approximately according to the Schultze-Hardy rule and thereby behaves as a rather normal electrostatically stabilized colloid, although steric stabilization plays role at high pHs.

2.2 Lignin uptake by cellulose fibres

Control of the redeposition of lignin onto cellulose fibres during cooking, washing, and bleaching has become an important issue for the overall pulping process control, in particular, with the introduction of displacement batch cooking procedures and increased water circulation closure. Redeposited lignin may also influence on the papermaking properties of fibres, such as surface properties and bonding between the fibres. Previous studies of the lignin uptake by cellulose fibres have largely taken a technical approach; specifically referring to alkaline cooking conditions, papermaking conditions, lignin precipitation induced by acidification, and more recently, pulp washing. It has been found that cellulose fibres can resorb dissolved lignin during the kraft cook (Surewich 1962; Janson et al. 1975; Moskovtsev et al. 1976a,b). This observation suggested the application of sorption cook processes, in which pulp yield increases due to the redeposition of dissolved lignin onto pulp fibres (Hartler 1978; Brattberg 1977; Corneer and Olausson 1977). This is achieved by acidification of black liquor at the end of the cook. Lignin precipitation induced by acidification has also been used in lignin removal processes (Hynninen 1989; Kumar et al. 1997; Srinivasan and Chatterjee 1995). It has been found that even acidified fibrous sludge can initiate the precipitation of lignin (Srinivasan and Chatterjee 1995). The adhesive properties of lignins were studied by sandwiching the powdered lignin between two small pieces of paper and measuring the bond strength (Goring 1962). Normally, lignins did not bond to paper when the sandwiches were made up in the dry or wet state. A bonding was found when lignin was soaked in a weak solution of NaOH, the sandwich made up wet, then dried and tested. The bond strength increased with the alkali concentration, as also did the sorption of sodium ion onto the lignin. The alkali induced bonding was ascribed to the mildly polyelectrolytic nature of the lignin. The sorbed alkali neutralizes the weakly acidic groups in the lignin inducing their ionisation. The free charges thus produced cause the lignin to swell like a neutralized polyelectrolyte gel. The lignin then develops adhesive properties and bonds when dried in a manner analogous to the behaviour of other alkali-based adhesives. The bonding was stronger with higher swelling lignins. Temperature affects the bonding: for dry pressing the bonding temperatures were within the range 125–320 °C, and for wet pressing 50–90 °C for different lignins (Goring 1962).

Some interesting attempts to make fibres sorb dissolved lignin under papermaking conditions have been reported (Lindström et al. 1977; Springer et al. 1985, 1986; Springer and Pires 1988; Rowan and Scott 1992). The effect of temperature and pH on lignin diffusion in a washing process (Strömberg 1991), and the effect of lignin concentration in the wash liquor on the washing rate (Jacobson and Nguyen 1997) have been discussed. Data on lignin precipitation in alkaline solutions and during pulp washing were reported by Sundin and Hartler (2000a,b). Kraft lignin adsorption onto pulp fibre surface was considered from a physical-chemical point of view by Norgren at al. (2001c). Pulp fibres and lignin under pulping conditions were treated as an anionic polymer system or a lignin-polysaccharide mixture and described in accordance with Scheutjens and Fleer theory (Fleer et al. 1993) as polyelectrolyte adsorption on an uncharged surface and on a charged surface. At a low NaCl concentration and high hydroxide concentration the adsorption was found to be low. With the increase of the pOH or the NaCl concentration, the adsorbed amount of lignin was increased rapidly. When the lignin solvency becomes poor, lignin self-aggregates and precipitates while fibres serve as a nucleus for phase separation (Norgren et al. 2001c).

Adsorption of kraft lignin onto bleached pulp fibres was reported as mg sorbed lignin per gram pulp and as ISO-brightness of pulp treated with kraft lignin solutions. The conditions were related to alkaline pulping at pOH 0.1–14 and NaCl concentrations at 75 °C and 175 °C. At pOH 3 in 1.4 M NaCl, the lignin adsorption was 14 mg/g fibre (Norgren et al. 2001c).

To my knowledge, no systematic studies on lignin sorption during mechanical pulping and bleaching processes have been reported.

Possible mechanisms of lignin uptake by cellulose fibres

Cellulosic fibres are negatively charged in aqueous solution, mainly due to the dissociation of carboxylic groups. Thus, in an aqueous medium, both cellulose fibres and lignin particles are negatively charged. Therefore, the two most important long-range surface forces in fibre-lignin systems should be van der Waals' attraction and electrostatic repulsion, with the latter becoming progressively weaker as ionic strength increases.

Theoretically, the uptake of lignin by cellulose can be caused by the following phenomena:

- Imbibition of dissolved lignin into fibre pores,
- Monolayer or multilayer physical adsorption of lignin fragments from the solution due to van der Waals' forces or hydrophobic interactions,
- Formation of acceptor-donor complexes (acid/base interactions) between lignin and cellulose,
- Chemical interactions between cellulose and lignin by radical mechanisms leading to the formation of strong covalent bonds.

Mechanisms of lignin uptake by cellulose fibres discussed in literature mainly refer to alkaline cooking conditions and fewer to pulp washing conditions. Kleinert (1965) found evidence of lignin grafting onto cellulose crystallites via a free-radical mechanism. In contrast, Moskovtsev et al. (1976a,b) suggested that all the lignin was attached to cellulose by physical adsorption. However, interactions between dissolved and residual lignin may result in the formation of chemisorbed complexes due to donor-acceptor reactions. Furthermore, hemicellulose-mediated association of lignin with cellulose has been suggested by Karlsson and Westermark (1997). It has been convincingly shown that cellulose fibres adsorb lignin-carbohydrate complexes even at room temperature due to physical interactions (Klevinskaja et al. 1979). Other mechanisms suggested are the precipitation of lignin induced either by lignin acidification (Hartler 1978; Hynninen 1989; Srinivasan and Chatterjee 1995) or by addition of metal ions (Sundin and Hartler 2000b).

The amount and location of sorbed lignin

It has been estimated, that the amount of lignin sorbed by the fibres under pulping conditions, is 0.7–2 % (Surewich 1962), up to 2 % (Moskovtsev et al. 1976a), or 0.09–0.67 % (Janson et al. 1975) of dry pulp weight, 14 mg/g fibre (Norgren et al. 2001c) and 1/5 by weight of the surface layers (Kleinert 1965). The width of the pores in the swollen cell wall is about 35 Å (Stone and Scallan 1965). The specific surface area of cellulose fibres (including pores) is around 100–200 m^2/g (Thode et al. 1958; Hernadi 1984; Budd and Herrington 1989), while the outer surface of the fibres if estimated from their dimension is much lower (10–20 m^2/g). Thus, it is obvious that the total surface of fibres is accessible only to low molecular weight lignin fractions so that the relatively high amounts of sorbed lignin must be due either to imbibition of low molecular weight lignin into the pores or the deposition of colloidal lignin particles on the outer surface.

Hartler (1978) showed that sorbed lignin is located in the secondary wall, and also as particles on both the outer surface and on the inner fibre lumen surfaces (under conditions of acidification of black liquor in the end of cook). According to Kleinert (1965), under alkaline cook conditions lignin does not penetrate into the cell walls and is chemically linked to alkali-sensitive cellulose pulp portions on the surface layers of the fibres. Springer and Pires (1988) suggested that lignin is sorbed onto the fibre surfaces under papermaking conditions, but discussed neither mechanism of attachment nor distribution of sorbed lignin.

The irreversibility of sorption

The amount of lignin sorbed irreversibly under pulping conditions was determined to be up to 0.91 % of pulp, after washing with alkaline solutions at 40–50 °C (Surewich 1962). The fraction of sorbed lignin that is irreversibly bound to the cellulose fibres has been found to be 1/4 (Moskovtsev et al. 1976a), 1/2 (Janson et al. 1975), and all (Kleinert 1966), depending on the extraction procedure. However, most of the sorbed lignin could be removed by extraction with hot alkali (Kleinert 1965; Moskovtsev et al.1976a). Furthermore, it has been shown that lignin sorbed into the fibre wall has a higher resistance against dissolution than lignin in particle form on the fibre surface (Hartler 1978).

Rowan and Scott (1992) reported that under papermaking conditions all the sorbed lignin could be removed even by stirring.

Of the adsorption mechanism suggested by different authors, radical reactions certainly will result in irreversible adsorption without chemical treatments, while the other interactions depend on solution conditions (ionic strength, temperature, pH, concentration and aggregation state of lignin) etc. and may induce reversible adsorption or absorption. Acidification or addition of metal ions could result in the direct precipitation of lignin on fibre surfaces. Alternatively, if repulsive electrostatic particle/surface interactions are weak, (e.g., at high ionic strength) the result could be formation of colloidal lignin particles that deposit on the surfaces. These adsorption processes could be completely or partially reversed by washing or changing pH.

It is difficult to compare the studies referred to above to each other because of the very variable conditions used.

2.3 Adsorption of polymers on cellulose fibres

Papermaking is a very dynamic and complex process. When a polymer is added to a papermaking suspension, it is quickly adsorbed on the surfaces of fibres, fines and fillers. To work properly, the polymer must be adsorbed on the fibre surface. Adsorption of polymers on cellulose fibres has been studied comprehensively and a few excellent reviews are available (Wågberg 2000; Wågberg and Ödberg 1989). Cationic polyelectrolytes represent the largest part of the polymers used in papermaking nowadays.

Generally, the polyelectrolytes are thought to act by charge neutralisation, suppressing the electrostatic repulsion between particles and/or polymer bridging in which particles are held together by individual macromolecules attached simultaneously to neighbouring particles. Because of the ionic character the behaviour of polyelectrolytes and their interaction with cellulose in aqueous media are affected by pH and ionic strength. The most feasible mechanism would be attachment of the cationic polymer to the carboxylic groups of the cellulose by ion exchange (Trout 1951; Allan and Reif 1971). Also, van der Waals forces including hydrogen bonds might contribute to the interaction between cellulose and cationic polymer (Kenada et al. 1967). The porosity of swollen cellulose complicates the adsorption mechanism. The accessibility of anionic sites on cellulose (carboxylic groups) depends on the polymer size, the porosity of cellulose and its accessibility to polymer (Alince 1974). According to Wågberg and Sjölund (1999), cationic polymers with radii of gyration 17–72 nm are restricted to the external surface of ECF bleached kraft pulp fibres. All the charges in the fibre wall are accessible only for molecules smaller than 9 nm.

The first step of polymer adsorption is the transport of the polymers to the surface of fibres. Then adsorption is believed to occur in two steps: first the polymer quickly deposits on the outer surface and then it slowly diffuses into the pores and lumens of the fibres. The adsorption of polymer onto a cellulosic fibre is schematically illustrated in (Ödberg et al. 1993).

In general the adsorption of polyelectrolytes on pulp fibres depends on the properties of the polyelectrolyte, such as charge density, molecular weight, degree of branching, stiffness, and morphology. Polyelectrolyte adsorption depends also on the properties of the fibres, such as their surface charge density, accessible surface area and porosity. The adsorption depends on the strength of the interaction of a polymer segment with the fibre surface, which depends on pH and ionic strength.

For cationic polyelectrolytes electrostatic interactions are the driving force of adsorption. For low molecular mass cationic polyelectrolytes at low salinity, there is often a one to one correspondence between charges on the fibres and adsorbed polymer charges. For higher molecular masses the porous nature of the fibres becomes important for the adsorption process.

Cationic starches (CS), which are usually starch ethers containing a quaternary ammonium group, are widely used to improve e.g. the dry strength and retention. Adsorption of cationic starch on microcrystaline cellulose was rather comprehensively studied by van de Steeg et al. (1993a,b,c). The literature of CS sorption on the pulp and its effect on paper properties is extensive (e.g. Nedelcheva and Stolikov 1978; Marton 1980; Marton and Marton 1976; Roberts et al. 1987; Tanaka et al. 1979; Wågberg and Björklund 1993; Hedborg and Lindström 1993; Bobacka et al. 1999). Normally the dosage of cationic starch amounts to 0.2 %–1.5 % of wet end solids. For isotherms of adsorption of cationic starches onto kraft pulp fibres see e.g. Wågberg and Björklund (1993). For isotherms of adsorption of PDADMAC onto pulp see e.g. Wågberg and Ödberg (1989).

If a cationic polymer is first adsorbed onto a cellulosic surface, an anionic polymer can then be adsorbed onto the fibres. This is the basis for some of the dual polymer retention aid systems. For the efficient adsorption of the anionic polymer, the adsorbed cationic polymer must have a loopy configuration. If the cationic polymer is lying flat on the surface after reconformation, the adsorbed amount of anionic polymer will be small except for the case where the cationic polymer is very highly charged. In this case the fibres are patchwise positively charged and anionic polymers adsorbs (Ödberg et al. 1993).

A variety of studies regarding complex formation have been reported over the last twenty years. When polyelectrolyte complexes are formed in solution, both stoichiometric and non-stoichiometric polyelectrolyte complexes can be formed, depending on different factors such as the molar mixing ratio, acidity/basicity of the polyelectrolytes used, ionic strength of medium, chain length or accessibility of the charges on the polyelectrolytes. Properties such as charge density, position and type (weak/strong) of the functional group, flexibility of the polymeric chains also affect the complex formation. The complexes either precipitate or coacervate from the solution or remain soluble if they carry an excess of charge (Ström et al. 1985; Kötz et al. 1996; Ström and Stenius 1981; Kötz 1993; Kekkonen et al. 2002).

Polyelectrolyte complexes of cationic and anionic polymers are introduced to enhance the paper strength. For example, cationic starch has been combined with anionic carboxymethyl cellulose providing a synergistic effect on the Mullen burst strength and tensile strength (Taggart et al. 1991). Carboxymethyl cellulose combined with cationic poly(amideamine) epichlorohydrin condensate provided a significant increase in strength of the paper, compared to sheets prepared with only the cationic condensate (Gärlund et al. 2003). Furthermore, building of polyelectrolyte multilayers on the fibre surface, when consecutive layers of cationic and anionic polymers are deposited on cellulosic fibres is a developing trend. With this approach considerable strength improvement is achieved even on beaten pulps (e.g. Wågberg et al. 2002).

Complexation of cationic polymer with anionic components of dissolved and colloidal substances (DCS) is used for removal of anionic components of DCS (Wågberg and Ödberg 1991; Sundberg et al. 1993).

2.4 Lignin association with polymers

Lignin can associate with both non-ionic polymers, such as polyethylenoxide (PEO), via a bridging flocculation mechanism (Lindström 1979) and with highly charged cationic polymers, such as PDADMAC, via ionic bonding and formation of colloidal and macroscopic complexes (Li and Pelton 1992). Bridging occurs when the thickness of the electrostatic double layer is sufficiently reduced by addition of an electrolyte or by charge reduction on the particle surface.

The formation of complexes between cationic polymers and kraft lignin or lignin sulphonates was studied e.g. by Ström and Stenius (1981), Li and Pelton (1992). The interactions between lignosulphonate and cationic polymers have been found to result in soluble complexes, colloids, and macroscopic precipitates, mainly depending on the polymer weight ratio and the molecular weight of lignosulphonate. High-molecular weight lignosulphonate reacts stoichiometrically with cationic polymers and forms a completely flocculated precipitate provided that the LS is present in excess of charge equivalence. With cationic polymer in excess both colloids and macroscopic precipitates are formed. Low molecular weight lignosulphonate forms only colloids regardless of which polymer is in excess, but the colloid is flocculated at the point of charge reversal. Unfractionated lignosulphonate forms both colloid and macroscopic precipitates regardless of which polymer is in excess. At point of charge reversal no colloid is formed (Ström and Stenius 1981).

It is generally known that oppositely charged polyelectrolytes form complexes over a broad range of stoichiometric ratios and that the complexes tend to be water-soluble unless they are nearly stoichiometric.

The complexation of cationic polyelectrolytes (polyamines and PDADMAC) with kraft lignin was viewed as complexation of oppositely charged polyelectrolytes, where PDADMAC was cationic polymer and kraft lignin anionic phenolic polymer (Li and Pelton 1992; Pelton 1999). The lignin/polyelectrolyte complex was mainly present as a macroscopic complex, although a stable colloidal phase was often obtained if either the lignin or cationic polymer was present in excess. Eighty to ninety percent of the lignin could be precipitated with PDADMAC. The precipitation yield was not sensitive to the molecular weight of the cationic polymer, the concentration of salt, or the detailed chemical structure of highly charged cationic polymers. The volume of cationic polymer required for the maximum yield of precipitate was inversely related to the polyelectrolyte concentration, indicating a stoichiometric interaction with lignin (Li and Pelton 1992).

At the optimum mixing ratio of about 80 % of the added lignin ends up in the precipitate, whereas less than 35 % of the added cationic PDADMAC formed precipitate. The experimental optimum mixing ratios were less than the estimates from charge balance, indicating that many of the anionic charges on lignin were not accessible to PDADMAC. This means that the precipitates are not stoichiometric based on charge: 75 % of the charges on the lignin are not bound to PDADMAC. It was proposed that the 20 % lignin that cannot be precipitated with cationic polyelectrolyte is present as a small highly charged polymer fragments that form water-soluble complexes with most of the added PDADMAC (Lappan et al. 1997*)*.

Addition of kraft lignin increases the cationic demand of pulp slurries and the adsorbed amounts of cationic starch (Huh and Lee 1999; Sundberg et al. 1993).

Lignin-polymer complexes can be used in some practical implementations: the use of sulfonated kraft lignin/PEO complexes as a dual retention system for newsprint and groundwood stocks was suggested by Pelton et al. (1981). They showed that the complexes improved fines retention without decreasing pulp brightness. The preferential formation of precipitating macroscopic lignin-PDADMAC complex in beds channels improved displacement washing (Pelton and Grosse 1994).

Lignin is also a surfactant, used in industry as a dispersant and as an emulsion stabilizer already from the mid 1930's. The surface activity of kraft lignin is higher than that of lignosulphonate (Gundersen et al. 2001). Therefore, lignin association with cationic polymers could also be viewed as cationic polymer/anionic surfactant interaction. For cationic polymer/anionic surfactant complexes, see e.g. Claesson et al. (1997, 1998); Merta and Stenius (1999a,b) and Bergström et al. (2002). Piculell and Lindman (1992) discussed the difference and similarities in polymer/polymer and polymer/surfactant mixtures.

There is no information on complexes formed between lignin and cationic starches.

2.5. Lignin thermomechanical properties

Lignin undergoes thermal softening. Glass transition temperatures are between 135–230 °C depending on the lignin isolation procedure. The molecular weight was also found to influence the transition with smaller molecules softening at lower temperatures. Sorbed water vapour had a marked effect: the softening temperature of a spruce lignin fell from 195 °C to 90 °C when 27 % water was adsorbed. Lignin softens at elevated temperatures and the water sorption markedly decreases the softening temperature. Glass transition temperature for alkali spruce periodate lignin was 193 °C at dry and 116 °C at moist (13 %) (Goring 1964).

2.6 Lignin films

Lignin at air-water interface

Numerous studies were dedicated to the lignin spreading, starting from the 1920’s (e.g. Wedekind and Katz 1929) and the behaviour of lignin surface layers at the air-water interface has been studied (e.g. Luner and Kempf 1970; Luner and Roseman 1986; Gilardi and Cass 1993; Oliveira et al. 1994; Cathala et al. 2000a,b). Most of the films are characterized by compression and expansion isotherms performed on a Langmuir trough. The two most common tests used to verify that the material is spread as a monomolecular film are a constant collapse area when the surface-active substance is spread from solutions of different concentrations, and a constant surface potential when the interface is scanned with the air electrode. Basic parameters obtained from such experiments are collapse pressure and corresponding average area per molecule, which give some insights into the spatial organization of molecules at the interface. The hysteresis between compression and expansion isotherms may account for lignin-lignin interactions.

Wedekind and Katz (1929) spread methyl-phenol and acetyl-phenol spruce phenol lignins and obtained a film of 10 Å thick, and calculated an area per molecule value of 83 $Å^2$. Loughborough and Stamm (1936) obtained a methanol maple lignin film 16 Å thick, and calculated an area per molecule value of 318 $Å^2$. Luner and Kempf (1970) spread mill-wood lignin (MWL), dioxane lignins and kraft lignin on water as monomolecular films and studied them with the trough technique. Ethanol-1,2-dichloro-ethane solution was found the most suitable spreading solvent. All lignins formed a coherent, gel-like film. Kraft lignins exhibit collapse pressure 16 mJ/m^2 and compressibility 0.0167–0.0171 m^2/mJ. Based on the values for collapse pressures and compressibilities, as well as the coherent nature of the lignin films, lignin belongs to Group II in Crisp's classification (Crisp 1946). The film thickness of the various lignins which differ widely in molecular weight and chemical treatment are similar and close to 17 Å at the extrapolated area at zero pressure, which is similar to the thickness of maple lignin films studied by Loughborough and Stamm, and the measured areas per monomer (phenyl propane unit) calculated from molecular models lying flat on the water are also constant and about 57 Å. The height of a phenyl propane unit is about 11 Å standing on the phenolic group. Areas per monomers for lignins are 10–12 Å, which suggests a high degree of cross-linking, which leads to molecular configuration where not every monomer is adsorbed at the interface and therefore cannot contribute to the area per molecule. The values of dipole moments per monomer were exceptionally low for kraft lignin. Lignin also showed hysteresis effects. Luner and Kempf suggested, that lignin at the air-water interface may be envisioned as forming a hydrogen-bonded film as a result of the preferred orientation of the water molecules in the vicinity of the adsorption sites of the macromolecule. As an alternative to hydrogen bonding hypothesis, hydrophobic interactions upon compression, leading to higher interaction energies was suggested (Luner and Kempf 1970).

For kraft lignin the limiting area per monomer unit was 12.1 a.u., the surface potential was 166 mV, the collapse pressure 5 mJ/m^2 and the compressibility 0.020 m^2/mJ (Luner and Roseman 1986) At 37 °C, an anomalous isotherm was observed which was ascribed to a "melting" of lignin. The lower unit areas at higher temperatures were ascribed to an increase of the solubility of lignin. The cross-linking of kraft lignins with formaldehyde did not change the values for extrapolated area, surface potential and collapse pressure, i.e. did not alter the adsorption characteristics of the lignin (Luner and Roseman 1986*)*.

Baumberger at al. (1997) reported that lignin (organosolv wheat straw) spreads into soft non-collapsing compressible films, the large relaxation behaviour of surface pressure after the dynamical component of the compression isotherms. Lignin molecules exhibit a rather high dilational modulus. Lignins have quite special surface properties related to the structure of the interfacial film and to the interactions between lignin molecules. These surface properties might determine the way lignins interact with other macromolecules in the fluid state and thereby in a solid state.

Cathala et al. (1998) studied such properties of lignin model compounds (dehydrogenation polymers=DHPs) as limiting area, the relaxation behaviour and dilational modulus. The compressibility behaviour of the interfacial films is determined by interactions between DHPs and these interactions are only governed by the crowding of the interface (Cathala et al. 1998). When DHPs are spread at the interface, the surface pressure increases abruptly between 0 and 9 mg/m^2, showing that molecules remain at the interface, and then stabilizes at a value of 6 mN/m. At the lowest concentration, good fits are obtained with one-layer model. At higher concentrations the experimental data were fit to two-or three-layer models. The distribution of the DHPs in the interface layer is not homogeneous: on the air side dense structure and a decreasing volume fraction toward the water side. As the amount of spread DHP increases, the volume fraction of the airside layer changes toward an increasingly "dry" state. Increase of lignin (or DHP) concentration favours self-association resulting in segregation between lignins and water and in the increase of the film thickness and in the formation of a denser layer on the air side (Cathala et al. 2000a,b). Neutron reflectivity experiments indicated that when the surface concentration increases with the spread amount from 0.81 to 3.5 mg/m^2 for guaiacyl DHP and from 1.01 to 2.85 mg/m^2 for guaiacyl/syringyl DHP, the thickness increases from 24 to 220 Å and from 45 to 183 Å for guaiacyl DHP and guaiacyl/syringyl DHP, respectively. At the same surface concentration guaiacyl DHPs form dense structures whereas guaiacyl/syringyl DHPs form layers more swollen by water (Cathala et al. 2000a). DHPs at the air-water interface form a gel-like phase containing a large amount of water. These films exhibit long relaxation times after compression as determined by dynamic surface pressure measurements, indicating where molecules form a physical network. At high surface concentrations a two-layer structure is observed with a water content of 50–60 % on the air side and 80–90 % on the bulk side (Cathala et al. 2000b).

Gundersen et al. (2001) studied the surface films of lignosulphonates and kraft lignin at different bulk concentrations, varying pH and different salts by Langmuir technique. The films exhibited a significant stability toward compression. At pH 6 and 8 the kraft lignin film has to be extensively compressed until the high compressible region at elevated pressure is observed. At pH 10 the adsorption is further reduced and the final area is too large to compress the film lignin into a multilayer. The kraft lignin film properties are equal in both acidic and alkaline solutions despite the fact that multilayer adsorption occurs at lower concentration at pH 4 than at pH 10. When the concentration is high enough to give rise to multilayer adsorption, the compressibility of the film is quite high. The surface activity of kraft lignin was higher than that of lignosulphonate. Kraft lignin form more rigid film than lignosulphonate. In region with reduced compressibility at intermediate film areas the surface pressure increases rapidly. A further compression gives a film with increased compressibility although lower than at large areas. This indicates that lignin is displaced from the surface and new layers, i.e. multilayers are formed. Multilayer films are readily compressible due to low rearrangement energy. Films adsorbed from aqueous NaCl solutions are governed by the swelling capacity of the molecular matrix and by increased amount of adsorbed material at high salinity. In solutions containing high concentrations of trivalent salts, the film had to be extensively compressed to obtain high surface pressures, which indicates extensive aggregation of the lignin molecules. With trivalent cations (Al^{3+}, Fe^{3+}) kraft lignin formed insoluble metalhydroxide complexes (Gundersen et al. 2001).

According to Aguie-Beghin et al. (2002), the spread layers of lignin at the air-water interface hold 70 % water, and the surface concentration of lignin is less than amount deposited. The significant loss of lignin molecules to the bulk occurs during the first hour after spreading. An increase of the spread surface concentration leads to an increase of the thickness and of the surface concentration in quasi-equilibrium conditions. After spreading or compression the kinetics of ellipticity and surface pressure imply a reorganization of the layers, which is more pronounced at high surface concentration. In addition to the surface layer, lignin exists in the bulk in a colloidal or aggregation state. The covalent structure of the adsorbed molecules is not different from that of molecules in the solution. The lignin molecules reach a quasi-equilibrium state in the interfacial layer.

Oliveira et al. (1994) characterised the organosolv lignin monolayers by surface pressure and surface potential measurements. The collapse process did not correspond to a breakdown in the monolayer structure, and a bi-layer seems to be formed when compression proceeds beyond the collapse pressure. The formation of such a bi-layer is irreversible, as demonstrated by the reproducibility of the second and subsequent compression-expansion cycles. At a given critical area surface potential increases, indicating the onset of structuring of the monolayer. This sharply decreases the dielectric constant at the film-water interface, resulting in increase in surface potential. The surface potentials were non-zero even at large areas per molecule, indicating the domains formation even at low molecular concentrations. The surface potential is not changed at the collapse pressure; moreover, the surface potential does not decrease even beyond collapse. This was ascribed to the stacking of molecules, possibly forming a bi-layer. The extrapolated area is generally increased with the molecular weight of the lignin. The reproducibility in the pressure-area isotherms for the second and subsequent compressions shows that a very stable molecular arrangement is attained (Oliveira et al. 1994).

These results suggest that lignin can crowd on the air-liquid interface and adsorb by variety of mechanisms, e.g, by formation of rather coherent, gel-like monolayer on the liquid surface, or by formation of bi-layers of different volume fractions. However, based on a two-dimensional pressure results it is not possible to forecast the adsorption behaviour of lignin on the solid, since the molecules are not mobile in the same way on a solid surface. It is essential, that in spreading experiments described above organic solvents were used (chlorophorm (Loughborough and Stamm 1936), dioxane/water mixture 9:1 (Cathala et al. 2000), mixture of ethanol and 1,2-dichlorethane (Luner and Kempf 1970), DMS-ethanol-dichlorethane mixture (Luner and Roseman 1986), chlorophorm or THF (Oliveira et al. 1994). When lignin is dissolved in aqueous alkali and becomes water-soluble, it would hardly form films on water.

The Langmuir-Blodgett films of lignin

Based on the gel permeation chromatography (Wayman and Obiaga 1974) and electron spin resonance (ESR) studies of lignin (Lindberg et al. 1975; Törmälä et al. 1975), it has been indicated that individual lignin globule consists of regions with different mobilities, which could be explained in terms of the fragmented structure of an individual globule. Alternative results for this hypothesis were confirmed by scanning tunnelling microscopy (STM) (Radotic et al. 1994), and in a computational study of lignin formation (Jurasek 1995). According to Radotic et al. (1994), the lignin model compound DHP consists of building units or modules assembled into larger assemblies called supermodules. Supermodules are interconnected into the overall lattice-like polymer structure with or without spherical regions. One module consists of about 20 monomers, while the supermodule contains about 500 monomers.

Constantino and co-workers were the first to produce LB films of lignin in 1996. Since then, the LB films of lignin (or lignin model compounds) have been intensively studied (e.g Constantino et al. 2000; Pasquini et al. 2002; Paterno and Mattoso 2001; Micic et al. 2000, 2001a,b). I think that the behaviour of lignin LB films is very important for understanding of lignin behaviour as an adsorbing specie and as an adsorbate, so the properties of the LB films of lignin put light on the mechanism of lignin adsorption on the cellulose and on the structure of the adsorbed layers.

Constantino et al. (2000) investigated the morphological features of LB films of lignin and composite of lignin and cadmium stearate by AFM. The lignin monolayer was rather unstable and transferrable. The surface of the LB film of lignin on mica was found to be smooth, comparable to that of an LB film of pure cadmium stearate. In the mixed LB film structure, a clear domain structure (of lignin and cadmium stearate) could be visualized. The surface roughness increased with increasing number of layer.

Pasquini et al. (2002) investigated the molecular organization of LB films of lignins with AFM and FTIR. Ethanol lignin films have a flat surface in comparison with saccharification lignin films. Saccharification lignin gave ellipsoidal aggregates oriented perpendicularly to the substrate. The ethanol lignin aggregates were preferentially oriented parallel to the substrate. The influence of strong polar groups appeared to determine molecular packing. The surface potential was particularly sensitive to the polar groups. Lignins with more carbonyl groups, such as ethanol lignin (more than saccharification lignin), had lower values of surface potential. This means that carbonyl groups contribute negatively to the surface potential, that is, these groups have the oxygen in the carbonyl linkage pointing to the air when the film is in the compressed state. Ethanol lignin and saccharification lignin displayed extrapolated areas of 194 and 182 $Å^2$ and maximum surface potentials of 110 and 200 mV, respectively, for films on pure water. The presence of polar groups led to films with a more uniform spatial arrangement, which seemed to be maintained during film transfer, yielding LB films with a lower roughness. The tendency to form aggregates and consequently less smooth surfaces depends on the type of lignin, or more specifically in this case, on the isolation method employed. Paterno and Mattoso (2001), studied self-assembled films of poly(o-ethoxyaniline) and sulfonated lignin. The important conclusion was that the tendency to form planes makes the lignin macromolecules capable of covering rough surfaces.

Micic et al. (2000) attempted the visualization of lignin supramolecular structures and presented the results of an environmental SEM (ESEM) investigation of a lignin model compound DHP. Four different levels of the supramolecular structure of lignin were found. The supramolecular organization was well dependent on the substrate surface characteristics, such as hydrophobicity, de-localized orbitals, and surface free energy (Micic et al. 2000).

The latter conclusion is very important and suggests that with regard to lignin adsorption on the cellulose fibres, the morphology of lignin-adsorbed layers will be dependent on the physicochemical characteristics of the fibres.

Lignin nanomechanical properties and lignin-lignin interactions were studied by combining atomic force microscopy and environmental SEM (Micic et al. 2001a). By using the lignin-coated AFM tip, strong attractive intermolecular forces between two individual lignin macromolecular globules responsible for holding lignin globules together in higher ordered structures were revealed. They suggested that lignin globules consist of at least 2 individual spherical layers, with space in between filled with solvent or gas (Micic et al. 2001a). The lignin model compound expresses different levels of structural organization. Lignin at the nano-scale range expresses elastic-viscoelastic properties. However, there is a large non-linearity involved in the globule attractions. On all force scans the existence of three different distinctive cohesion peaks during the cantilever retraction was observed within the distance which corresponds to the diameter of individual globules, in the range 400–800 nm. This was ascribed to the onion-like, layered structure of lignin globule (Micic 2001b).

This evidently suggests that lignin can be adsorbed onto the cellulose fibres by formation of multilayers on the fibre surface due to intermolecular attractive forces. Lignin can adsorb onto the lignin layer already adsorbed on the fibre surface, i.e. one layer of lignin could induce the adsorption. This resembles another interesting phenomenon of a different nature: the grafting of dissolved lignin on the residual lignin in the pulp under alkaline pulping conditions (Moskovtsev 1976b).

The wetting properties of lignin

Lee and Luner (1972) determined the wetting characteristics of different lignins, including softwood and hardwood kraft lignins. The solid films were prepared by evaporation and by heat molding. The contact angle measurements were done in the liquid-air-solid phase and in the liquid-liquid-solid phase. The critical surface tension of wetting, the surface energy, the hydrogen bond force component of the surface tension, the adhesion tension etc. were reported. For hardwood lignin at 20 °C with water the work of adhesion was 108 mJ/m^2, intermolecular dispersion forces 59.8 mJ/m^2, and critical surface tension of wetting was 36 mJ/m^2 as calculated by the Zisman method. The authors concluded that lignin was of hydrophilic and amorphous nature. When a liquid interacts with lignin or cellulose, even when “dry”, the total energy is mainly determined by nondispersion forces. This might be of crucial importance for the mechanism of lignin adsorption by cellulose (Lee and Luner 1972).

3 EXPERIMENTAL

3.1 Materials

3.1.1 Kraft lignin

The kraft lignin used was precipitated from black liquor, CURAN 100 (Lignotech AB, Sweden). The weight average M_w of lignin, as determined by gel permeation chromatography (KCL, Finland), was $5.8 \cdot 10^3$ with polydispersity 2.1, (used in papers III–V) and $7.15 \cdot 10^3$ with polydipersity 2.4 (used in papers I, II and V). A stock lignin solution was prepared by dissolving lignin powder in 0.1M NaOH. The solution was stirred before use for 48 hrs to allow all the lignin to dissolve. Prior to sample preparation, the pH of the solution was adjusted using concentrated HCl. Furthermore, NaCl was added to obtain the desired ionic strength.

3.1.2 Cationic polymers

A cationic polyelectrolyte, poly-dimethyldiallylammonium-chloride, PDADMAC (Fig. 1) ($1 \cdot 10^5 < M_w < 3 \cdot 10^5$) carrying one charge per monomer unit was used. The charge density of the polymer was $6.19 \cdot 10^{-3}$ mol/g and it was obtained from Allied Colloids Ltd., Yorkshire, England. The molecular structure of PDADMAC is shown in Figure 1. Concentration of stock solution used was 1.42 g/l.

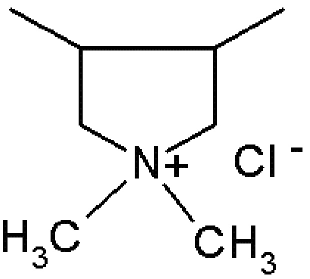
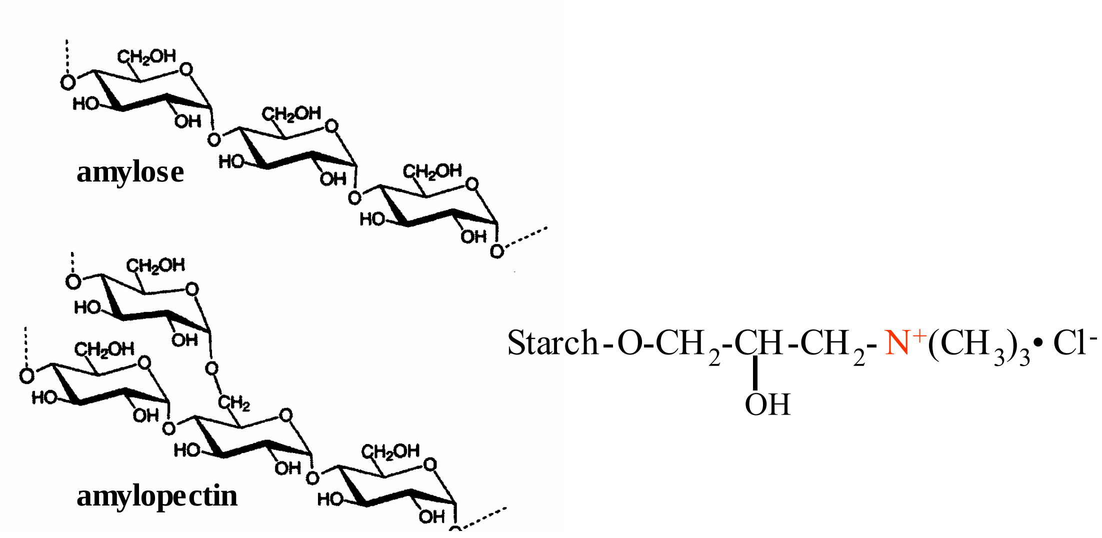


Fig. 1. PDADMAC

A quaternary substituted starch (2-hydroxy-3-trimethylammoniumpropyl starch) with different degrees of substitution (DS) (0.045, 0.2, 0.75), synthesized from potato starch

(Raisio Chemicals, Finland) was used. The structure of CS is shown in Fig. 2. The weight average molecular weight (M_w) of CS was $1.6 \cdot 10^6$ with polydispersity 7.9 for DS 0.045, $8.8 \cdot 10^5$ with polydispersity 2.1 for DS 0.2, and $4.5 \cdot 10^5$ with polydispersity 2.3 for DS 0.75. Since starch was depolymerised with sodium hypochlorite before cationization, the amylose and amylopectin fractions could not be separated in the SEC chromatograms. The stock starch solutions (10 g/l and 3 g/l) were prepared as described by Merta and Stenius (1999a).



$$\text{Starch-O-CH}_2\text{-}\underset{\text{OH}}{\text{CH}}\text{-CH}_2\text{-}\text{N}^+(\text{CH}_3)_3 \cdot \text{Cl}^-$$

Fig. 2. Cationic starches: amylose and amylopectin, and a quaternary substituent.

3.1.3 Salts

NaCl, $CaCl_2$ and $AlCl_3$ were analytical grade. In the range of $CaCl_2$ concentrations used in this work (up to 8 mM) there will be no precipitation of $Ca(OH)_2$ even at pH 12 (the solubility product of $Ca(OH)_2$ is $5.3 \cdot 10^{-6}$ mol/l). Thus, calcium is present in the aqueous solutions as Ca^{2+} and $CaOH^+$ ions; the latter is a major form of soluble Ca(II) at pH ≥ 11 (Sillen and Martell 1964, 1971).

Appropriate amounts of 1 M $AlCl_3$ (pH 3.5) were added to lignin dispersions and the pH was adjusted to 7, 10, 11, and 12 using 5M NaOH.

3.1.4 Cellulose fibres

Pulp A (used in papers I and II): ECF bleached spruce kraft pulp was obtained from a Finnish pulp mill. The pulp was beaten to SR^0 35. In order to remove fines fraction (< 200 mesh) the pulp was Bauer McNett fractionated according to the SCAN-M 6:69

standard. The surface charge of the pulp A, as determined by polyelectrolyte adsorption (PDADMAC, $M_w > 3 \cdot 10^5$, charge density $6.2 \cdot 10^{-3}$ eq/g), was 62 μmol/g.

Pulp B (used in papers III and IV): ECF bleached softwood kraft pulp was obtained from a Finnish pulp mill. The pulp was beaten to SR^0 24. The fines fraction was not removed. The fines fraction was determined by Bauer-McNett classification method. Pulp contained 4 % fines that pass through the 200-mesh wire. The surface charge of the pulp B, as determined by polyelectrolyte adsorption was 12 μmol/g.

Metal ions were removed from both pulps by acid treatment with 0.01 M HCl, whereupon the fibres were converted to sodium form using 1 mM $NaHCO_3$ according to the procedure described by Swerin et al. (1990). Both pulps were washed thoroughly with deionised water after both treatments until the water surrounding the fibres had a conductivity less than 5 µS/cm.

3.1.5 Mica

Mica (used in paper IV) was ruby red mica, from Electron Microscopy Sciences, USA. Freshly cleaved mica is reported to have one charge per 50 $Å^2$, which corresponds to a charge density of 0.32 C/m^2 (Evans and Wennerström 1999).

3.2 Methods

3.2.1 Samples preparation

Lignin samples of different concentration and electrolyte composition were prepared volumetrically from the stock solution (papers I–V). Pulp samples were stirred with lignin samples at room temperature (papers I–IV), whereupon the fibres were separated by filtration in a Bühner funnel.

Cationic polymers were added in two different ways (papers II–IV). Either cationic polymer was mixed with the lignin in solution, followed by addition of the substrate (mica or pulp, abbreviated as M and F respectively), or the substrate was first equilibrated with cationic polymer solution, and then added to the lignin solution. The first adsorption strategy is further abbreviated as M+CS*L or F+CS*L, and M+P*L or F+P*L for CS and PDADMAC, respectively. The second adsorption strategy is further abbreviated as M*CS+L or F*CS+L, and M*P+L or F*P+L, depending on whether CS or PDADMAC was used.

After equilibration substrates were separated from the solution (papers II–IV). Sorption of lignin in the pulp was measured in terms of the kappa number of the pulp, which was determined according to SCAN-C 1:77 (new ISO 302) standard. The lignin content (LC, %) was calculated from the kappa number as LC = kappa number/6.546 (Kyrklund and Strandell 1969). The pulp sheets were dried at room temperature between smooth surface board sheets. Samples for both ESCA (papers II and III) and AFM (papers II and IV) analysis were taken from these sheets.

3.2.2 Electrophoretic mobility

The movement of charged colloidal particles in an electrolyte solution in an applied electric field is termed electrophoresis. Rate of migration, also called velocity of migration, ν, is the distance of migration divided by time. The electrophoretic mobility of a particle (μ) is the observed rate of migration of a particle (ν) divided by strength of applied electric field (E) in a given medium. Two forces act on the particle surface per unit area: electric force F_e and a viscous force F_h that are given by:

$$F_e = \sigma E \qquad /1/$$

where σ is charge density of the particle surface,

$$F_h = \eta \nu / (1/\kappa) \qquad /2/$$

where η is viscosity of the solution , $1/\kappa$ is Debye length.

At equilibrium electric force is balanced by viscous force, so

$$\sigma E = \eta \nu / (1/\kappa) \qquad /3/$$

Electrophoretic mobility is proportional to the surface charge density of the particle:

$$\mu = \sigma / \eta \kappa \qquad /4/$$

Smoluchowski’s mobility formula for the electrophoretic mobility of a colloidal particle is expressed as

$$\mu = \zeta (\varepsilon_r \varepsilon_0 / \eta) \qquad /5/$$

where ζ is zeta potential, ε_r and ε_0 are the relative permittivity of the liquid and the permittivity of a vacuum, respectively.

Henry derived mobility formulas for spheres of radius r and an infinitely long cylinder of radius r that are appreciable for low zeta-potential and any value of κr. Henry's formula for the electrophoretic mobility μ of a spherical colloidal particle is expressed as

$$\mu = \zeta\,(\varepsilon_r\varepsilon_0/\eta)\,f(\kappa r) \qquad /6/$$

where $f(\kappa r)$ is Henry's function.

Henry's mobility formula includes the retardation effect but does not take into account the relaxation effect (the distortion of the equilibrium double layer).

An accurate analytic expression for the electrophoretic mobility of a spherical colloidal particle was derived by Ohshima (1998).

The electrophoretic mobility depends on pH, ionic strength, viscosity, temperature and dielectric constant of the suspending liquid.

For fundamentals of electrophoresis and calculations of electrophoretic measurements data see excellent review by Ohshima (1998).

The electrophoretic mobility of dissolved lignin and lignin/CS and lignin/PDADMAC complexes samples was measured with a Coulter Delsa 440 instrument (Doppler Electrophoretic Light Scatter Analyser). Lignin solutions of different concentration (1–20 g/l), ionic strength (0.025 M NaCl, 0.1 M NaCl, and 0.1 M NaOH), and pH (12.8 and 7) were made in the same way as in adsorption and SAXS/USAXS studies, but before measuring the electrophoretic mobility, the solutions were diluted 1/20, to ensure that the conductivity was below 1 mS/cm. Lignin/CS and lignin/PDADMAC complexes were otherwise made in the same way as in adsorption studies, but the solutions were diluted 1/20, to ensure that the conductivity was below 1mS/cm. The measurements were conducted at run time 120 sec, voltage 5 V, frequency 500 Hz, and at constant temperature (25 °C).

3.2.3 Colloid titration

Colloid titration is based on the tendency for low-molecular weight linear polyelectrolytes to form polyelectrolyte complexes that are stoichiometric with respect to charge. In this method, a solution or a dispersion is titrated with an oppositely charged standard polyelectrolyte solution. What is actually measured is the capacity of the mixture to adsorb a polyelectrolyte of opposite net charge. The end point occurs when the net charge of the complexes is zero (Terayama 1952).

Lignin sols were titrated with an oppositely charged polyelectrolyte using a Mütek PCD 03 particle charge analyser to detect the end point. PDADMAC was used for anionic sols and sodium polyethenesulfonate was used for cationic sols. PDADMAC with M_w $1•10^5–3•10^5$ and CD 6.19 meq/g was obtained from Allied Colloids Ltd., Yorkshire, England. Sodium polyethenesulfonate with M_W $1.9•10^4$ and CD 7.69 meq/g was obtained from MT-Instruments Oy, Finland).

3.2.4 Ultra Small Angle X-Ray Scattering

Small Angle X-ray Scattering (SAXS) is used to measure the dimensions and electron density distribution of molecular structures and assemblies with sizes from 1 to 100 nm and can be extended to several microns with Ultra-Small Angle X-ray Scattering (USAXS). The applications cover various fields, from metal alloys to synthetic polymers in solution and in bulk, biological macromolecules in solution, emulsions, porous materials, nanoparticles, etc. The major advantage of the SAXS lies in its ability to provide structural information about partially or completely disordered systems. The method makes it possible to study the structure of particles in solution and to analyse structural changes in response to variations in the composition of the solution and external conditions.

A typical SAXS experimental set-up is shown in Fig. 3. A monochromatic beam of incident wave vector $\mathbf{k}_i$ is selected and falls on the sample. The scattered intensity is collected as a function of the scattering angle 2θ. Elastic interactions are characterised by zero energy transfers, such that the final wave vector $\mathbf{k}_f$ is equal in modulus to $\mathbf{k}_i$. The relevant parameter to analyse the interaction is the momentum transfer or scattering vector $\boldsymbol{q}=\mathbf{k}_i-\mathbf{k}_f$, defined by $q=(4\pi/\lambda)\sin\theta$. The standard unit for q is $Å^{-1}$.

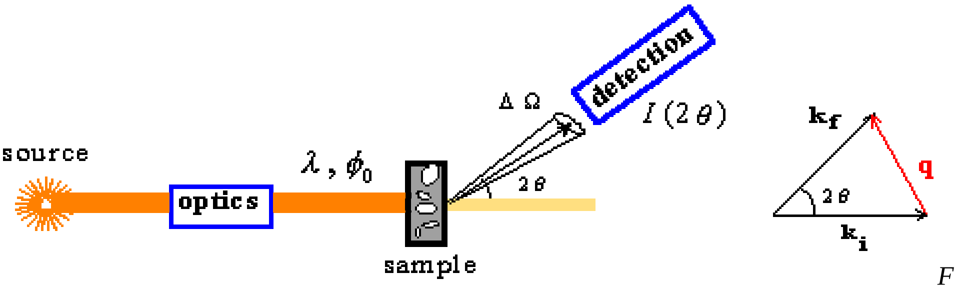


Fig. 3. Schematic view of a typical scattering experiment.

The scattered intensity $I(q)$ is the Fourier Transform of the correlation function of the electronic density $\rho(r)$, which corresponds to the probability to find a scatterer at position r in the sample if another scatterer is located at position 0: elastic x-ray scattering experiments reveal the spatial correlations in the sample. Small angle scattering experiments are designed to measure $I(q)$ at very small scattering vectors $q \approx (4\pi/\lambda)\theta$, with 2θ ranging from few micro-radians to a tenth of a radian, in order to investigate systems with characteristic sizes ranging from crystallographic distances (few Å) to colloidal sizes (up to few microns). The number of photons scattered by one sample is proportional to its total volume V and to its electronic contrast. In the simple case of a binary system for instance, like scattering objects of density ρ_1 embedded in a solvent of density ρ_2, the electronic contrast is $\Delta\rho=\rho_1-\rho_2$. The higher the contrast between particles and solvent, the more intense the scattered signal. The experimental intensity is usually fitted in order to determine the density $\rho(r)$, the size, the shape and the internal structure of one elementary scatterer, as well as the structure and the interactions between scatterers. The determination of physical quantities, such as molecular weight, particle volume, specific surface or osmotic compressibility, is feasible only if $I(q)$ is measured on absolute scale. As shown in Fig. 3, part of the incident beam is absorbed in the material. The number of photons scattered in the solid angle $\Delta\Omega$ in the direction 2θ have to be normalised with respect to the number of photons transmitted through the sample. This implies to control several parameters: the sample thickness e (cm) and transmission T, the incident flux of photons ϕ_0 (photons/s) and the solid angle of one pixel of the experiment $\Delta\Omega$. The absolute intensity can then be obtained in absolute units (cm^{-1}).

The size and the shape of "particles" are of fundamental interest to understand the microstructure of a heterogeneous material or complex fluid. Small angle X-ray scattering gives valuable information, providing that the contrast is sufficient. Experimentally, form factors can only be measured in the dilute regime where particles can be considered as independent scatterers without any interactions. In this case, the intensity is directly proportional to the contrast $\Delta\rho$, the volume fraction ϕ and the volume of one particle V_P and the form factor of a single particle $P(q)$. Form factors have been theoretically derived for spheres, cylinders, disks, rods, micelles, lamellas or Gaussian polymers, which are the basic shapes encountered in soft condensed matter.

The distance distribution function $p(r)$ represents the probability of finding two points in the particle separated by a distance r (Porod 1982; Feigin and Svergun 1987). The largest diameter of the particle can be obtained from the $p(r)$ function.

An excellent review of structural studies of macromolecules by SAXS is available (Svergun and Koch 2003).

During the last few years, *ab initio* methods for analysis of macromolecular shapes have become one of the major tools for SAXS data analysis in terms of three-dimensional models. Several programs are publicly available on the Web. The performance of *ab initio* shape determination programs DALAI GA, DAMMIN, and SAXS3D was compared by Takahashi et al. (2003). Optional symmetry and anisometry restrictions, absent in other programs, lead to a better performance of DAMMIN on symmetric models. Practical applications of *ab initio* shape determination range from individual macromolecules to large macromolecular complexes. DAMMIN program was used in this work for analysis of shape of lignin particles. The details on experimental set up used in this work are given in paper V. An example of USAXS image of dissolved kraft lignin obtained in this study is shown in Fig. 4.

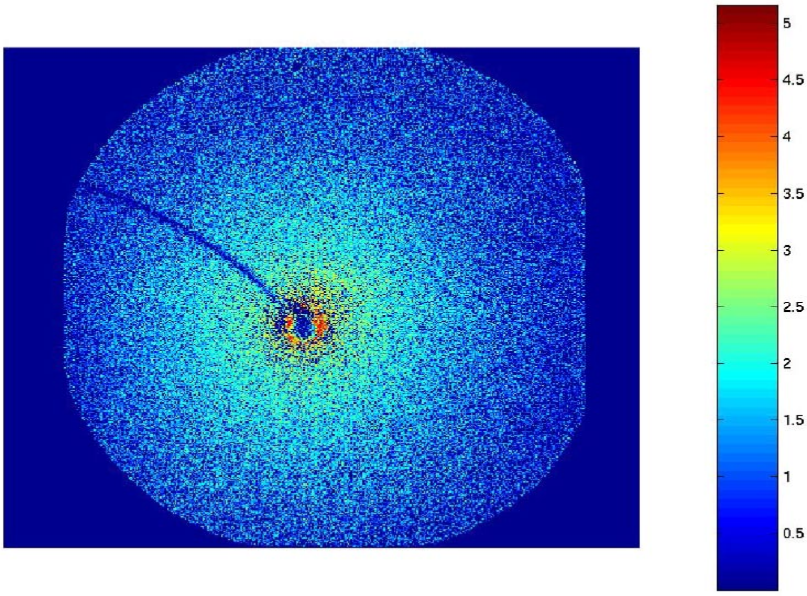


Fig. 4. An example of USAXS image of kraft lignin solution obtained in this study (5 g/l in 0.1 M NaOH). Logarithmic scale.

3.2.5 Electron Spectroscopy for Chemical Analysis

The surface chemical composition of cellulose fibre samples was determined using ESCA (XPS). The pulp sheets were dried at room temperature between two board sheets that had a smooth surface. Samples for ESCA were taken from these sheets.

ESCA is a versatile surface analytical technique that can be applied for a variety of material. It provides very useful chemical-state information and, besides, interpretation of ESCA spectra is relatively straightforward. ESCA is based on the photoelectric effect. Sample is placed in a vacuum chamber and its surface is irradiated with monochtromatic X-rays. Fig. 5 shows the processes of photoelectron and Auger electron emission under irradiation.

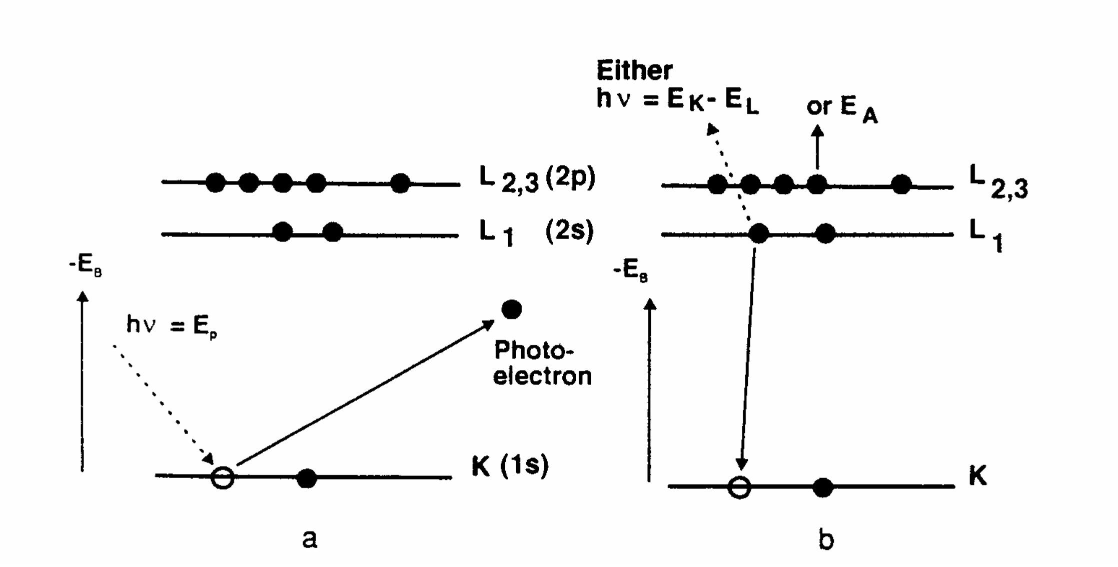


Fig. 5. ESCA principle. Photoelectron (a) and Auger electron (b) emission (adopted from Stenius and Vuorinen 1999).

Electrons with binding energies smaller than the energy of the exciting X-ray are ejected out of material. The emitted core electrons are then collected by an analyser and their kinetic energies are being measured. The kinetic energy, E_k, is given by:

$$E_k = h\nu - E_b - \Phi \qquad /7/$$

where $h\nu$ is the energy of the X-ray beam and Φ is the reduction in kinetic energy due to a electrostatic charge of the sample, which arises when photoelectrons are emitted (Riviere 1990). The term E_b describes the binding energy of the electrons, which is characteristic of each element in the sample. Therefore the origin of the element can be identified from equation /7/ by measuring the kinetic energy of the emitted electrons. ESCA is a very surface sensitive technique since the photoelectrons can move freely only for short distances in the material before they collide with the atoms of the material and lose energy. As the depth of analysis increases the intensity of escaping electrons decreases exponentially due to the fact that photoelectrons interact with the atoms of the material. The thickness of material required to reduce the initial intensity of electrons to $1/e$ of its original value is called the escape depth of electrons and is a constant for a given material at constant density. This means that about 95 % of the signal intensity at the detector is collected from a distance 3λ. Hence, if the take-off angle of the electrons is 90 degrees, the depth of analysis is about 3λ (Briggs and Riviere 1990), which corresponds to an analysis depth of 6–12 nm for polymeric materials.

The penetration depth can be reduced by changing the angle between the sample and the analyser.

As a consequence of photoelectron emission, which creates a hole in the core level, secondary processes occur. The hole is filled by an electron from a higher level, releasing an amount of energy that can either radiate (X-ray fluorescence) or be transferred to another electron, which is then emitted (Fig. 5b). Such electrons are called Auger electrons. Auger peaks always appear in wide scan ESCA spectra. However, in spectrometers particularly designed for Auger emission spectra (AES), the initial emission of electrons is obtained by irradiating the surface with an electron probe beam. AES does not depend on the energy of the incident X-ray radiation. However, the position of Auger peaks in ESCA spectra depends on the X-ray source since the binding energies in ESCA spectra are always corrected for the energy of the X-ray source. Auger peaks have been extensively used in studies of the chemistry of metal surfaces, but applications of the method to fibres or paper are scarce.

Determination of surface lignin

The use of ESCA to study cellulose fibres was pioneered by Dorris and Gray (1978). Since then, the ESCA technique has been used in many studies of fibres surface chemistry, including the surface composition of wood pulp fibres (e.g. Dorris and Gray 1978; Carlsson 1996).

There are two alternative ESCA methods for lignin analysis. The first one is based on determination of oxygen-to-carbon atomic ratios, which are different for cellulose and lignin (Laine and Stenius 1994; Johansson et al. 1999). In the other method, the carbon high-resolution C (1s) spectrum is deconvoluted and the lignin content is derived from the relative concentration of carbon bound only to other carbon atoms (denoted C-C component). Such carbon atoms are not present in chemically pure cellulose. Thus, the C-C component in the C (1s) spectrum, originating from carbon atoms that have no oxygen neighbours is due to lignin only, provided that there are no extractives (fatty and rosin acids, sterols etc.) present in the fibre surface (Dorris and Gray 1978a,b).

Here lignin quantification based on the C-C percentages is used. However, before quantification, results from the two analyses are correlated and compared with adequate references so that experiments recorded from contaminated specimens can be discarded, as described by Johansson (2002).

The analysis was performed with a Kratos Analytical AXIS 165 electron spectrometer using a monochromatic Al (K_α) X-ray source run at 100 W. Analyses were made on an area of about 1 mm^2 at three different locations on the sample. The measurement depth was 2–10 nm. The binding energies in the high-resolution spectra were charge-corrected using a tabulated value of 285.0 eV for the C (1s) components (the C-C bond) as described in (Bearnson and Briggs 1992). For samples with small but detectable amounts of nitrogen (N 1s), additional spectra were determined to find out the surface concentration of catonic starch. In the more detailed analysis of the carbon peak, the division of the chemical shift into four categories suggested by Dorris and Gray (1978) and Carlsson and Ström (1991) was used. The categories are carbon bonded to other carbons and hydrogen only (C1), carbon with one oxygen bond (C2), carbon with two oxygen bonds (C3) and carbon with three oxygen bonds (carboxyl groups, C4).

Pure cellulose contains theoretically only C2 and C3 carbons. Lignin contains 49 % C1 carbon. Hence, if the sample contains only cellulose and lignin, the surface coverage of lignin, ϕ_{lignin}, can be determined from the relative amount of C1 carbon. However, a small C1 peak is almost always detected even in fully bleached pulp samples. This is mainly due to adsorption of airborne contaminants. In the present case, account has also to be taken of the amount of lignin present in the pulp surface before the adsorption of complexes, as well as the amount of PDADMAC and cationic starch affecting the C1 peak. Hence, the surface coverage of adsorbed lignin was calculated using the equation

$$\phi_{lignin} = \frac{C1 - a}{49\%} \times 100\% \qquad /8/$$

where the constant a is a correction factor for the presence of contaminants and background lignin and $C1$ is the area of the C1 peak divided by the total area of the C (1s) peak. The amount of C1 in the unmodified pulp sample was 5 % (paper II) or 10 % (paper III) and hence these values of a were used in the calculations.

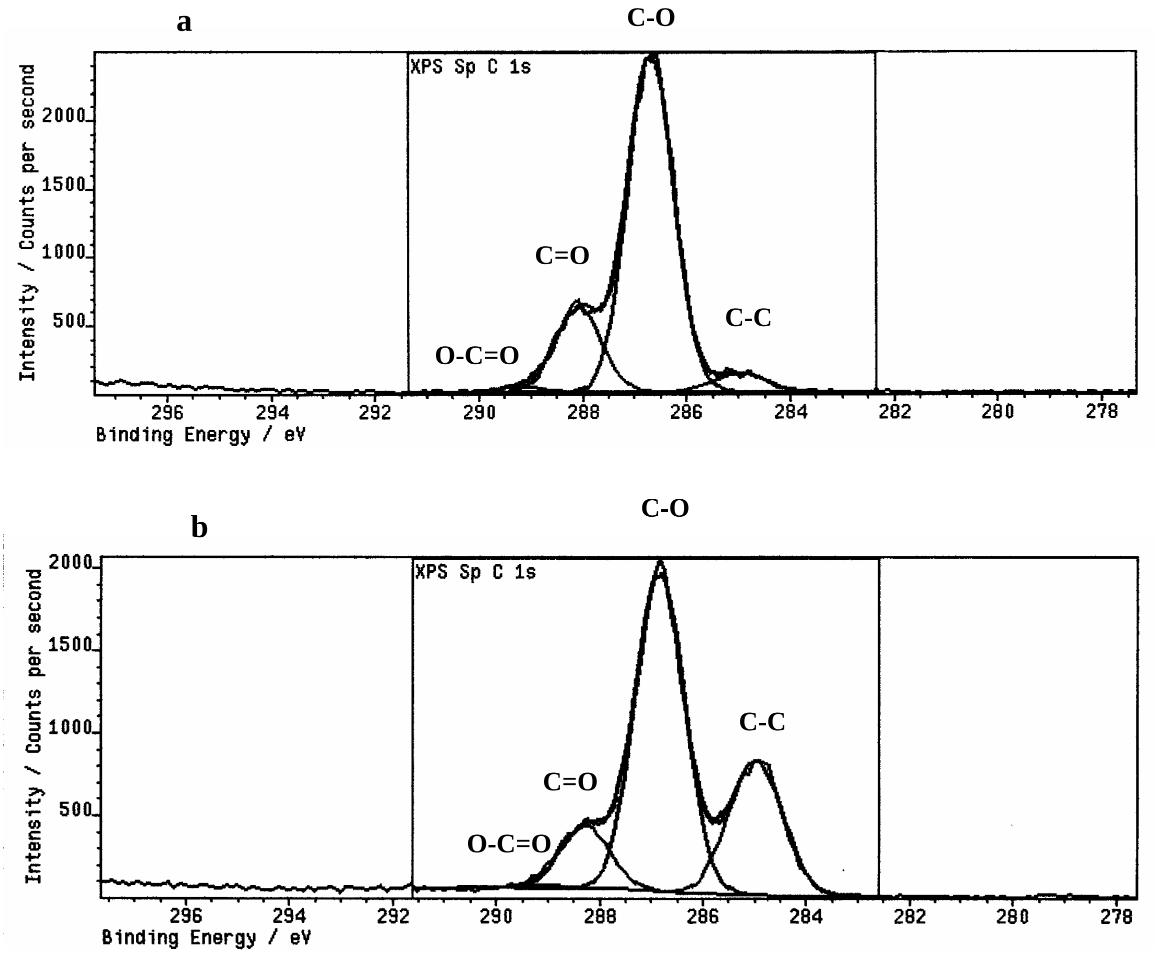


Fig. 6. High resolution C 1s spectra with component fitted carbon region for (a) pure ECF bleached kraft pulp and (b) pulp with sorbed lignin (lignin was sorbed from aqueous solution at pH 7, ionic strength 0.1 M (NaCl), lignin concentration 2000 mg/l (b).

3.2.6 Confocal Laser Scanning Microscope

A Confocal Laser Scanning Microscope (CLSM) was used to identify and locate lignin in the fibres after adsorption. The unique feature of the CLSM is its non-destructive sectioning capability. When obtaining an image from a section of a thick, translucent object, the confocal principle provides an enhanced lateral resolution. The light coming from the specimen is focused through a small aperture, which ensures that data is obtained from one particular level of the specimen only (Fig. 7). Trials using a CLSM in fluorescence mode showed that lignin is strongly excited by blue light, thus indicating the feasibility of using a CLSM to study lignin content and distribution. Differences in intensity were assumed to correlate with the concentration of lignin in the fibre cell walls (Moss et al. 1999).

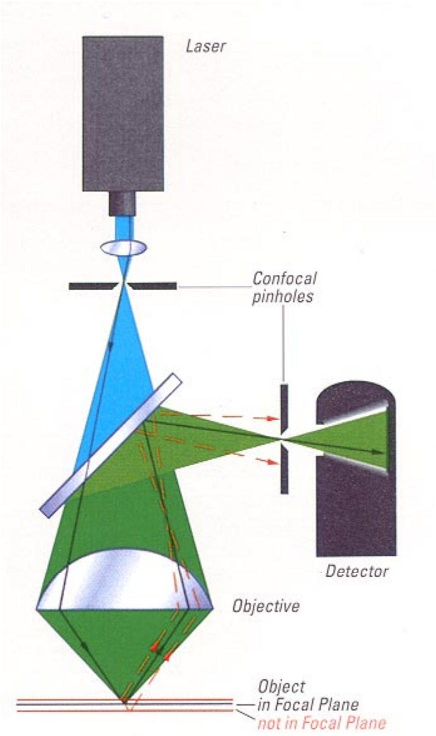


Fig. 7. Schematic diagram of CLSM instrument.

Fibre preparation for CLSM. Samples of hand sheets were embedded under vacuum in an epoxy resin. After congealing, the surfaces of the resin blocks were ground down until cross-sections of the fibres could be clearly seen, and then the surfaces were polished. In addition, fibres after adsorption were placed onto a glass and examined both when wet and after drying. The surface of paper handsheets prepared from the sorption pulp were also examined as such.

CLSM examination. All samples were examined with a Leica CLSM in fluorescence mode using an excitation wavelength of 490 nm. Immersion oil was applied to the surface of the resin block and cross-sections examined using an x40/1.3 oil immersion objective. All samples were examined under similar operating conditions. Microscope parameters (i.e. laser power, voltage, pinhole size and offset) were kept constant as far as possible. The laser power was 20 mW, the offset was zero.

3.2.7 Contact angle and drop volume measurements

Wetting involves the interaction of a liquid with a solid. It can be the spreading of liquid over a surface, the penetration of a liquid into porous medium, or the displacement of one liquid by another. The contact angle, θ, is a quantitative measure of wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, vapour and solid intersect (Fig. 8). If the angle θ is less than 90° the liquid is said to wet the solid. If it is greater than 90° it is said to be non-wetting. A zero contact angle represents complete wetting.

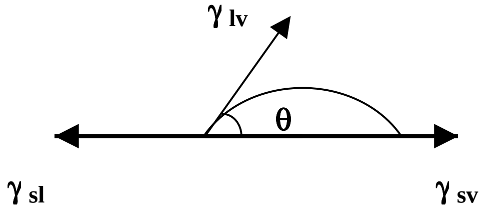


Fig. 8. Contact angle definition. The vectors γ_{lv}, γ_{sv}, and γ_{sl} refer to the interfacial energies of the liquid/vapour, solid/vapour and solid/liquid interfaces. The vectors do not represent stresses in the solid surface, but forces on the fluid at the three-phase boundary.

The contact angle of a drop on an ideal solid (smooth, flat, homogeneous, non-deformable) is related to the interfacial energies at the three phase boundary by the classical Young's equation :

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \qquad /9/$$

where γ_{lv}, γ_{sv}, and γ_{sl} are the vectors for interfacial energies of the liquid/vapour, solid/vapour and solid/liquid interfaces, respectively.

The contact angle measured on a rough surface (called the Wenzel angle, θ^*) does not obey Young's equation; it is related to the equilibrium (Young) angle θ, from

$$\cos \theta^* = r \cos \theta \qquad /10/$$

where r is the ratio of the true wetted area to the apparent area (the area if the surface were smooth) and can be taken as a measure of surface roughness.

Roughness results in local changes in the contact angle and hence the shape of contact lines. Instead of being a straight line in the case of planar substrates, the three-phase contact line tends to wander on the x - y plane due to the roughness. Surface roughness amplifies the wetting. Since $r > 1$, the wetting gets better in hydrophilic situations ($\theta^* < \theta$ for $\theta < 90°$) and worse in hydrophobic ones ($\theta^* > \theta$ for $\theta > 90°$).

The effect of drop size on contact angle has been well documented (e.g. Chan 1994). This effect is caused by solid surface imperfections: heterogeneity, roughness, instability, deformation. Although contact angle varies with drop size, this effect is usually insignificant for a drop of volume greater than 10 µl (e.g. Berg 1993).

The reliability of contact angle measurements on paper is debatable, since the papers are rough, porous and inhomogeneous. Wetting of paper sheet is affected by the hydrophobicity of the fibres, pores and cavities and the morphology of the surface.

Despite this, contact angle measurements are frequently used. Presently there is a good understanding of the factors that control the equilibrium contact angle on solid surfaces that are both inhomogeneous and rough (Wenzel 1936; Oliver et al. 1980; Oliver and Mason 1980; Marmur 1996; Brandon and Marmur 1996; Marmur 1996; Chow 1998; Bico et al. 1999; McHale et al. 2000; Della Volpe et al. 2000).

Water absorbance by paper

The theory of water transport into paper has been discussed rather extensively (Scallan 1978; Stannet and Williams 1978; Schuchardt and Berg 1990, 1991; Salminen 1988).

One of the mechanisms for water uptake is capillary pressure, under which water penetrates inside paper. When the contact angle is less than 90°, the positive capillary pressure pulls the liquid into the pores. The penetration of a liquid drop into a porous substrate is often described as a wicking process. Contact angle, pore radius and sheet void fraction are controlling parameters. Another mechanism involves molecular diffusion of water into fibre cell wall, accompanied by swelling.

In this work, water absorbency was measured by changes in water drop volume (papers I and IV).

Static contact angles and drop volumes were measured using a KSV CAM 200 computer-controlled video based instrument (KSV Instruments Ltd., Finland). The instrument includes a CCD video camera, a frame grabber, an adjustable sample stage and a LED light source. A water drop (14 µl) was allowed to fall onto the solid from a syringe tip to produce a sessile drop. Images were captured at a rate of 1 per second for 4 minutes.

The contact angles were calculated by curve fitting of the captured drop profile to the theoretical shape predicted by the Young-Laplace equation. The software (CAM 200) fits the Young-Laplace equation to the shape of the drop utilizing all points on the drop profile. The tangent to the curve assigned where the curve intersects the baseline. The angle between this tangent and the baseline is the contact angle. The contact angle was measured on 3 different points of each sample and the adsorption series were repeated at least twice. The reproducibility of contact angle measurements on different samples prepared in the same way was ±5° or better. The drop volumes were calculated by curve fitting of the captured drop profile to the shape of a calibration sphere of known volume. The initial drop volume was 14 µl ±7 %.

3.2.8 Paper technical properties

Paper technical properties were measured according to SCAN standards. Details are given in papers I–III.

4 RESULTS AND DISCUSSION

4.1 Lignin in solution

The solution and colloid properties of lignin have been studied rather comprehensively and are well understood (e.g. Lindström 1979b, 1980a; Lindström and Westman 1980; Nyman and Rose 1986), meaning that they were not the objectives of this study as such. In order to correlate lignin sorption by the cellulose fibres and lignin state in the solution, colloid behaviour of lignin solutions employed in the sorption studies have been characterised. For better understanding of interfacial properties of lignin and lignin adsorption mechanism, it was important to determine the size and shape of lignin particles in the solutions used in adsorption experiments and in the layers of lignin adsorbed on fibres. By that means the structure (size and shape) of adsorbed lignin particles revealed by AFM (papers II and IV) and size and shape of lignin particles in the solution revealed by USAXS (paper V) could be compared.

In the early stage of this thesis (papers II and IV) it was assumed that most probable lignin particles in aqueous solution would be rather globular between 20–200 nm (Lindström 1979; Gupta and Goring 1960). However, based on more recent reports as well as our own study (Garver and Callaghan 1991, Richter et al. 1998, Norgren and Lindström 2000, paper V), it can be concluded that both globular and elongated shapes are likely, and the size would be about 1.5–2.5 nm for primary lignin particles. Sizes exceeding 40–150 nm are most probably typical for lignin agglomerates (Richter et al. 1998, Garver and Callaghan 1991). Thus, the clear distinguishing is needed between primary particles and agglomerates.

Results from measurements of electrophoretic mobility and size of pure lignin in aqueous solution are shown in Table 2.

Table 2. Electrophoretic mobility and size of kraft lignin in aqueous and alkaline solutions

C mg/l	**pH**	**Solution**	***R_g*** nm	**Thickness** nm	**Width** nm	**Mobility** $\mu m\ s^{-1}V^{-1}cm$
1000	7	NaCl 0.1 M	2.2	n.d.	n.d.	-2.0
2000	7	NaCl 0.025 M	3.5	n.d.	n.d.	-2.4
5000	7	NaCl 0.025 M	2.3	1.2 ±0.2	2.5 ±0.5	-2.1
10 000	7	NaCl 0.025 M	2.6	1.4 ±0.2	3.0 ±0.5	-2.7
20 000	12.8	NaOH 0.1 M	1.6	1.0 ±0.2	2.0 ±0.5	-4.0

Note that the mobility was measured in diluted solutions (1/20), whereas USAXS measurements were conducted on initial samples without dilution. Thus, actual concentrations of lignin and ionic strength in mobility measurements were 20 times lower than specified in Table 2. While this dilution may certainly have an influence on the actual magnitude of the mobility (due to expansion of the diffuse double layer), it should not have an effect on the sign and the relative magnitude of the mobility, as the only simple ions in solution are Na^+ and Cl^-, which are not specifically adsorbed. The radius of gyration R_g of the dissolved kraft lignin particles was reasonably well determined with SAXS/USAXS and varied between 1.6–3.5 nm, depending on the pH and concentration. The shape of the $p(r)$ functions indicates that the shape of the particles is markedly elongated, i.e. the particles must be more rod-like than flat disk (Svergun and Koch 2003). On the basis of the DAMMIN models the lignin particles in the solutions are elongated and are about 1 nm thick and 2.5 nm wide (paper V).

It is of interest to consider how the radius of gyration and the size in general depend on the chemical environment and the charge of the particles. The electrophoretic mobility is proportional to the surface charge density of the particle and depends on the pH, ionic strength, viscosity, temperature, and the dielectric constant of the suspending liquid. The mobilities of the dissolved lignin are shown in Table 2. For comparison with earlier zeta-potential results, see Dong et al. (1996). The negative charge of lignin in alkaline solutions is predominantly due to dissociation of phenolic hydroxyls (pK_a about 9.5) (Sjöström 1993). As a result, the lignin particle in alkali is more charged and more mobile than in neutral solution. The mobilities at pH 7 vary between 2.0 and 2.7 $\mu m\ s^{-1}\ V\ cm^{-1}$. Increasing the ionic strength will compress the diffuse double layer around the lignin particle. Increase of particle size has been reported to take place both upon increase and decrease of pH. Increase of particle size due to increase of pH was ascribed to polyelectrolyte swelling due to breaking of intramolecular hydrogen bonds and dissociation of ionisable functional groups (e.g. Chupka et al. 1970, Garver and Callaghan 1991), while the association due to decrease of pH was ascribed to formation of intramolecular hydrogen bonds: when the carboxylic groups are protonized, intramolecular hydrogen bonds are formed in the loose surface region of the particle, and intermolecular hydrogen bonds are formed between the particles (Lindström 1979b). The decreasing charge density of lignin when the pH decreases also promotes the formation of associated complexes (Sarkanen et al. 1984). According to SAXS measurements a slight increase (up to 50 %) in the particle radius (implying about a three-fold increase in volume) occurred when pH decreased from 13 to 7 at constant ionic strength 0.1 M. Thus, there was no indication of the formation of large associated complexes or aggregates. Norgren et al. (2002) reported that very high salt concentrations are needed for extensive self-aggregation to occur and that the resulting aggregates are fractal. On the other hand, according to ultrafiltration and light-scattering studies reported by Woerner and McCarthy (1988), large stable complexes of kraft lignin exist in neutral and weakly alkaline solutions. As alkalinity is increased, these complexes are broken to yield small molecules. When alkalinity is decreased from pH 13.8 to 8.5, large stable associated complexes (M_w up to 200 000) grow from smaller lignin molecules (M_w 3500). An associated complex would most probably give a power-law type intensity curve in SAXS, but such intensity curves were not seen. This means that there either was no association when pH decreased from 12.8 to 7 in aqueous solutions of kraft lignin or that the size of the associated complexes must be larger than about 100 nm.

It cannot be excluded that some of the increase of the particle size taking place as pH decreases was due to occasional association of macromolecules. The intensity and the dimensions extracted from it would then be an average over such aggregates and single particles. However, in turbidity studies (paper I) the extinction coefficient did not change with changes in lignin concentration in NaCl solution. Thus there was virtually no formation of colloidal particles in NaCl solutions at pH 12.8–7.

The following picture emerges: due to dissociation of phenolic hydroxyls lignin acquires negative charge in alkaline solution, which results in high electrophoretic mobility and strong electrostatic repulsion between the lignin particles. The repulsion prevents association of lignin particles in the solution, which is consistent with the small diameters of lignin particles measured by SAXS. When pH decreases the negative charge on lignin is partly neutralised which leads to a decrease in the electrophoretic mobility of the lignin particle. However, the electrostatic repulsion between the lignin particles is still sufficient to prevent extensive association in neutral solution.

On the basis of the low resolution shapes obtained by DAMMIN the lignin particles consist of oblate and prolate parts, which have associated into elongated structures. The shape remains irregular but elongated at different concentrations of lignin and in different aqueous solvents. This is in contrast to another study, (Garver and Callaghan 1991) where acetylated lignin in 1.0 M $CHCl_3$ solution was found to be an oblate ellipsoid with axial ratio less than 18 using NMR. We found the thickness of the dissolved lignin particles to be about 2 nm, which is consistent with results of Luner and Kempf (1970). The reason why a more oblate shape is observed in surface studies of lignins could be a coiling of the elongated macromolecule.

Colloidal behaviour of lignin

The lignin remained soluble at all pH (12–7) in NaOH/NaCl solution. Ca^{2+} neutralized the negative charge on lignin (Fig. 9), which promoted precipitation and coagulation. In 4 mM $CaCl_2$ the colloid was rather stable at all pHs. In 8 mM $CaCl_2$, coagulation and sedimentation occurred at all pHs (from 12 to 7). The effect of aluminium ions on lignin charge increased with decreasing pH; while at pH 12 the charge of lignin was scarcely affected by introducing the aluminium, at pH 7 aluminium rendered the lignin cationic (Fig. 9) or neutralized it at higher lignin concentration. These results are in a good agreement with Dong et al. (1986), who reported reduction of zeta potential on kraft lignin with introduction of $CaCl_2$ and charge reversal with introduction of $AlCl_3$ and with e.g. Sundin and Hartler (2000a), who reported precipitation of kraft lignin from alkaline solutions with Ca^{2+} and Al^{3+} ions.

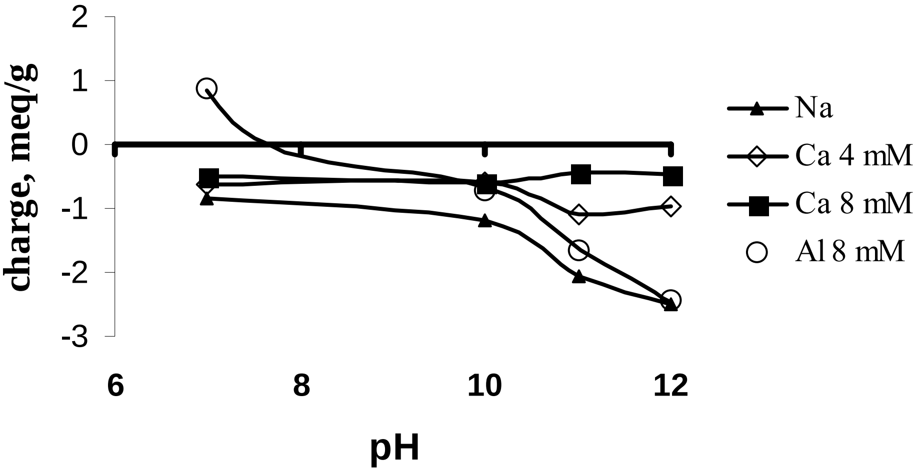


Fig. 9. Effect of electrolytes on lignin charge as determined by colloidal titration. Ionic strength 0.1 M NaCl, lignin concentration 500 mg/l (paper I).

According to Lindström (1980), the critical coagulation concentration (c.c.c.) of all salts increases for kraft lignin with increasing pH. For a kraft lignin sol c.c.c. = 6 mM $CaCl_2$ (lignin concentration 0.1 g/l, at pH 6.2 and 25 °C). According to Nyman and Rose (1986), the c.c.c. for a kraft lignin sol at pH 12.8 is about 9 mM $CaCl_2$. It was found in this study that for lignin concentrations below 5 g/l in 0.1 M NaCl, the addition of 8mM $CaCl_2$ rapidly coagulated the lignin at all pH.

The metal ions can be ranked according to their effect on dissolved lignin charge and colloidal stability as follows:

Na < Al < Ca (pH12–10), and Na < Ca << Al (pH 7).

4.2 Lignin uptake from aqueous solutions and dispersions

The examples of isotherms of lignin uptake by fibres are shown in Fig. 10.

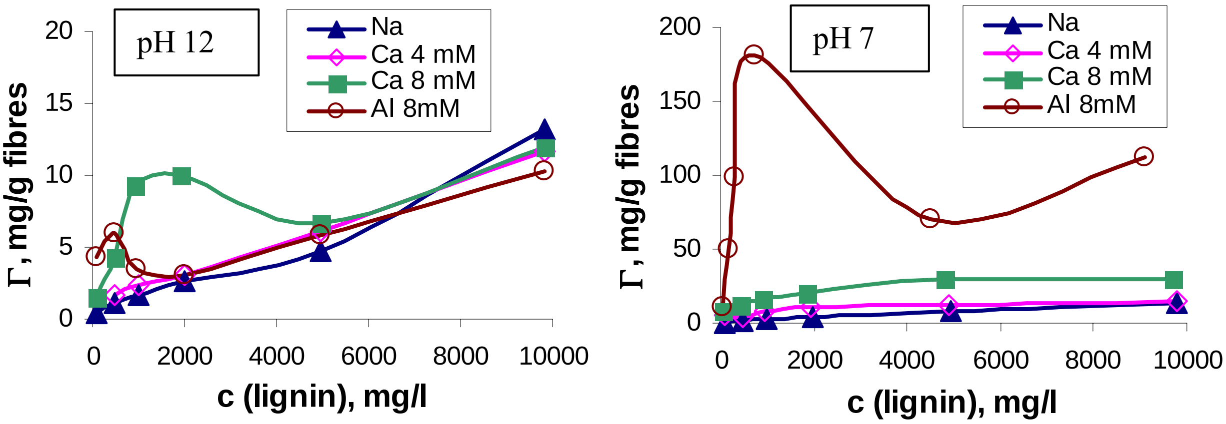


Fig. 10. Isotherms of lignin uptake with ionic strength 0.1 M NaCl.

While in the presence of monovalent simple ions only the adsorbed amount depended linearly on lignin concentration in the solution, introduction of calcium and aluminium in some cases resulted in a sharp maximum in the isotherm of lignin uptake.

Lignin uptake by the fibres correlated directly with lignin phase behaviour (results presented in Figs 1 and 4 in paper I). Maximum lignin uptake by the fibres corresponded to the ranges of maximum lignin sedimentation from the solution in the whole pH range with calcium (8 mM) and at pH 7 with aluminium. When aluminium completely removed lignin from the solution (Fig. 10), the fibres sorbed striking amounts of lignin. The amount of lignin deposited on the fibres also depended on the charge of lignin particle. Maximum lignin deposition on fibres corresponded to the range of neutralization of lignin charge. In a given ionic medium (pH, background ionic strength) the ratio of simple electrolyte to the dissolved lignin determined whether lignin aggregated and precipitated from the solution, thereby dramatically increasing the lignin uptake by the fibres. The occurrence of an optimum salt/lignin ratio makes it easy to understand why at constant concentration of simple salt, higher concentrations of lignin in the solution sometimes lead to less lignin uptake and retention in the fibres than low lignin concentrations (Fig. 4 in paper I). These results are consistent with results of Sundin and Hartler (2000 b) that show that the kappa number of the pulp increases with increasing calcium concentration in the solution. In my experimental work, I observed that when Ca^{2+} was added to fibres in equivalent amount, and followed by addition of lignin solution, lignin sols coagulate indicating that calcium was drawn from the fibres to the lignin, and thereby, higher calcium affinity to lignin than to cellulose. This is in good agreement with Torre et al. (1992), who showed that lignin has a higher capacity for calcium retention than cellulose.

Fig. 11 illustrates the good agreement between total amount of uptaken lignin and lignin detected on the fibre surface (data from papers I and II, one point-surface coverage at Ca 4 mM was not included in paper II).

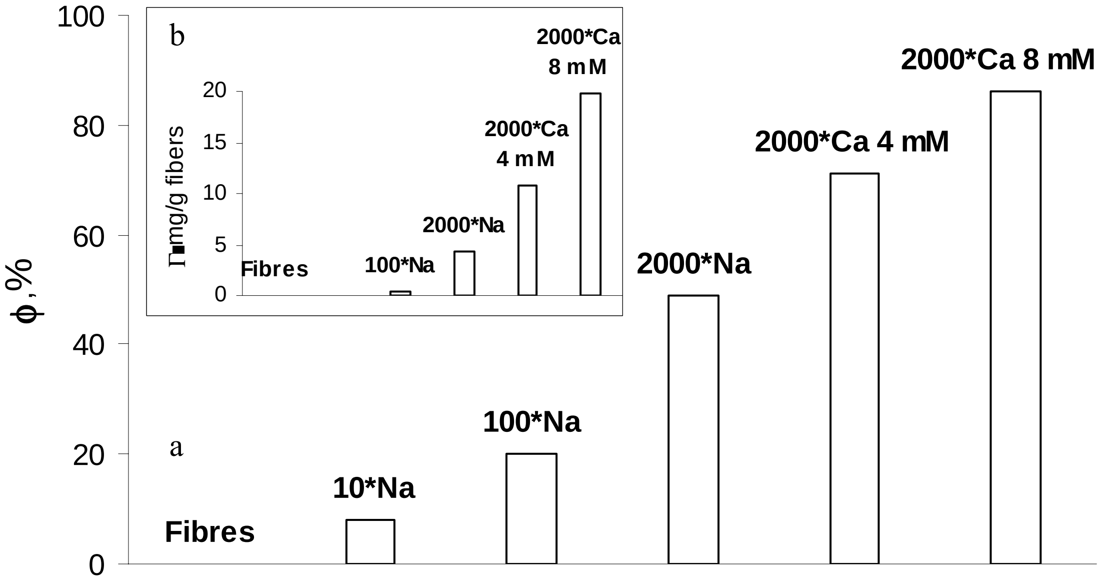


Fig. 11. Lignin uptake by fibres from aqueous solutions with simple salts. pH 7, ionic medium is 0.1 M NaCl. Numeric values in column data labels stand for concentration (mg/l) of lignin solution added to the fibres. Indexes Ca 4 mM and Ca 8 mM stand for addition of calcium chloride in correspondent concentrations. (a) surface coverage of fibres with lignin taken up as determined by ESCA (at %), (b) total amount of lignin taken up by the fibres calculated from the kappa number (papers 1 and II).

All the lignin sorbed by the fibres from aqueous solutions containing only monovalent simple ions could be washed away by simple rinsing. The van der Waals' interactions between lignin and fibres in aqueous dispersion should be weak in this case, as they did not overcome the electrostatic repulsion between lignin and fibres. This was verified by direct measurement of the effect of dissolved lignin on the interactions between cellulose surfaces in aqueous solution. The results of such measurements by AFM are shown in paper I. Although the results must be regarded as preliminary and a more detailed study of the effect of different ions is warranted in order to obtain a more complete picture, they show that the presence of lignin has no effect on the interaction between the cellulose surfaces. The interactions are just screened by ionic strength as expected for the electrostatic repulsion between diffuse double layers. This would certainly not be the case if there were any significant adsorption of lignin. Thus, for the negatively charged lignin, van der Waals' interactions are not sufficiently strong to induce adsorption.

When calcium/lignin particles are flocculated and precipitated from the solution lignin deposited on the fibres and became trapped in filtrates. However, washing with pure water easily removed this lignin. The aluminium-lignin precipitate impeded drainage and got stuck in the filtrates, impeding washing.

Paper samples containing lignin were studied with CLSM using the cross-cut technique. In the absence of lignin, pure bleached pulp fibres appeared faint in blue light. After sorption some lignin was distributed throughout the cell wall, but the major part was located on the outermost layer of the fibres (Fig. 9 in paper I). When calcium-lignin flocs were precipitated onto the fibres, the lignin content in the fibres was increased (higher intensity of the images) and the lignin formed thicker layers around the fibres (about 1.5–3 μm). At the same time, part of dissolved lignin seemed to penetrate through the cell wall, which was indicated by higher image intensity throughout the whole cross-cut of the fibres (Fig. 9 in paper I).

The results showed that the lignin uptake from aqueous solutions was governed by the coagulation with salts and a filtration effect.

4.3 Lignin/cationic polymer complexes in the solution

Electrophoretic mobilities

A few things about electrophoretic mobility measurements should be pointed out. Firstly, it is the net charge of the particle at the slipping plane between the liquid and the particle that determines the mobility, not the total charge. Secondly, the mobility is not an exact measure of the charge of the complex; the size and conformation of the complex and the binding of simple counter ions inside the slipping plane will also affect its mobility. Especially close to electroneutrality these effects make it difficult to determine the exact point of zero mobility. Hence, it is not possible to precisely determine how much PDADMAC or cationic starch is needed to neutralise the lignin sol.

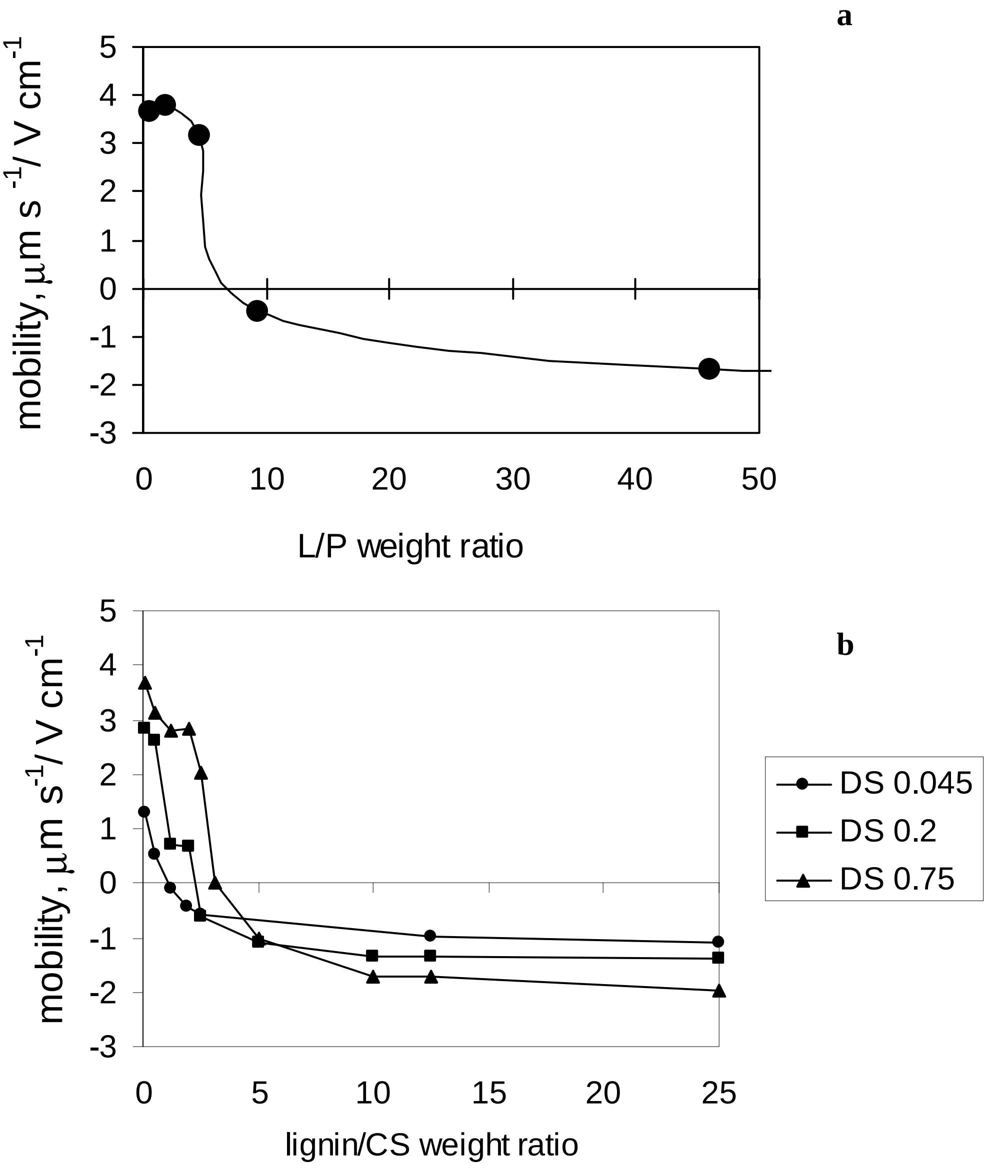


Fig. 12. Electrophoretic mobility of lignin/PDADMAC (a) and lignin/CS (b) complexes. Polymer concentrations were: (a) 1 mg/l PDADMAC, 2–50 mg/l lignin, (b) 4 mg/l starches, 0.5–100 mg/l lignin. pH was 7, ionic medium was 5 mM NaCl. For reference: before the dilution for mobility measurements, in initial solutions concentrations were (a) 21.8mg/l PDADMAC, 40–1000 mg/l lignin, (b) 80 mg/l starches, 10–2000 mg/l lignin, pH was 7, ionic medium was 0.1 M NaCl. The polymer weight ratios in diluted samples were as in initial solutions.

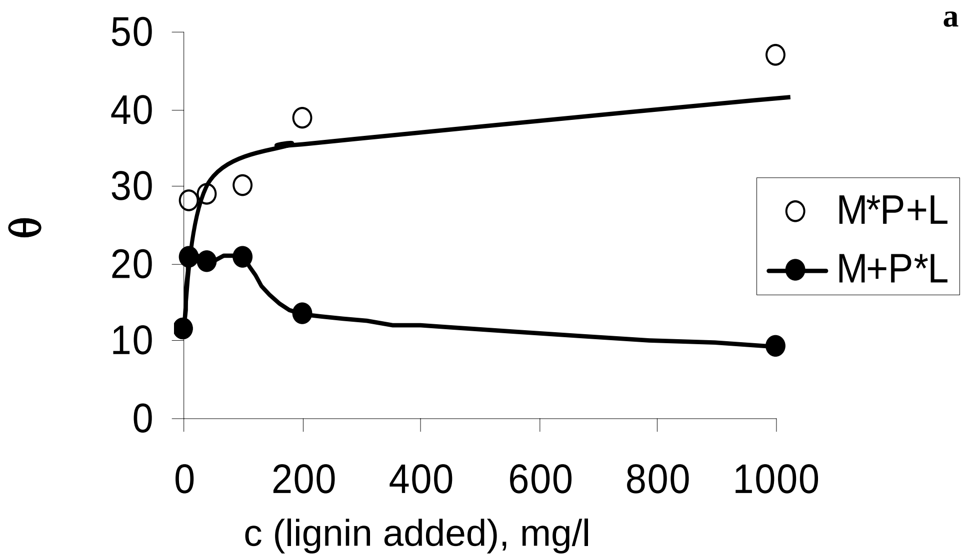
Kraft lignin and cationic polymers (PDADMAC and CS) formed both soluble and insoluble complexes in aqueous solutions. As expected, the lignin/cationic polymer charge ratio determined the sign and the mobility of the complex. Fig. 12a shows mobility of lignin/PDADMAC complexes. Fig. 12b summarizes the effect of DS of starch on the complex mobility. The electrophoretic response of lignin to addition of PDADMAC and CS appeared to be charge-dependent. As could be expected, starch with high DS bound more lignin before charge neutralization than starch with low DS. Being the most charged cationic polymer, PDADMAC bound most of the lignin before charge neutralisation.

A decrease in the concentration of salt did not affect the electrophoretic mobility of the complexes significantly (paper III). Indeed, increasing the ionic strength in the polycation/polyanion system is expected primarily to increase the amount of water bound in the complexes, without changing the weight ratio of the polymers (Ström and Stenius 1981).

Precipitation of lignin/PDADMAC and lignin/CS complexes was not measured. The electrophoretic mobility data indicated charge neutralization at lignin/PDADMAC ratio about 6. Since precipitation is expected near charge neutralization point, it was assumed that maximum precipitation of lignin/PDADMAC complex should occur at lignin/PDADMAC ratio 6. Pelton (1999) showed that for complex precipitation the optimum mixing ratio PDADMAC to lignin is around 0.175, which in terms of lignin/PDADMAC ratio is about 6.

4.4 Adsorption on mica surface

Cleaved mica was selected as a substrate in order to eliminate effects of roughness and surface heterogeneities. Cleaved mica was wetted instantly and completely by water. When lignin was adsorbed onto polyelectrolyte-coated mica surfaces the contact angle first increased as the concentration of lignin in solution was increased. At a lignin concentration of about 200 mg/l the contact angle reached a plateau (see the open circles in Fig. 13a for the M*P+L case and Fig. 13b for the M*CS+L case).



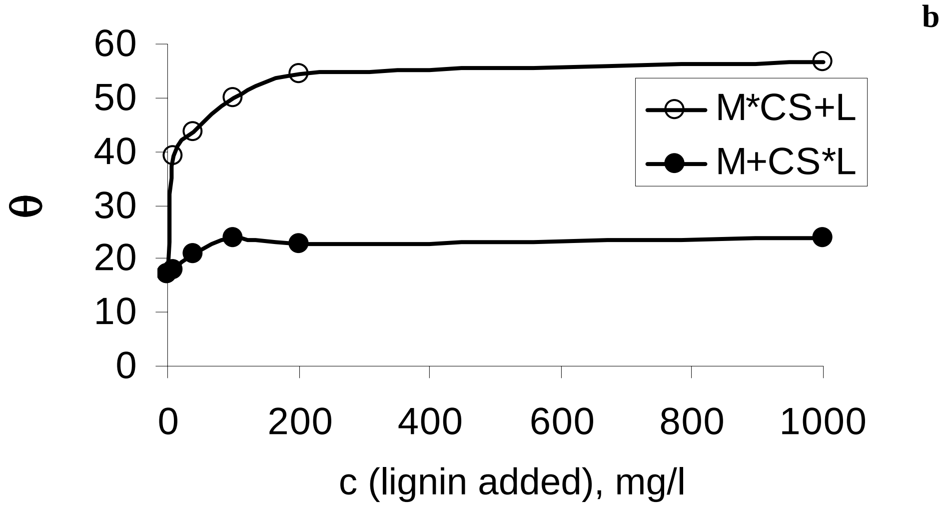


Fig. 13. Contact angle of water on mica as a function of lignin concentration in the solution (pH 7, 0.025 M NaCl). Lignin is adsorbed in the presence of CS (DS 0.2), conc. 80 mg/l and of PDADMAC, conc. 20 mg/l). The contact angle was recorded 10 s after deposition of water drop. Filled circles: polyelectrolyte was introduced into the lignin solution; open circles: polyelectrolyte was pre-adsorbed on mica before lignin adsorption.

This increase in contact angle obviously was associated with adsorption of lignin onto the solid substrate. The more lignin adsorbed onto the surface, the higher the contact angle. Evidently, lignin adsorbed onto cationic polymer-treated mica conveyed hydrophobic moieties to the hydrophilic substrate and lowered the adhesion of water to the surface, whereas the influence of adsorbed lignin/cationic polymer complexes preformed in the solution was small. This suggested that the structure of the adsorbed lignin/cationic polymer layer depended on the addition sequence, which was verified by AFM examination of the mica surface (paper IV). The similarity between the wetting of mica treated with cationic polymer only and mica treated with the cationic lignin/cationic polymer complexes formed in the solution suggests that in the adsorbed complex the hydrophilic cationic polymer is wrapped around a core containing less hydrophilic lignin.

4.5 Adsorption on cellulose fibres

Fig. 14 shows the isotherms of lignin adsorption on pulp fibres in the presence of PDADMAC and cationic starch.

When the fibres were pre-coated with cationic polymer before adsorption of lignin the adsorbed amount of lignin increased when the concentration of lignin increased until it reached a plateau at a lignin concentration of about 200 mg/l. Thus, anionic lignin was adsorbed onto cationised fibres, until the cationic charge on the fibre surface was neutralized. When lignin and cationic polyelectrolyte were mixed in solution the adsorption of the lignin/polyelectrolyte complex on the fibre surface depended on the net surface charge of the complex. Lignin was irreversibly adsorbed onto fibres from cationic complexes. As expected, there was virtually no adsorption of anionic complexes onto the anionic fibres. The surface coverage of lignin as determined by ESCA roughly followed the same trend as the total amount of lignin in the sample (Figs 15 and 16). The very high percentage of C-C bonds in the surface indicated by ESCA shows that there must be a substantial enrichment of the adsorbed lignin on the fibre surface.

In support of this result, the lignin in fibres could be observed by CLSM as thin layers around fibres (Figs 17a and 17b). The pure bleached pulp and CS or PDADMAC treated fibres appeared very faint in blue light. Bright spots indicate lignin. With cationic starch, adsorbed lignin seemed to be unevenly distributed throughout the paper cross cut and was located on the outermost surface of the fibres as a thin layer without penetrating the cell wall (Fig. 4 in paper III). Similarly with PDADMAC, thin fluorescent layers around fibres cross sections were detected (Fig. 17b).

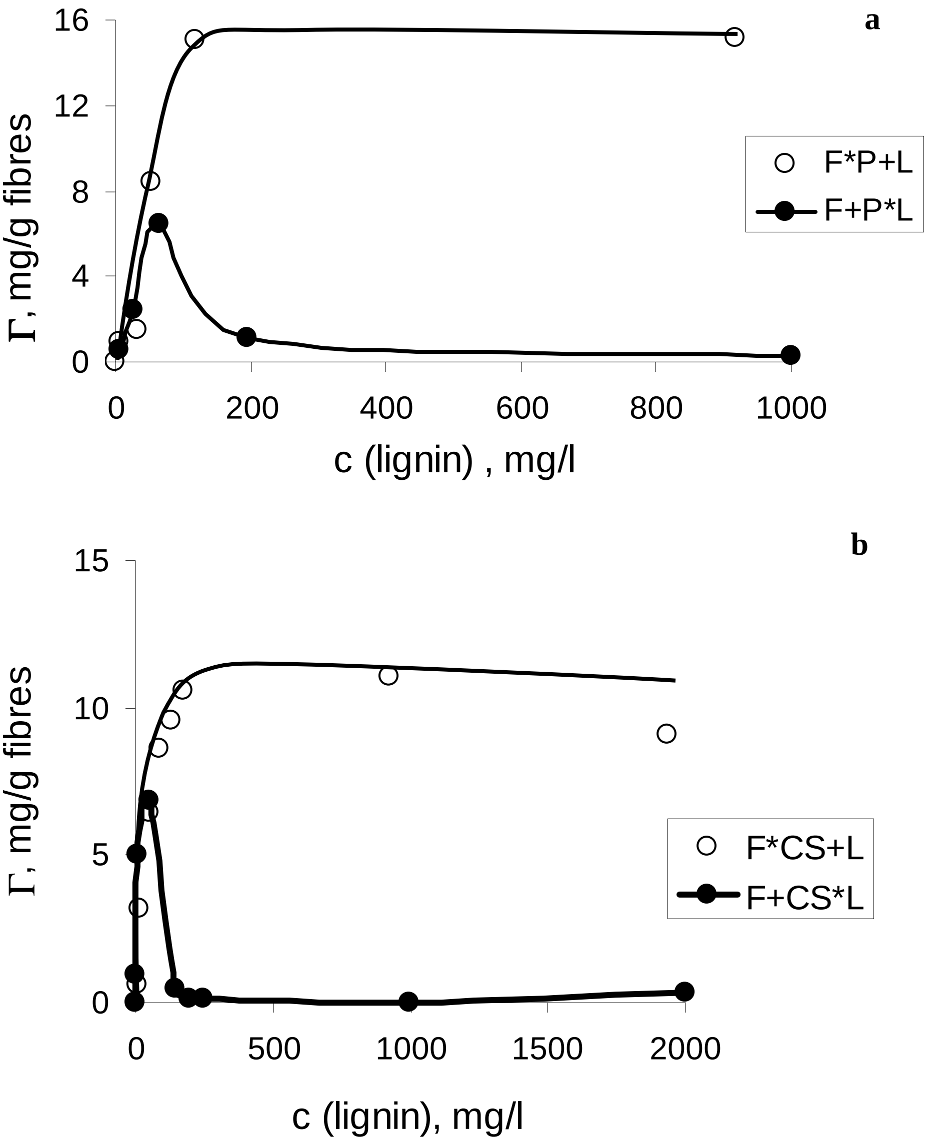


Fig. 14. Isotherms of lignin adsorption on cellulose fibres as calculated from the kappa number. (a) the amount of PDADMAC used was 20 mg/l (4 mg/g pulp), pH 7, 0.1 M NaCl, (b) the amount of CS used was 80 mg/l CS (DS 0.2) (1.2 mg/ g pulp), pH 7, 0.025 M NaCl. Filled circles: polyelectrolyte was introduced into the lignin solution; open circles: polyelectrolyte was pre-adsorbed on the fibres before lignin adsorption (papers III and IV).

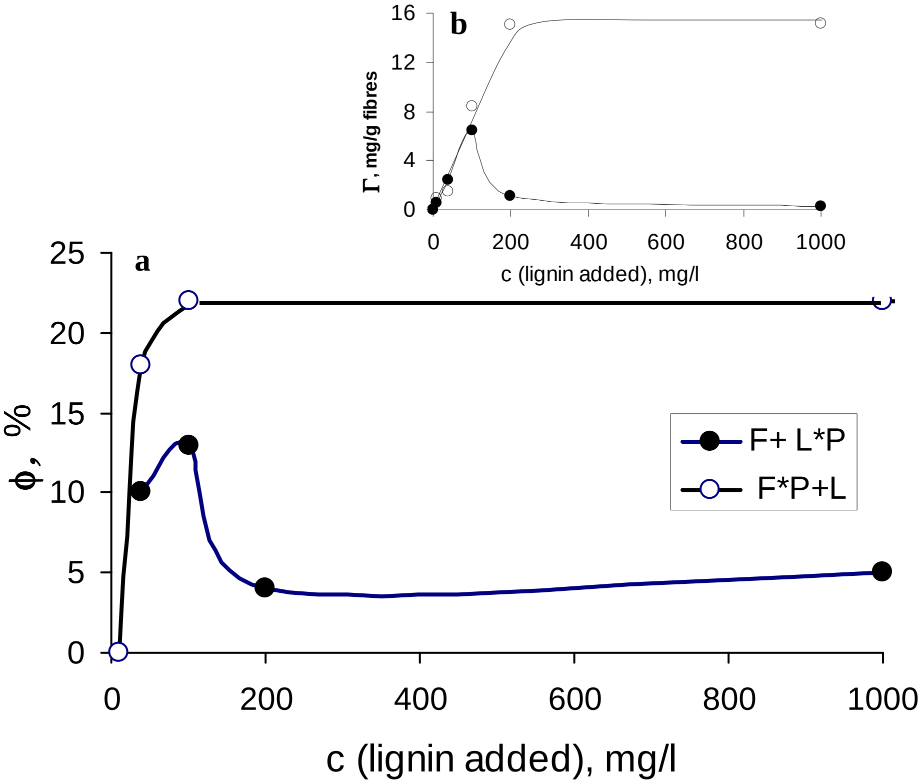


Fig. 15. Lignin uptake by fibres from aqueous solutions (pH 7, 0.1 M NaCl) in the presence of PDADMAC. a) Surface coverage of fibres by lignin determined by ESCA (at %) b) total amount of lignin taken up by the fibres calculated from the kappa number (papers II and IV). In (a) the amount of PDADMAC used was 21.8 mg/l or 3.8 mg/g of o.d. pulp. In (b) the amount of PDADMAC used was 20 mg/l or 4 mg/g fibres. Filled circles: PDADMAC introduced into the lignin solution; open circles PDADMAC pre-adsorbed on the fibres before lignin adsorption.

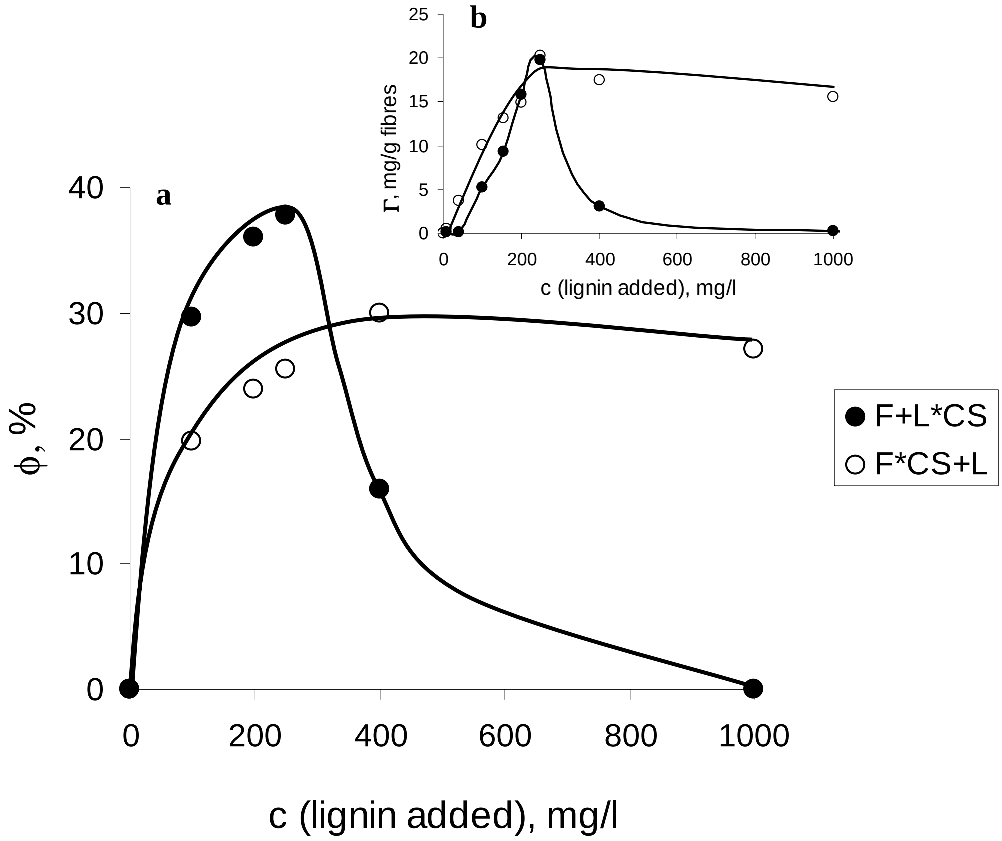


Fig. 16. Lignin uptake by fibres from aqueous solutions in the presence of CS (DS 0.75, pH 7, 0.025 M NaCl. a) Surface coverage of fibres by lignin determined by ESCA is shown and b) retained total amount of lignin adsorbed by the fibres (calculated from determination of kappa number) (paper III). Addition of CS was 80 mg/l or 1.1 % o.d. pulp. Filled circles: CS introduced into the lignin solution; open circles CS pre-adsorbed on the fibres before lignin adsorption.

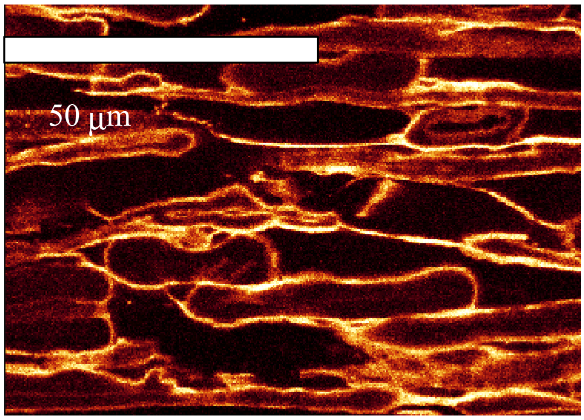


Fig. 17a. CLSM image of fibres with lignin adsorbed onto CS treated fibres (handsheet) (paper III). CS addition 400 mg/l, lignin addition 500 mg/l.

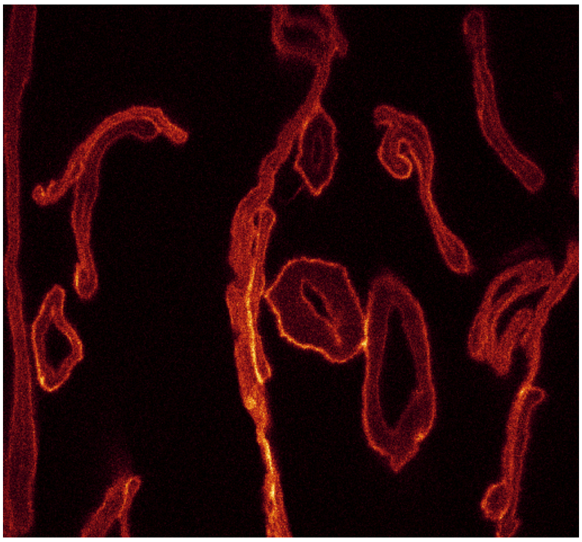


Fig. 17b. CLSM image of fibres (Bühner sheet) with lignin adsorbed onto PDADMAC-treated fibres. PDADMAC addition 3.8 mg/l, lignin addition 2000 mg/l.

The shape of isotherms of lignin adsorption onto CS or PDADMAC treated fibres (Fig. 14) suggested the formation of lignin monolayer on the cationised fibre surface. The adsorption isotherms of PDADMAC or CS on fibres were not measured. Assuming that adsorption of cationic polymers onto pulp is electrostatically driven, the maximum adsorbed amounts of PDADMAC would be 10 mg/g on pulp A (pulp surface charge 63 μmol/g, paper II) and 2 mg/g on pulp B (pulp surface charge 12 μmol/g, paper IV). The actual addition of PDADMAC was 4 mg/g pulp. Because adsorption of polyelectrolytes on oppositely charged surfaces generally is very strong, the adsorbed amount could be assessed as 4 mg PDADMAC/g on pulp A and 2 mg/g on pulp B. In the same way, the maximum adsorbed amounts of CS (DS 0.2) onto pulp B would be 17 mg/g on pulp B, actual amount added was 11 mg/g pulp, and it can be assumed that all of this was adsorbed on the pulp (papers III and IV).

The amounts of lignin attached in relation to the amounts of lignin that according to mobility data are required to neutralize the charges of cationic polymers were quite reasonable. For example, when 11 mg CS (DS 0.2)/g pulp was adsorbed, the lignin/CS ratio at the plateau level was about 1 (12 mg lignin/g pulp/11 mg CS/g pulp), while the lignin/CS ratio at the pzc of the complex in the solution was about 2. The lignin/PDADMAC ratio at the plateau level was about 8 (16 mg lignin/g pulp/2 mg PDADMAC/g pulp), while the lignin/PDADMAC ratio at the pzc of the complex in the solution was about 6. This showed that a significant part of CS and PDADMAC charge was consumed by neutralization of the lignin and that maximum adsorption of lignin on PDADMAC- and CS-treated fibres results in overcompensation, i.e. the surface becomes negative again.

To facilitate comparison with mobilities and wetting results, adsorption data for the two different adsorption sequences for the lignin/CS (DS 0.2) are presented in Fig. 18.

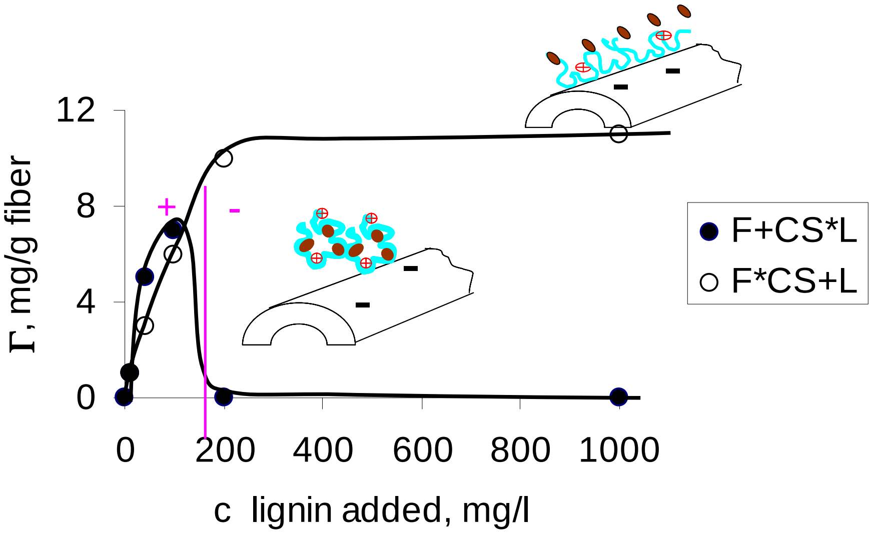


Fig. 18. Illustration of lignin adsorption on cellulose fibres in the presence of cationic polymer. The amount of CS (DS 0.2) was 80 mg/l (1.2 mg/g pulp). In the solution pH 7, 0.025 M NaCl. Filled circles: CS was introduced into the lignin solution. Open circles: CS was pre-adsorbed on the fibres before lignin adsorption. The vertical line at about 160 mg/l marks electroneutrality: to the left of the line the complexes in the solution are cationic and to the right of the line anionic.

4.6 Lignin’s interfacial behaviour

Generally, the surface properties of an adsorbed polymer layer are determined by the properties of both the polymer and the substrate. Thus, if lignin shows similarities in organization and wetting behaviour on smooth non-porous mica and on rough porous fibrous substrates, these similarities probably originate from intrinsic behaviour of lignin at the interface. On the other hand, dissimilarities would originate from the difference between surface properties of the two substrates. Hence, comparison of lignin behaviour on these two chemically and morphologically different substrates should shed light on interfacial properties of lignin. In particular, my target was to answer the following questions:
i) What is the correlation between the wetting and the morphology of adsorbed lignin layer?
ii) To what extent is lignin wetting properties and organization on solid substrate controlled by the underlying substrate and to what extent by intrinsic properties of lignin?

When a polyelectrolyte-coated mica was immersed into a lignin solution, the smooth hydrophilic surface acquired a granular coverage and concomitantly hindered wetting (paper IV). The following conclusions can be drawn: the increase in contact angle and in surface coverage can only be associated with the adsorption of lignin onto the solid substrate, and the adsorbed granular lignin covered the hydrophilic substrate with hydrophobic moieties. The impeded wetting in this case was consistent with a layered surface structure in which a hydrophilic layer of cationic polymer was decorated with granules of hydrophobic lignin.

Lignin adsorbed as a granular monolayer onto fibres pre-coated with cationic polymer in the same way as on mica. Evidently, the cohesion of lignin itself was stronger than the adhesion between lignin and the cationic polymer-covered fibre surface. Kraft lignin was found to occur in aqueous solutions as rod-like particles with a diameter of 2 nm (paper V), whereas the size of the granules that were seen on mica in the AFM images was about 40 nm. This means that granules observed in AFM images were likely composed of about 20 primary lignin particles held together by strong cohesive forces. However, some differences in granular structures depending on substrate and polyelectrolyte were observed (paper IV). PDADMAC is a linear highly charged polyelectrolyte and thus it adsorbed in a flat conformation, while CS is branched and has a low charge density and consequently adsorbed in a more extended conformation, leading to a more irregular structure of the adsorbed layer.

With both CS and PDADMAC, the granular layer of adsorbed lignin was capable of impeding water adhesion and rendering both mica and sheet surfaces substantially less hydrophilic at higher lignin concentration. However, with PDADMAC the adsorbed dispersed lignin granules were less water-repellent than the layer of diffuse lignin granules on CS-treated substrates. This is very reasonable in view of the higher charge density of the PDADMAC. Clearly, both the properties of the substrate and of the cationic polymer affected the organization and the wetting properties of the adsorbed lignin.

When cationic polymer was mixed with lignin before adsorption on mica, the surface became covered with patches (paper IV) that grew in number and in size when the lignin concentration was increased, as long as the complex was cationic. The patchy appearance of the adsorbed layer indicated that adhesion between the lignin/CS complex and mica is stronger than cohesion within the complex, i.e. between lignin and cationic polymer. Wetting was essentially the same as without added lignin, i.e. the adsorbed patches did not render the substrate less hydrophilic. Thus the mica surface partially covered by lignin/polyelectrolyte patches was more hydrophilic than mica covered with a granular lignin layer. However, before attributing the difference in wetting to a different morphology or shape only, the adsorption strategies had to be taken into consideration. The direct dissimilarity between the two cases was related to the sequence of adding the polymers.

When the lignin solution was equilibrated with a pre-coated polymer surface, lignin was expected to be adsorbed onto the positive sites on the adsorbed layer of cationic polymer. As a result, the substrate should become covered by droplets of bare lignin. On the other hand, if the polymeric complex was formed in the solution prior to adsorption, either the lignin or the cationic polymer could be concentrated on the surface. Which one would depend on the location of lignin molecules: they can be either outside the complex particle or immobilized inside the core.

The results showed that the complexes that were retained on the surface had a cationic net charge and a low lignin/cationic polymer ratio. Consequently, it is highly likely that lignin was immobilized inside the complex particle. If that is the case and the complex adsorbed onto the solid substrate as such, the more hydrophobic lignin was wrapped inside the cationic polymer so that hydrophilic moieties of the cationic polymer were oriented towards the solid substrate. Investigations on the complex structures in the solution are needed to verify this explanation. On the other hand, the possibility of re-conformation of the components of the complex on the solid substrate cannot be excluded. However, since the surface covered with the polymer/lignin patches was rather hydrophilic, it is likely that the lignin stayed wrapped inside a polymer core and it was the cationic polymer that screened the hydrophobic moieties of lignin.

With PDADMAC, large blobs of the complex were unevenly distributed on the fibre surface (paper I), while with CS, the complex spread on the fibre surface forming a film. Evidently, with PDADMAC, the cohesion within the complex was stronger than the adhesion between the complex and the fibre: as a result, complexes formed blobs on the fibre surface. With CS, the adhesion between the complex and the fibre was stronger than the cohesion within the complex, i.e. between lignin and CS. This gave rise to film formation.

Neither the blob structure nor the film was capable of making the fibrous matrix water resistant, although with CS the complex somewhat impeded water penetration. This was probably because the lignin was immobilized inside the polyelectrolyte core in the same way as for complexes on mica.

With wetting results on the fibrous matrix only, it was not possible to verify whether the lignin/PDADMAC complex conveyed hydrophobic moieties to fibres or not. The evaluation of the effect of lignin/PDADMAC complex on the wetting of the fibrous matrix was difficult because the rate of penetration depended not only on the surface energy of the fibres, but also on the porosity of the fibre matrix. However, comparison with the results on the nonporous mica showed that the lignin/PDADMAC complex adsorbed on fibres was rather hydrophilic as such. The mica results also showed that either the lignin/CS complex was somewhat less hydrophilic than the lignin/PDADMAC complex or else it rendered the surface less hydrophilic due to better coverage.

It has been reported in literature that lignin is capable of self-organisation on solid substrates; the structures are very different depending on the lignin chemical make-up and on the substrate (Constantino et al. 2000; Micic et al. 2000; Paterno and Mattoso 2001; Pasquini et al. 2002) Depending on polar groups, lignin could be oriented parallel to the substrate resulting in a flat surface or as ellipsoidal aggregates oriented perpendicularly to the substrate (Pasquini et al. 2002). Paterno and Mattoso (2001) studied self-assembled films of poly-(o-ethoxyaniline) and sulfonated lignin and concluded that the tendency to form planes makes lignin macromolecules capable of covering rough surfaces. Micic et al. (2001) gave evidence that there are strong intermolecular forces responsible for holding lignin globules together in higher-ordered structures, which agrees with the observed granule formation. Lignin monolayers have been reported to be unstable and transferable (Constantino et al. 2000).

In this study, the lignin layer on underlying cationic polymer was very stable and exhibited low hydrophilicity. Since lignin tended to form granules on both smooth non-porous and rough porous substrates, it can be concluded that a specific interfacial property of lignin, namely to form granules in water, leads to granules that are strong enough so that they do not spontaneously spread out to form a film on cationised substrates, although they bind to them by electrostatic interactions.

When lignin formed complexes in solution, it covers the substrate with large blobs, patches and films, depending on the nature of the polymer and the substrate. Evidently, competition between internal cohesion, the cohesion of water and adhesion to the substrate governed the interfacial organization of lignin.

4.7 Effect of lignin and lignin/cationic polymer complexes on paper technical properties

Lignin

Paper sheets were prepared from pulps after lignin adsorption, with lignin present in the water. In the sheets lignin seemed to be strongly bound to the fibres. Obviously, drying was responsible for binding of trapped lignin to the fibrous mat.

When the lignin solution contained only sodium ions and there was no precipitation from the solution, lignin binding to fibres upon drying resembled the behaviour of lignin in the "sandwich" experiments reported by Goring (1962). Lignin dissolved in alkaline solution acquires mildly polyelectrolyte nature and swells like a neutralised polylectrolyte gel. The lignin gel then develops adhesive properties and binds when dried in a manner analogous to the behaviour of an alkali-based adhesives. Table 2 in paper I summarizes the effect of metal ions added to lignin solution on paper properties. Unsurprisingly, the paper brightness decreased with the increase in lignin content of the pulp, and the darkest paper was obtained with aluminium at pH 7, when the aluminium-lignin sol turned into viscous suspension, which glued to the fibres.

Paper strength properties were not significantly changed when lignin was adsorbed on the fibres with sodium and calcium, but the paper was somewhat weakened in the presence of aluminium (paper I). Also, aluminium that precipitated on the fibres alone somewhat lowered the sheet strength. However, the Scott-Bond strength of sheets prepared with aluminium-lignin at pH 7 increased. According to Lindström et al. (1977), lignin alone does not significantly affect the strength properties of the sheet, whereas Springer et al. (1986) found that sorbed lignin lowers the sheet strength.

Lignin impeded water penetration inside the sheet (Fig. 7 in paper I). Aluminium-lignin rendered paper hydrophobic.

When aluminium-lignin was taken up by the fibres, the structure of paper sheets was different: the thick lignin layers were located between the fibres forming a “triple decker” structure, and the thickness of the lignin layers increased with increasing lignin concentration in the solution (up to 30 μm in the case of lignin concentration in the solution 2 g/l) (paper I). This could explain the noticeable increase in Scott-Bond observed only in this sheet.

Lignin/PDADAMAC and lignin/CS complexes

Sheet brightness was affected by adsorbed lignin/PDADMAC and lignin/CS complexes. The brightness decreased more as more lignin was adsorbed (Fig. 20) (papers II and III).

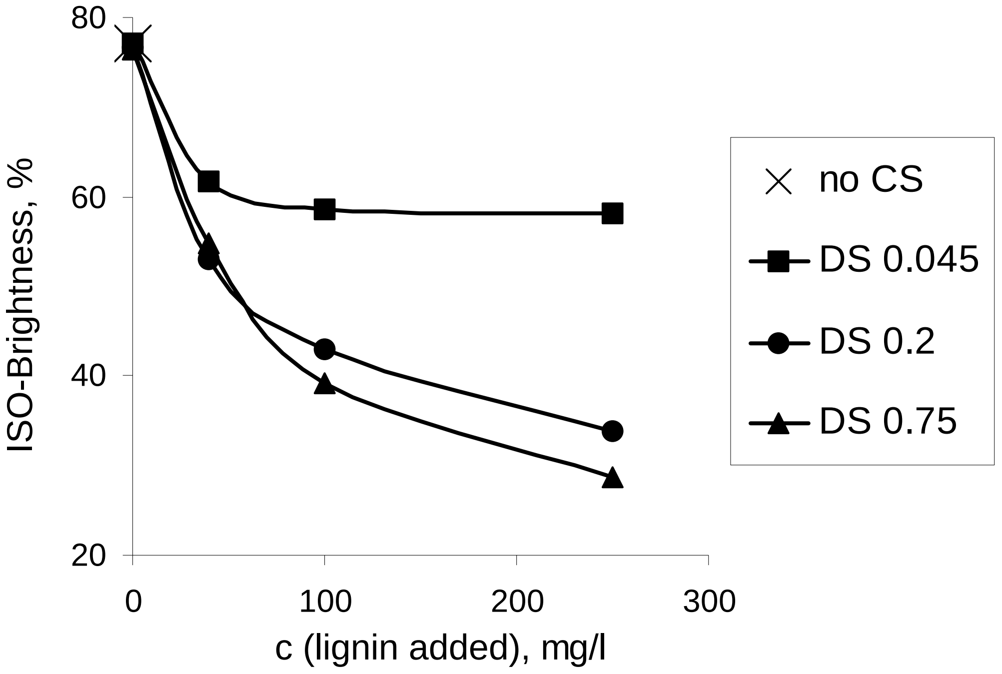


*Fig. 20. Effect of lignin adsorbed in the presence of CS on the ISO-Brightness. Lignin adsorbed onto CS treated fibres (F*CS+L). Addition of CS was 80 mg/l (1.1 % pulp), and of lignin 40, 100, and 250 mg/l.*

The strength properties generally increased (Fig. 21). The increase in the paper strength brought about by lignin/CS complexes was greater than the increase due to addition of CS alone. While PDADAMC alone did not increase the paper strength, lignin adsorbed onto PDADMAC-treated fibres increased Scott Bond (paper II) It was suggested that the cationic polymers and the negatively charged lignin form a complex akin to a water rich gel on the fibre surface, which gives rise to a large contact area between fibres and a resulting increase in the bonding upon drying.

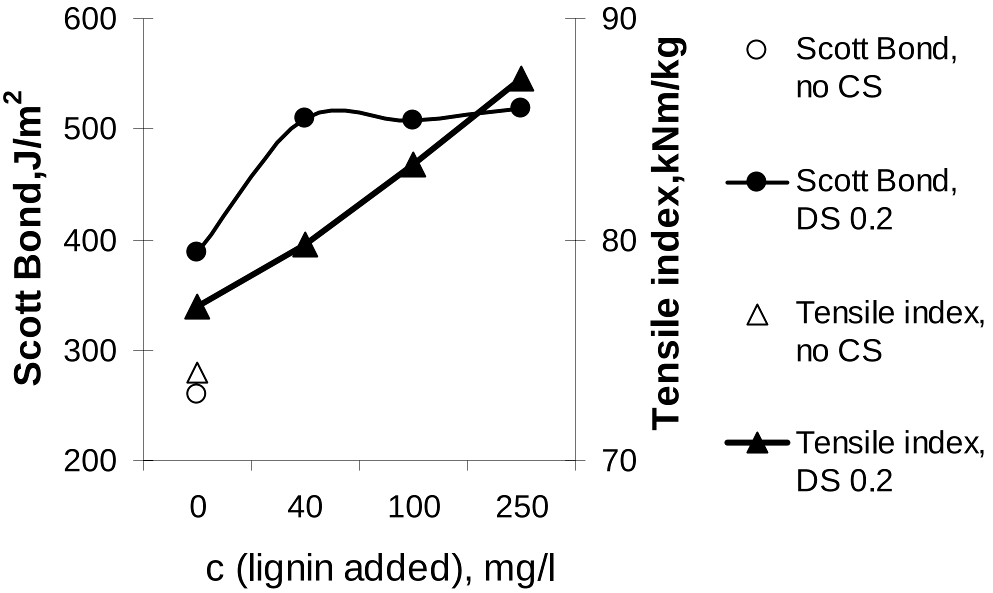


*Fig. 21. Effect of lignin adsorbed onto CS treated fibres (F*CS+L) on the tensile strength and Scott Bond. Addition of CS (DS 0.2) was 80 mg/l (1.1 % pulp), and of lignin 40, 100, and 250 mg/l. Standard deviations in tensile index measurements were up to 10 %, in Scott Bond up to 5 %.*

The structure of the lignin/cationic polymer complex may have an effect on the paper properties. Thus, either lignin or cationic polymer can be concentrated on the outmost contact area between the fibres, depending whether the lignin is outside the complex particle or immobilized inside the polymer core. The effect on the paper strength properties and brightness was generally the same with cationic lignin/CS complexes formed in the solution and with lignin adsorbed onto CS-treated fibres; with similar adsorbed amounts of lignin, the addition strategy did not influence the strength development significantly. However, the addition strategy did have an effect on the wetting properties of paper: with the same amount of adsorbed lignin paper was hydrophilic or rather water resistant depending on the sequencing of polymer addition.

The sheets prepared from pure fibres with adsorbed PDADMAC and CS were hydrophilic and hence water penetrated the sheet in a few seconds. When lignin was adsorbed onto the PDADMAC and CS-treated fibres the wetting dynamics of the fibrous matrix changed (see

Fig. 22a). While the lowest lignin addition (10 mg/l) had no effect on water penetration, it was already impeded with lignin addition 40 mg/l. The addition of 100 mg/l to CS-treated fibres rendered the fibrous matrix capable to hold the water drop on the surface with only minor penetration into the porous sheet. Further adsorption of lignin at higher lignin concentrations inhibited the water penetration into the porous sheet almost completely. In addition, the contact angle increased (Fig. 22b). The corresponding amounts of adsorbed lignin are shown in Fig. 18. This suggested the existence of a critical lignin addition (adsorption), above which adsorbed lignin impedes the water absorbing capacity of a porous sheet. With lignin/CS and lignin/PDADMAC complexes formed in the solution, sheets were rather hydrophilic in general, although the adsorbed cationic complexes did reduce penetration to some extent. Because contact angles measured on papers is greatly dependent on the sheet density, surface structure and time, it was difficult to compare the results with other reports. As an example, Wågberg (2000) studied spreading of liquid droplets on model papers where the surface structure, the bulk structure and the surface energy had been altered in a controlled way. The wetting kinetics is reported only for very short times, i.e. 10 seconds. Additions of an alkyl ketene dimer (AKD) increase the contact angles on papers up to 70–110° depending on the AKD dosage and the induced roughness (Wågberg 2000). Still, it could be concluded that the efficiency of the complexes studied in this paper as hydrophobing agents is certainly lower than that of AKD.

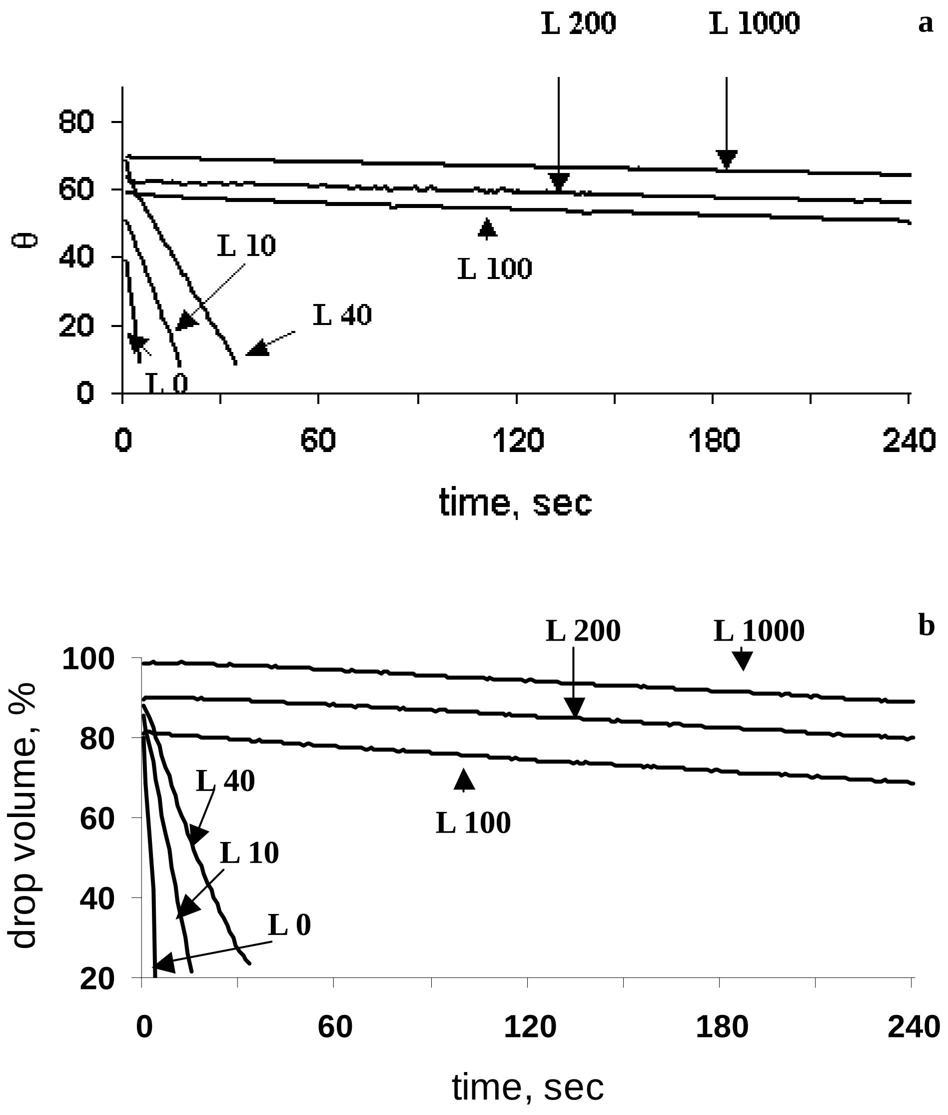


Fig. 22. Effect of adsorbed lignin on the wetting dynamics of fibrous matrix. Lignin was adsorbed from solutions of specified concentrations onto CS-pretreated fibres. a) contact angle, b) drop volume.

CONCLUDING REMARKS

1) The following picture of the interactions between lignin solutions and fibres at room temperature emerges: Dissolved lignin is imbibed into cellulose fibres from true lignin solutions and precipitated from coagulated lignin dispersions. In the former case the amount of sorbed lignin increases linearly with lignin concentration. Both colloidally stable and colloidally unstable lignin can be formed in the solution of calcium and aluminium depending on electrolytes concentration and pH. Adding calcium and aluminium to the solutions induces precipitation of lignin flocs onto the fibres as long as there is sufficient calcium and aluminium in the solution to neutralize the negative charge on lignin and cause rapid coagulation and precipitation of lignin from the solution. These particles are deposited on the fibres and retained in fibre mat during filtration, which significantly increases the uptake of lignin. Maximum adsorption occurs when the flocs are more or less neutral. In alkaline solutions, calcium ions were more efficient than aluminium while in neutral solutions aluminium had a much greater effect. Most of the uptaken lignin bonds to fibres loosely and can be easily removed by washing with water. Thus, there is no indication of true molecular adsorption of lignin under any of the conditions investigated.

2) From a practical point of view, this implies that at least low temperatures lignin can be easily and quantitatively washed away from fibres as long as the only simple cations in solution are sodium ions. Very likely, the situation is similar for other simple monovalent cations. In $CaCl_2$ solutions, when the calcium/lignin particles are flocculated and precipitated from the solution, lignin will deposit on the fibres and becomes trapped in filtrates. However, washing with pure water will easily remove this lignin. At neutral pH aluminium ions will cause serious hindrance of pulp washing.

3) Both the sorption studies and measurements of interaction forces by AFM indicate that the net van der Waals interactions between lignin and fibres in aqueous dispersion are apparently very weak and do not overcome the electrostatic repulsion between lignin and fibres, even when the negative charge on lignin is very small. The attachment of lignin to fibres is mainly governed by imbibition into the fibres with solution and flocs retention in fibre mat due to filtration effect.

4) In sheets lignin seems to be strongly bound to the fibres. Obviously, drying is responsible for binding of imbibed and trapped lignin to the fibrous mat.

5) Uptaken lignin changes the paper structure and lowers the brightness. Noticeable effect on sheet strength was observed only when lignin was precipitated with aluminium. Uptaken lignin impeded wetting, and aluminium-lignin rendered sheet hydrophobic.

6) The driving force for adsorption of lignin/CS and lignin/PDADMAC complexes on chemical pulp fibres is primarily electrostatic: adsorption takes place as long as the fibre surface and the lignin are oppositely charged. When the charge density of cationic polymer increases the amount of lignin bound in the complex increases and, hence, lignin retention in the fibres increases.

7) Adsorption of complexes is highly dependent on the sequence of addition of lignin and cationic polymer. If the complexes are formed in solution prior to adsorption on the fibres there is a relatively sharp maximum in adsorption at lignin/cationic polymer ratios below the isoelectric point. If complexes are formed directly on the fibre surface (adsorption of lignin on fibres treated with cationic polymer) the isotherm reaches a plateau value.

   From a practical point of view this means that the same polymer concentrations will result into maximal or zero lignin adsorption, depending on which species are first contacted with the fibres. The adsorption isotherms give a clue to acceptable levels of dissolved and colloidal lignin e.g. under conditions of water circulation closure. Whereas low lignin concentrations (some tens milligrams per litre) result into irreversible adsorption on fibres in the presence of cationic polymer, high lignin concentrations (grams per litre) are much less risky in terms of retention unless the cationic polymer was pre-adsorbed onto the fibres prior to contact with lignin-containing water. With pre-adsorbed cationic polymer, very high lignin concentrations (grams per litre) are no more dangerous than low ones (milligrams per litre), which means that washing from very high till low, yet dangerous lignin levels is pointless.

8) Adsorbed lignin/CS complexes have a significant influence on paper properties. Adsorbed complexes are located on the outermost surface of the fibres, which leads to loss in brightness. The strength properties are generally increased. Moreover, the increase brought by the lignin/CS complex is greater than the increase due to the addition of CS alone. Adsorbed lignin/cationic polymer complexes impede wetting. When sufficient level of lignin adsorption is reached, water is prevented from penetrating inside the sheet. The structure and wetting of lignin layers are first and foremost determined by the sequencing of polymers addition.

9) The positive effect of a cationic and an anionic component on the strength properties is well known fact. In present case, lignin acts as natural anionic component, boosting both the strength and water resistance of paper. The only disadvantage is decreased brightness. Yet, strengthened, water-resistant, brownish lignin/CS-papers could find their implementation e.g. in packaging technology.

10) An important interfacial characteristic of lignin is its tendency to adsorb on cationised substrates in water in the form of well-defined individual granules or as diffuse aggregated granules, depending on the substrate. The individual granules are lignin agglomerates, consisting of about 20 primary lignin particles that are held together by strong cohesive forces. Granular lignin decorating a hydrophilic substrate conveys hydrophobic moieties to the surface and lowers the adhesion of water to the surface, which is another important interfacial characteristic.

11) When lignin is allowed to form complexes with cationic polymers in the solution, it forms either blobs or patches and films on the substrate (depending on the cationic polymer used), and does not convey hydrophobic moieties to the solid substrate. It is likely that cationic polymer screens the lignin at least partly from contact with water. The competition between internal cohesion, water cohesion and adhesion to the substrate govern the interfacial organization of lignin. The morphology of adsorbed layer and the location of bare lignin in the layer are responsible for the wetting properties. The structure and wetting of lignin layers are first and foremost determined by the sequencing of polymers addition.

REFERENCES

Aguie-Beghin, V., Baumberger, S., Monties, B., Douillard, R. (2002). Formation and characterization of spread lignin layers at the air/water interface. *Fr. Langmuir* **18**(13), 5190–5196.

Alekseev, A., Reznikov, V., Bogomolov, B., Sokolov, O. (1971). Hydrodynamic properties of Björkman lignin. *Khim. Drev.* **7**, 31–36.

Alince, B. (1974). Polyethylenimine adsorption on cellulose. *Cellul. Chem. Technol.* **8**(6), 573–590.

Allan, G., Reif, W. (1971). Fibre surface modification. Part 6. The Jack-in-the-Box effect: A new mechanism for the retention of polyethylenimine and other polyelectrolytes by pulp fibres. *Svensk Papperstidn.* **74**(2), 25–31.

Barros, A.M., Dhanabalan, A., Constantino, C.J.L., Balogh, D.T., Oliveira, O.N. Jr. (1999). Langmuir monolayers of lignins obtained with different isolation methods. *Thin Solid Films* **354**(1,2), 215–221.

Baumberger, S., Aguie-Beghin, V., Douillard, R., Lapierre, C., Monties, B. (1997). Properties of grass lignin layers at the air-water interface. *Industrial Crops and Products* **6**(3,4), 259–263.

Bearnson, G., Briggs, D. (1992). High resolution XPS of organic polymers. Wiley, London.
Berg, J.C. (ed.) (1993). Wettability. Marcel Dekker, USA.

Bergström, M., Kjellin, U.R.M., Claesson, P.M., Pedersen, J.S. and Nielsen, M.M. (2002). A Small-Angle X-ray Scattering Study of Complexes Formed in Mixtures of a Cationic Polyelectrolyte and an Anionic Surfactant. *J. Phys. Chem. B* **106**, 11412–11419.

Bico, J., Marzolin, C., Quére, D. (1999). Pearl drops. *Europhys. lett.* **47**(2), 220–226.

Bobacka, V., Näsman, J., Kreutzam, N. and Eklund, D. (1999). Adsorption of cationic starch onto peroxide-bleached TMP fibres - Influence of interfering wood substances. *Pap. Puu* **81**(1) 59–62.

Bogolitsyn, K., Rjabeva, N., Volkova, N. (1995). Behaviour of native lignins in organic solvents. International Symposium on Wood and Pulping Chemistry, 8th, Helsinki, June 6–9, Association of Finnish Paper Engineers, **2**, 101–105.

Brandon, S. and Marmur, A. (1996). Simulation of contact angle hysteresis on chemically heterogeneous surfaces. *J. Colloid Interface Sci.* **183**, 351–355.

Brattberg, T. (1977). Increasing kraft pulp yield by sorption of organic matter (3), carbon dioxide as a pH-decreasing agent. STFI Medd. Ser. A. no. 475: 12 p./Sept. 1977.

Briggs, D. and Riviere, J. (eds) (1990). Spectral interpretation. In “Practical Surface Analysis - Auger and X-ray Photoelectron Spectroscopy. (Briggs D. and. Seah M. P (Editors), vol 1, 2nd ed, pp. 85–41. Wiley Interscience.

Brown W. (1967). Solution properties of lignin. Thermodynamic properties and molecular weight determination. *J. Appl. Polym. Sci.* **11**(11), 2381–2396.

Budd, J. and Herrington, T. (1989). Surface charge and surface area of cellulose fibres. *Colloids Surf. A* **36**, 273.

Carlsson, C.M.G. and Ström, G. (1991). Adhesion between plasma-treated cellulosic materials and polyethylene. *Surf. Interface Anal.* **17**(1991), 511–515.

Carlsson, G. (1996). Surface composition of wood pulp fibres, relevance to wettability, sorption and adhesion. Doctoral Thesis, Royal Institute of Technology, Stockholm.

Cathala, B.; Aguie-Beghin, V.; Douillard, R.; Monties, B. (1998). Properties of model compounds of lignin (dehydrogenation polymers=DHPs) at the air/water interface. *Polymer Degrad. Stabil.* **59**(1–3), 77–80.

Cathala, B., Lee, L.T., Aguie-Beghin, V., Douillard, R. and Monties, B. (2000). Equipe Biochim. Organization Behavior of Guaiacyl and Guaiacyl/Syringyl Dehydrogenation Polymers (Lignin Model Compounds) at the Air/Water Interface. *Langmuir* **16**(26), 10444–10448.

Cathala, B., Puff, N., Aguie-Beghin, V., Douillard, R. and Monties, B. (2000) Structural investigation of dehydrogenation polymer (models of lignin) films at the air-water interface by neutron reflectivity. *CS Symposium Series: “Lignin: Historical, Biological, and Materials Perspectives”* **742**, 278–290.

Chan, C.-M. (ed.) (1994). Polymer surface modification and characterization. Hanser/Gardner Publications, Cincinnati.

Chow, T. (1998). Wetting of rough surfaces. *J. Phys. Condens. Matter* **10**(27), L445–L451.

Chupka, E., Obolenskaya, A. and Nikitin, V. (1970). Effect of the internal structure of lignin on some of its properties. *Khim. Drev.* **5**, 53–58.

Claesson, P.M., Dedinaite, A., Fielden, M., Kjellin, M. and Audebert, R. (1997). Polyelectrolyte-Surfactant Interactions at Interfaces. *Prog. Colloid Polymer Sci.* **106**, 24–33.

Claesson, P.M., Fielden, M.L., Dedinaite, A., Brown, W. and Fundin, J. (1998). Interactions between a 30% Charged Polyelectrolyte and an Anionic Surfactant in Bulk and at a Solid-Liquid Interface. *J. Phys. Chem.* **102**, 1270–1278.

Constantino, C.J.L., Dhanabalan, A., Curvelo, A.A.S. and Oliveira, O.N. Jr. (1998). Preparation and characterization of composite LB films of lignin and cadmium stearate. *Thin Solid Films* **327–329**, 47–51.

Constantino, C.J.L., Juliani, L.P., Botaro, V.R., Balogh, D.T., Pereira, M.R., Ticianelli, E.A., Curvelo, A.A.S. and Oliveira, O.N., Jr. (1996). Langmuir-Blodgett films from lignins. *Thin Solid Films* **284–285**, 191–194.

Constantino, C., Dhanabalan, A., Cotta, M., Pereira-da-Silva, Curvelo, A, and Oliveira Jr, O. (2000). Atomic force microscopy (AFM) investigation of Langmuir-Blodgett (LB) films of sugar cane bagasse lignin. *Holzforschung* **54**(1), 55–60.

Corneer, I.. and Olausson, J. (1977). Increasing kraft pulp yield by sorption of organic matter (2), pulp processing and pulp properties. STFI Medd. Ser. A. no. 474, 12 p.

Crisp, D. (1946). Surface films of polymers. Part 1. Films of the fluid type. *J Colloid Sci* **1**(49), 49–70.

Della Volpe, C., Penati, A., Peruzzi, R., Siboni, S., Toniolo L. and Colombo C. (2000). The combined effect of roughness and heterogeneity on contact angles: the case of polymer coating for stone protection. In: “Apparent and microscopic contact angles”, Eds: J. Drelich, J. S. Laskowski, K.L. Mittal. PART 3. Wetting of heterogeneous, rough and curved surfaces.

Dong, D., Fricke, A., Moudgil, B. and Johnson, H. (1996). Electrokinetic study of kraft lignin. *Tappi J.* **79**(7), 191–196.

Dorris, G. and Grey, D. (1978a). The surface analysis of paper and wood fibres by ESCA (electron spectroscopy for chemical anaysis). I. Application to cellulose and lignin. *Cellul. Chem. Technol.* **12**(1), 9–23.

Dorris, G. and Grey D. (1978b). The surface analysis of paper and wood fibres by ESCA. II. Surface composition of mechanical pulps. *Cellul. Chem. Technol.* **12**(6), 721–734.

Ducker, W.A., Senden, T.J. and Pashley, R.M. (1991). Direct measurements of colloidal forces using an atomic force microscope. *Nature (London, U.K.)* **353**, 239–241.

Evans, F. and Wennerström H. (eds) (1999). “The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet”, 2nd Edition. John Wiley & Sons, Inc. p. 460.

Feigin, L. and Svergun, D. (1987). “Structure analysis by small X-ray and neutron scattering“, Plenum Press, New York.

Fengel D. and Wegener G. (1989). “Wood Chemistry, Ultrastructure, Reactions”, Walter de Gruyter, Berlin p. 611.

Fleer, G., Cohen-Stuart, M. and Scheutjens (1993). In: Polymers at Interface, T. Cosgrove and B. Vincent (Eds.), Chapman&Hall, London.

Gardon, J. and Mason, S. (1958). Polyelectrolytic properties of lignosulfonic acids. *Chemical and Engineering Data Series* 3(1), 115–119.

Gardon, J. and Mason (1955). Physicochemical studies of lignosulphonates. II. Behaviour as polyelectrolytes. *Can. J. Chem.* **33**, 1491–1501.

Gärlund, L., Wågberg, L. and Gernandt, R. (2003). Polyelectrolyte complex for surface modification of wood fibres. II. Influence of complexes on wet and dry strength of paper. *Colloids Surf. A* **218**, 137–149.

Garver, T. and Callaghan P. (1991). Hydrodynamic of kraft lignins. *Macromolecules* **24**(2), 420–430.

Gilardi, G. and Cass, A. (1993). Associative and colloidal behavior of lignin and implications for its biodegradation in vitro. *Langmuir* **9**(7), 1721–1726.

Goring, D. (1962). The physical chemistry of lignin. *Pure Appl. Chem.* **5**, 233–253.

Goring, D. (1964). Lignin. *Trend (London)*, no **3**, 9–15.

Gross, S., Sarkanen, K. and Schuerch, C. (1958). Determinations of molecular weight of lignin degradation products by three methods. Analytical Chemistry. **30**(4): 518–521.

Gundersen, S.A., Ese, M-H. and Sjoblom, J. (2001). Langmuir surface and interface films of lignosulfonates and kraft lignins in the presence of electrolyte and asphaltenes: correlation to emulsion stability. *Colloids Surf. A* **182**(1–3), 199–218.

Gupta, P. and Goring, D. (1960). Physicochemical studies of alakali lignins. III. Size and shape of the macromolecule. *Can. .J. Chem.* **38**(2), 270–279.

Hartler, N. (1978). Sorption cooking: yield increase for unbleached alkaline pulps through sorption of organic substances from black liquor. *Svensk Papperstidn.* **81**(14), 457–463.

Hedborg, F. and Lindström, T. (1993). Adsorption of cationic starch on bleached softwood cellulosic fibres. *Nord. Pulp Pap. Res. J.* **8**(2), 258–263.

Hernadi, A. (1984). Accessibility and specific surface of cellulose measured by water vapour sorption. *Cellul. Chem. Technol.* **18**, 115–124.

Huh, D.M. and Lee, H.L. (1999). Influence of conductivity and anionic trashes on adsorption behavior of cationic starches. *Palpu Chongi Gisul* **31**(3), 10–18.

Hynninen, P. (1989). Lignin removal process (LRP). *Pap. Puu* **71**(5), 553.

Ingmansson W.L. and Thode E.F. (1959). Factors contributing to the strength of a sheet of paper. *Tappi J.* **42**, 83–93.

Jacobson, S. and Nguyen, K. (1997). Modelling the effect of fibre properties and operating conditions on diffusion washing of different eucalypt kraft fibres. Appita '97, 249.

Janson, J.P., Stenlund I.B. and Sågfors, P.E. (1975). Differences in colour and strength of kraft pulps from batch and flow cooking. *Pap. Puu* **5**, 387.

Johansson, L-S. (2002). Monitoring Fibre Surfaces with XPS in papermaking processes. *Microchimica Acta* 138, 217–223.

Johansson, L-S. Campbell, J., Koljonen, K. and Stenius, P. (1999). Evaluation of surface lignin on cellulose fibres with XPS. *Appl. Surf. Sci.* **144–145**, 92–95.

Jurasek, L. (1995). Toward a three-dimensional model of lignin structure. *J. Pulp. Pap. Sci.* **21**(8), J274–J279.

Karlsson, O. and Westermark, U. (1997). The significance of glucomannan for condensation of cellulose and lignin under kraft pulping conditions. *Nord. Pulp Pap. Res. J.* **12**(2).

Kekkonen, J., Lattu, H. and Stenius, P. (2002). Formation, adsorption and interactions of poly-DADMAC/pectic acid complexes. *J. Pulp. Pap. Sci.* **28**(1), 6–12.

Kenada, D., Kindler, W. and Meyer, F. (1967). Studies of adsorption of cationic polyelectrolytes on pulp using streaming current detection. *Tappi J.* **50**(7), 381–387.

Kettunen, H. and Niskanen, K. (2000a). On the in-plane tear test. *Tappi J.* **83**(4), 83.

Kettunen H. and Niskanen K. (2000b). Microscopic damage in paper. Part I: Method of Analysis. *J. Pulp Pap. Sci.* **26**, 35–40.

Kleinert, T. (1965). Lignin grafting onto cellulose during alkaline pulping. *Holzforschung* **19**(6), 179–183.

Klevinskaya, V.Ya.., Gromov, V.S., Treimanis, A.P. and Kreitsberg, Z.N. (1979). Kinetics of birchwood lignin-carbohydrate complex sorption by cellulose. *Khim. Drev. (Riga)* **6**, 52.

Kötz, J. (1993). Phase behaviour of polyanion-polycation aggregates and possibilities of utlization. *Nord. Pulp Pap. Res. J.* **1**, 11–14.

Kötz, J., Köpke, Schmidt-Nacke, G., Zarras, P. and Vogl, O. (1996). Polyanion-Polycation Complex Formation as a Function of the Position of theFunctional Groups. *Polymer* **37**, 2775 & **37**(13), 2775–2781.

Kumar, D., He, Z., and Hynninen, P. (1997). LRP process: experiment on agro mill effluents. *Inpaper Int.* **1**(2), 29.

Kyrklund, B. and Strandell, G. (1969). Applicability of the chlorine number for evaluation of the lignin content in pulp. *Pap. Puu* **51**(4a), 299–305.

Laine, J. and Stenius, P. (1994). Surface characterization of unbleached kraft pulps by means of ESCA. *Cellulose* **1**, 145–160.

Lappan, R., Pelton, R., McLennan, I., Patry, J. and Hrymak, A. (1997). Kraft lignin-polyDADMAC precipitate formation. *Ind. Eng. Chem. Res.* **36**(4), 1171–1175.

Lee, S.B. and Luner, P. (1972). Wetting and interfacial properties of lignin. *Tappi J.* **55**(1), 116–121.

Li, P. and Pelton, R. (1992). Wood pulp washing 1. Complex formation between kraft lignin and cationic polymers. *Colloids Surf.* **64**, 217–222.

Lindberg, J., Bulla, I. and Törmalä, P. (1975). Spin labeling studies on constituents of wood. II. Correlation times of spin probes and rigidity of network structure in isolated lignin. *J. Polym. Sci., Polym. Symp. Edit.* **53**, 167–171.

Lindström, T. (1979a). Flocculation of kraft lignin sols with polyethylene oxide. *Separation Sci Tech.* **14**(7), 601–610.

Lindström, T., Söremark, C. and Westman, L. (1977). The influence on paper strength of dissolved and colloidal substances in white water. *Svensk Papperstidn.* **80**, 341–345.

Lindström T. (1979b). The colloidal behaviour of kraft lignin. Part I. Association and gelation of kraft lignin in aqueous solutions. *Colloid Polym. Sci.* **257**, 277–285.

Lindström, T. (1980a). The colloidal behaviour of kraft lignin. Part 2. Coagulating of kraft lignin in the presence of simple and complex metal ions. *Colloid Polym. Sci.* **258**(2), 168–173.

Lindström, T. (1980b). The colloidal behaviour of kraft lignin. Part III. Swelling behaviour and mechanical properties of kraft lignin gels. *Colloid Polym. Sci.* **258**, 390–397.

Lindström, T. and Westman, L. (1982). The colloidal behaviour of kraft lignin. Part IV. Syneresis and hysteresis in swelling of kraft lignin gels. *Colloid Polym. Sci.* **260**, 594–598.

Loughborough, D.L. and Stamm, A.J. (1936). Molecular properties of lignin solutions. From viscosity, osmotic pressure, boiling-point raising, diffusion, and spreading measurements. *J. Phys. Chem.* **40**, 1113–1133.

Luner, Ph., and Roseman, G. (1986). Monomolecular film properties of isolated lignins. *Holzforschung* **40**, 61–66.

Luner, Ph. and Kempf, U. (1970). Properties of lignin monolayers at the air-water interface. *Tappi J.* **53**(11) (Pt. 1), 2069–2076.

Maier, L., Bogolitsyn, K. and Ivanova, M. (1997). Determination of the hydrodynamic dimensions of technical lignins by laser correlation spectroscopy. *Zh. Prikl. Khim. (Sankt-Peterburg)* **70**(3), 487–489.

Marmur A. (1996). Equilibrium contact angles: theory and measurement. *Colloids Surf. A* **116**, 55–61.

Marmur, A. (1996). Contact angles in constrained wetting. *Langmuir* **12**, 5704–5708.

Marton, J. (1964). On the structure of kraft lignin. *Tappi J.* **47**(11), 713–719.

Marton, J. and Marton, T. (1976). Wet end starch. I. Adsorption of starch on cellulose fibres. *Tappi Annual Meeting. Prepr.*, 283–291.

Marton, J. (1980). The role of surface chemistry in fines-cationic starch interactions. *Tappi J.* **63**(4), 87–91.

McHale, G. Rowan, S.M., Newton, M.I. and Käb, N.A. (2000). Estimation of contact angles on fibers. In: "Apparent and microscopic contact angles", Eds: J. Drelich, J. S. Laskowski, K.L. Mittal. PART 3. Wetting of heterogeneous, rough and curved surfaces.

Merta, J. and Stenius, P. (1999a). Interactions between cationic starch and mixed cationic surfactants. *Colloids Surf. A.* **149**(1–3), 367–377.

Merta, J. and Stenius, P. (1999b). Interactions between cationic starch and anionic surfactants. III. Rheology and structure of the complex phase. *J. Dispersion Science and Technology* 20(1&2), 677–697.

Micic, M., Radotic, K., Benitez, K, Ruano, M., Jeremic, M., Moy, V., Mabrouki, M. and Leblanc, R. (2001a). Topographical characterization and surface force spectroscopy of the photochemical lignin model compound. *Biophys. Chem.* **94**, 257–263.

Micic, M. Benitez, I., Ruano, M., Mavers, M., Jeremic, M., Radotic, K., Moy, V. and Leblanc, R. (2001b). Probing the lignin nanomechanical properties and lignin-lignin interactions using th eatomic force microscopy. *Chem. Phys. Lett.* **347**(1,2,3), 41–45.

Micic, M., Jeremic, M., Radotic, K., Mavers, M. and Leblanc, R. (2000). Visualization of artificial lignin supramolecular structures. *Scanning* **22**(5), 288–294.

Moskovtsev, N., Chupka, E. and Nikitin, V. (1976a). Adsorption of lignin substances by cellulose during alkaline pulping. *Khim. Drev. (Riga)* **1**, 70.

Moskovtsev, N., Chupka, E. and Nikitin, V. (1976b). Nature of reaction of dissolved lignin with cellulose and residual lignin during alkaline pulping. *Khim. Drev. (Riga)* **2**, 44.

Moss. P., Nyblom, I., Sneck, A. and Hyvärinen, H. (1999). Characterisation methods for fibres and paper. *Workshop Proceedings, PTS,* Munich, 2-3 Dec 1999.

Nedelcheva M.P. and Stolikov, G.V. (1978). Cationic starch adsorption by cellulose. I. *J. Colloid Interface Sci.* **66**(3), 475–482.

Norgren, M., Edlund, H., Wågberg, L., Lindström, B. and Annergren, G. (2001a). Aggregation of kraft lignin derivatives under conditions relevant to the process, part I: phase behaviour. *Colloids Surf. A* **194**, 85.

Norgren, M., Edlund, H., Wågberg, L., Lindström, B. and Annergren, G. (2001b) Fundamental physical aspects on lignin dissolution in the digester. *11th International Symposium on Wood and Pulping Chemistry (ISWPC), June 1-14 (2001)*, Nice, **1** (2001), pp. 37–40.

Norgren, M. and Edlund H. (2001c): Stabilization of kraft lignin solutions by surfactant additions. *Colloids Surf. A.* **194**, 239–248.

Norgren, M. and Lindström, B. (2000). Physico-chemical characterization of fractionated kraft lignin. *Holzforschung* **54**(5), 528–534.

Norgren, M., Edlund, H. and Wågberg, L (2002). Aggregation of lignin derivatives under alkaline conditions. Kinetics and aggregate structure. *Langmuir* **18**, 2859–2865.

Nyman, V. and Rose, G. (1986). The colloidal behaviour of kraft lignin and lignosulfonates. *Colloids Surf. A* **21**, 125–147.

Obiaga, T. and Wayman, M. (1973). Molecular weight distribution of lignin during alkaline pulping. *Svensk Papperstidn.* **76**(18), 699–703.

Ödberg, L., Tanaka, H. and Swerin A. (1993). Kinetic aspects of the adsorption of polymers on cellulosic fibres. *Nord. Pulp Pap. Res. J.*, **1**(8), 6–9.

Ohshima, H. (1998). Interfacial electrokinetic phenomena. In: Ohshima, H., Furusawa, K. (Eds). Electrical phenomena at interfaces. Fundamentals, measurements, and applications. 2nd edition. Surfactant science series volume 76. Marcel Dekker Inc. New York, Basel, Homg Kong. Chapter 2.

Oliveira Jr. O., Constantino, C., Balogh, D. and Curvelo, A. (1994). Langmuir monolayers of lignins from pinus caribaea hondurensis sawdust. *Cellul. Chem. Technol.* **28**, 541–549.

Oliver, J., Huh, C. and Mason, S. (1980) An experimental study of some effects of solid surface roughness on weting". *Colloids Surf. A* **1**, 79–104.

Oliver, J. and Mason, S. (1980). Liquid spreading on rough metal surfaces. *J. Materials. Sci.* **15**, 431.

Pasquini, D., Balogh, D. Antunes, Constantino C, Curvelo, A., Aroca, R. and Oliveira, Jr., O. (2002). Surface Morphology and Molecular Organization of Lignins in Langmuir-Blodgett Films. *Langmuir* **18**(17), 6593 –6596.

Paterno, L.G. and Mattoso, L. (2001). Effect of pH on the preparation of self-assembled films of poly(o-ethoxyaniline) and sulfonated lignin. *Polymer* **42**(12), 5239–5245.

Peart, C. and Ni, Y. (2001). UV-VIS spectra of lignin model compounds in the presence of metal ions and chelants. *J. Wood Chem. Tech.* **21**(2), 113–125.

Pelton R.H. (1999). Colloid-polymer interactions. From fundamentals to practice, (Farinato R.S. and Dubin P.L., Eds.) Polymer-colloid interactions in pulp and paper manufacture. John Wiley Sons, Inc., Dublin, p 51–82.

Pelton, R., Allen, L. and Nugent, H. (1981). Novel dual-polymer retention aids for newsprint and groundwood specialities. *Tappi J.* **64**(11), 89–92.

Pelton, R. and Grosse, B. (1994). Polymer-enhanced displacement of lignin solution from model packed beds. *J. Pulp Paper Sci.* **20**, 91–94.

Porod, G. (1982). Small angle x-ray scattering. In; Glatter, O.,Kratky, O., Eds. Academic Press: London, Chapter 2.

Piculell L. and Lindman, B. (1992). Association and aggreagation in aqueous polymer/polymer, polymer/surfactant and surfactant/surfactant mixtures: Similarities abd differences. *Adv. Colloid Scie.* **41**, 149–178.

Radotic, K., Simic-Krstic, J., Jeremic, M. and Trifunovic, M. (1994). A study of lignin formation at the molecular level by scanning tunneling microscopy. *Biophys. J.* **66**(6), 1763–1767.

Richter, W., Zaenker, H. and Nitsche, H. (1998). Lignin colloids in aqueous solution. Forschungzentrum Rossendorf e.V., FZR, pp. 76–77.

Riviere, J. (1990). Instrumentation. Practical surface analysis. Vol 1. Auger and x-ray photoelectron spectroscopy, 2nd. Ed. (Briggs and Seah, eds) John Wiley&Sons, Chichester, pp. 19–83.

Roberts, J.C., Au, C.O., Clay G.A. and Lough, C. (1987). A study of the effect of cationic starch on dry strength and formation using C14 labelling. *J. Pulp and Paper Sci.* **13**(1), 1–5.

Rowan, D. and Scott, W. (1992). Colloidal properties of dissolved kraft lignin. *1992 Papermakers Conference, Tappi Proceedings*, pp. 59–61.

Rudatin, S., Sen., Y. and Woerner, D. (1989). Association of kraft lignin in aqueous solution in *Proceedings of ACS Symposium series* **397**, 144–154.

Salminen, P. (1988). Water transport into paper. The effect of some liquid and paper variables. *Tappi J.* **9**, 195–200.

Sarkanen, K. and Ludwig, C. (1971). Lignins: occurrence, formation, structure and reactions. J. Wiley&Sons, New York.

Sarkanen, S., Teller, D., Abramowski, E. and McCarthy, J. (1982). Lignin. 19. Kraft lignin component conformation and associated complex configuration in aqueous alkaline solution. *Macromolecules* 15, 1098–1104.

Sarkanen, S., Teller, D., Stevens, C. and McCarthy, J. (1984). Lignin. 20. Associative behavior between kraft lignin components. *Macromolecules* **17**, 2588–2597.

Scallan, A. (1978). The accomodation of water within pulp fibres. In: Fiber water interaction in paper making. V. 1. 1977 6th Fundamental Reasearch Symposium, Technical Division, BPBIF, 9–27.

Schmidt, B., König, S., Svergun, D., Volkov, V., Fischer,G. and Koch M. (1995). Small-angle X-ray Solution Scattering Study on the Dimerization of the FKBP25mem from L.pneumophila. *FEBS Lett.* **372**, 169–172.

Schuchardt, D. and Berg, J. (1990). Liquid transport in composite cellulose-superabsorbent fiber network. *Wood Fiber Sci.* **23**(3), 342–357.

Sillen, L. and Martell, A. (1964 & 1971). Stability constants of metal ion complexes, *The Chemical Society, London, Special Publications* **17**(1964) & **25**(1971).

Sjöholm, E. and Norman, E. (2000). Charge density of lignin samples from kraft cooking of birch wood. J. Wood Chem. Tech. **20**(4), 337–356.

Sjöström, E. (1993). In “Wood chemistry, Fundamentals and applications”, 2nd ed., Academic Press, New York, p. 163.

Springer, A.M., Dullforce, J.P. and Wegner, T.H. (1985). The effect of closed white water system contaminants on strength properties of paper produced from secondary fibre. *Tappi J.* **68**(4), 78–82.

Springer A.M., Dullforce J.P. and Wegner T.H. (1986). Mechanism by which white water system contaminants affect the strength of paper produced from secondary fibre. *Tappi J.* **69**(4), 106–110.

Springer, A.M. and Pires, E. (1988). Combined effect of fibre fines and dissolved organics on tissue properties. *Tappi J.* **71**(4), 141.

Srinivasan, G. and Chatterjee, A. (1995). Improved environmental management in an agro based mill – a case study. *IPPTA* **7**(4), 49.

Stannet, V. and Williams, J. (1978). The transport of water in cellulosic materials. In: Fiber water interaction in paper making. V. 1. 1977 6th Fundamental Reasearch Symposium, Technical Division, BPBIF, 497–513.

Stenius, P. and Vuorinen, T. (1999). Direct characterization of chemical properties of fibres. In: Sjöström, E. & Alén, R. (eds.), Analytical Methods in Wood Chemistry, Pulping and Papermaking. Germany, Springer-Verlag, pp. 149–192.

Stone, J. and Scallan, A. (1965). A study of cell wall structure by nitrogen adsorption. *Pulp Pap. Can.* **66**(8), T407–T414.

Ström, G. Barla, P. and Stenius, P. (1985). Formation of polyelectrolyte complexes between pine xylan and cationic polymers. *Colloids Surf. A* **13**, 193–207.

Ström, G. and Stenius, P. (1981). Formation of complexes, colloids and precipitates in aqueous mixtures of lignin sulphonate and some cationic polymers. Colloids Surf. A. **2**, 357–371.

Strömberg, B. (1991). Washing of low bleach chemical consumption. *Tappi J.* **74**(10), 113.

Sundberg, A., Ekman, R., Holmbom, B., Sundberg, K. and Thornton, J. (1993). Interactions between dissolved and colloidal substances and a cationic fixing agent in mechanical pulp suspensions. *Nord. Pulp Pap. Res. J.* **1**(8), 226–231.

Sundin, J. and Hartler, N. (2000a). Precipitation of lignin by metal cations in alkaline solutions. *Nord. Pulp Pap. Res. J.* **15**(4), 306.

Sundin, J. and Hartler, N. (2000b). Precipitation of kraft lignin by metal cations during pulp washing. *Nord. Pulp Pap. Res. J.* **15**(4), 313.

Surewicz, W. (1962). The sorption of organic components from cooking liquor by cellulose fibres; its relation to the “Dangerous cooking crest” in alkaline pulping (1). *Tappi J.* **45**(7), 570–578.

Svergun, D. and Koch, M. (2003). Small-angle scattering studies of biological macromolecules in solution. *Rep. Prog. Phys.* **66**, 1735–1782.

Swerin A., Glad-Nordmark G. and Ödberg L. (1997). Adsorption and flocculation in suspensions by two cationic polymers - simultaneous and sequental addition. *J. Pulp Paper Sci.* **23**, J389–J393.

Swerin, A., Ödberg, L. and Lindström, T. (1990). Deswelling of hardwood kraft pulp fibres by cationic polymers. The effect of wet pressing and sheet properties. *Nord. Pulp Pap. Res. J.* **5**, 188–196.

Taggart, T.E., Schuster, M.A. and Schellhamer, A.J. (1991). Papermaking using cationic starch and carboxymethyl cellulose or its additionally substituted derivatives. Patent. (Betz PaperChem, Inc., USA). U.S. (1991), 13 pp. CODEN: USXXAM US 5061346 A 19911029. Application: US 88-240774 19880902.

Takahashi, Y., Nishikawa, Y. and Fujisawa, T. (2003). Evaluation of three algorithms for ab initio determination of three-dimensional shape from one-dimensional solution scattering profiles. *J. Appl. Crystallogr.* **36**, 549–552.

Tanaka, H., Tachiki, K. and Sumimoto, M. (1979). Adsorption of cationic polymers onto bleached kraft pulp. *Tappi J.* **62**(1), 41–44.

Terayama, H. (1952). Method of colloid titration (a new titration between polymer ions). *J. Appl. Polym. Sci.* **8**(2), 243.

Thode, E., Swanson, J. and Becher, J. (1958). Nitrogen adsorption on solvent-exchanged wood cellulose fibres: indications of “total” surface area and pore-size distribution. *J. Phys. Chem.* **62**, 1036–1039.

Törmälä, P., Lindberg, J. and Lehtinen, S. (1975). Spin-labelling studies on constituents of wood. *Pap. Puu* **57**, 601–605.

Torre, M., Rodriguez, A. and Saura-Calixto, F. (1992). Study of the interactions of calcium ions with lignin, cellulose, and pactin. *J. Agric. Food Chem.* **40**(10), 1762–1766.

Trout, P. (1951). The mechanism of the improvement of the wet strength of paper by polyethylenimine. Tappi J. **34**(12), 539–544.

Van de Steeg, H., de Keizer, A., Cohen Stuart, M. and Bijsterbosch, B. (1993a). Adsorption of cationic starches on microcrystalline cellulose. *Nord. Pulp Pap. Res. J.* **1**, 34–40.

Van de Steeg, H., de Keizer, A., Cohen Stuart, M. and Bijsterbosch, B. (1993b). Adsorption of cationic amylopectin on microcrystalline cellulose. *Colloids Surf. A* **70**, 77–89.

Van de Steeg, H., de Keizer, A., Cohen Stuart, M. and Bijsterbosch, B. (1993c). Adsorption of cationic potato starch on microcrystalline cellulose. *Colloids Surf. A* **70**, 91–103.

Wågberg L. and Åsell I. (1995). The action of cationic polymers in the fixation of dissolved and colloidal substances part 2. *Colloids Surf. A* **104**, 169–184.

Wågberg L. and Lindström T. (1987a). Kinetics of polymer-induced flocculation of cellulosic fibers in turbulent flow. *Colloids Surf A.* **27**, 29–42.

Wågberg L. and Lindström T. (1987b). Some fundamental aspects on dual component retention aid systems. *Nord. Pulp Pap. Res. J.* **2**, 49–55.

Wågberg L. and Ödberg L. (1991). The action of cationic polyelectrolytes used for the fixation of dissolved and colloidal substances. *Nord. Pulp Pap. Res. J.* **6**, 127–135.

Wågberg, L. (2000). Spreading of droplets of different liquids on specially structured papers. *Nord. Pulp Pap. Res. J.* **15**(5), 598–606.

Wågberg, L. (2000). Polyelectrolyte adsorption onto cellulose fibres. A review. *Nord. Pulp Pap Res J.* **15**(5), 586–597.

Wågberg, L. and Sjölund (1999). Kinetics of polyelectrolyte adsorption on cellulosic fibres. Pre-symposium of the 10th ISWPC: Recent advances in paper science and technology. Korea Tappi, June 2-4, 1999, 34–42.

Wågberg, L. and Björklund, M. (1993). Adsorption of cationic potato starch on cellulose fibres. *Nord. Pulp Pap Res J.* **4**(8), 399–404.

Wågberg, L., Forsberg, S., Johansson, A. and Juntti, P. (2002). Engineering of fibre surface properties by application of the polyelectrolyte multiplayer concept. Part 1: Modification of paper strength. *Pulp Pap. Sci. J.* **28**(7), 222–227.

Wågberg, L. and Ödberg, L. (1989). Polymer adsorption on cellulosic fibres. Nord *Nord. Pulp Pap Res J.* **2**, 135–140.

Wayman, M. and Obiaga, T. (1974). The modular structure of lignin. *Can. J. Chem.* **52**, 2100–2102.

Wedekind, E. and Katz, J. (1929). Zur Erkenntnis des Lignins, I. Mitteil: Chemische und physikalische Untersuchungen der Phenol-Lignine. Ber. **62** 1172 –1177.

Wenzel, R. (1936). Surface roughness and contact angle. *Ind. Eng. Chem.* **28**, 988–994.

Woerner, D., McCarthy, J. (1988). Lignin 24. Ultrafiltration and light-scattering evidence for association of kraft lignins in aqueous solutions. *Macromolecules* **21**(7), 2160–2166.

Yaropolov, N. and Tishchenko, D. (1970a). Structure and properties of aqueous solutions of alakali lignins. (2). Study of the intermolecular reactions in purely aqueous solutions of lignin by means of additives, *Zh. Prikl. Khim.* **43**(6), 1351–1356.

Yaropolov, N. and Tishchenko, D. (1970b). Structure and properties of aqueous solutions of alakali lignins. (1). Viscosities of purely aqueous solutions of kraft lignins. *Zh. Prikl. Khim.* **43**(5), 1120–1126.

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