

# Adsorption of Water-Soluble, Nonionic Polymers onto Cellulosic Fibers

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## Synopsis

The adsorption of 12 different nonionic water-soluble polymers, methylcellulose (MC), hydroxypropylcellulose (HPC), polygalactomannan (PGM), polyglycidol (PGD), polyacrylamide (PAAm), methylolated polyacrylamide (MPAAm), polymethacrylamide (PMAAm), three differently hydrolyzed poly(vinyl acetate)s (PVAs), poly(vinyl methyl ether) (PVME), and poly(vinyl pyrrolidone) (PVP) onto bleached kraft pulp (BK), unbleached kraft pulp (UK), and a groundwood pulp (MP) has been investigated under aqueous conditions with attention to the functional groups in the polymers and the chemical character of the pulps. It was found that the adsorption was often selective toward one of the pulps. In order to gain some additional information on these interactions, some adsorption experiments were also performed on acetylated pulps. Some polymers (PGD, PAAm, MPAAm, and PVA 124) having both proton donating and accepting capability were not adsorbed onto any of the pulps. This was attributed to intramolecular hydrogen bonding in these polymers. Some polymers (PVA 224, PVME, and PVP) were strongly adsorbed onto UK but not at all onto BK. It was suggested that in these cases the adsorptive interaction was between phenolic and/or catecholic groups in the lignin on the UK and proton accepting sites on the polymers. However, for three polymers (MC, PGM, and PMAAm), a more general type of hydrogen bonding interaction was considered. For some polymers (HPC, PMAAm, and PVA 420) having hydrophobic groups, it was suggested that hydrophobic interactions were important for the adsorption.

## INTRODUCTION

Water-soluble polymers are widely used in papermaking operations to improve the dry strength properties of paper or to impart wet strength, and high molecular weight polymers are used as flocculants or retention aids. The task is to find suitable polymers which are adsorbed to the different kinds of cellulosic fibers used for papermaking.

Since cellulosic fibers are negatively charged in aqueous suspensions, most of the polymers used in papermaking are cationic. The adsorption of cationic polyelectrolytes onto cellulosic fibers is therefore a comparatively well-investigated field, whereas the adsorption of nonionic polymers has been much less investigated. Much of the work which has been done has been concerned with the adsorption of various gums and mucilages and not with the adsorption of synthetic polymers onto cellulose.<sup>1</sup>

Recently, the selective adsorption of polyethylene oxide onto different cellulosic fibers was studied<sup>2</sup> in order to gain information about the functional groups on the pulps responsible for the adsorptive interaction. It was shown in that

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work that different pulps could be selectively flocculated with polyethylene oxide and subsequently separated from each other by a microflotation procedure. This has a practical significance in the search for new fractionation methods by which the quality of wastepaper can be improved.

Another important task is to find functional chemical groups with strong adsorptive interactions to cellulosic surfaces, so that the formulation of industrial chemicals used in pulp and papermaking can be improved. Depending on the types of chemical and mechanical treatments to which the wood has been subjected, different pulps are expected to have different surface characteristics with regard to their contents and types of lignin, cellulose and hemicellulose. Different pulps are thus expected to show different affinities toward polymers.

The object of the present investigation was to study the adsorption of a range of nonionic polymers (12) from aqueous solutions onto three different types of pulp (bleached kraft, unbleached kraft, and stone groundwood). Particular attention was paid to the relation between the adsorptivity of the polymers and their functional group. The adsorption of nine polymers onto acetylated pulps was therefore also studied in order to obtain further information regarding the polymer-fiber surface interactions.

## EXPERIMENTAL

### Adsorbents

The unbleached kraft pulp (UK) was prepared in a laboratory digester utilizing chips from Scotch Pine (*Pinus sylvestris*), as has been described before.<sup>3</sup> The *H*-number after shives removal was 28. The bleached pine kraft pulp (BK) (Imperial Anchor) was obtained in dry lap form from Iggesund Bruk, Sweden. Both kraft pulps were beaten in a Valley beater to 25° SR. The spruce (*Picea abies*) stone groundwood pulp (MP) was obtained from Bure AB, Sweden. The freeness of this pulp, as given by the supplier, was 100 mL CSF.

The fine material fractions of all these pulps were removed using a Celleco filter and the >200 mesh fraction was collected and used in the subsequent experiments. After having been screened, the pulps were stored in a refrigerator in a 0.1% formaldehyde solution in order to prevent bacterial growth. The hydrodynamic specific surface was determined to be 0.99 m<sup>2</sup>/g for the BK, 1.42 m<sup>2</sup>/g for the UK, and 1.85 m<sup>2</sup>/g for the MP by permeability measurements using the Kozeny-Carman equation.<sup>4</sup>

Acetylated bleached kraft pulp (ABK) and acetylated unbleached kraft pulp (AUK) were also prepared from BK and UK. Prior to acetylation, the pulps were solvent-exchanged from water to acetone, air-dried at room temperature, and finally oven-dried at 105°C for 5 h. These pulps were then soaked in a mixture of 50% pyridine and 50% acetic anhydride (10 g dry pulp/L mixture) at room temperature and allowed to stand overnight. The acetylated pulps were washed with distilled and deionized water and stored in a refrigerator until use. Prior to the adsorption experiments, all the pulps were washed with 0.1*N* hydrochloric acid on a sintered glass filter with medium porosity in order to remove adsorbed metal ions and finally thoroughly washed with distilled and deionized water in order to eliminate water-soluble components which are extracted from the pulps

during storage and disturb the determination of polymer concentration by refractometry. Afterward the pulps were dewatered on the glass filter to a solids content of approximately 25% and were then used in the adsorption experiments.

### Polymers

The polymers used as adsorbants were as follows:

**Methyl Cellulose (MC).** A commercial product, Methocel A15 was kindly supplied by Dow Chemical Co. The approximate molecular weight and the degree of substitution were given by the manufacturer as 15,000 and 1.8, respectively.

**Hydroxypropyl Cellulose (HPC).** A commercial product, Klucel H was kindly supplied by Hercules Powder Inc. The approximate molecular weight and the degree of substitution were given by the manufacturer as 1,000,000 and 4.0, respectively.

**Polygalactomannan (PGM).** A product, E 1162 from Accurate Chemical and Scientific Corp. was used (69.8% mannose; 30.2% galactose). The intrinsic viscosity was determined to be 13.4 dL/g in deionized water at 25°C.

**Polyglycidol (PGD).** This polymer was kindly furnished by Dr. Vandenberg of Hercules Powder Inc. The viscosity of this sample was given as  $\eta_{sp}/c = 15.2$  dL/g in a 0.1% aqueous solution at 25°C.

**Polyacrylamide (PAAm).** A PAAm from Allied Colloids, Ltd., was used. The average molecular weight was  $4.6 \times 10^6$  as calculated from the equation by Collison et al.<sup>5</sup> using the intrinsic viscosity ( $\eta = 16.9$  dL/g) in deionized water at 25°C.

**Methylolated Polyacrylamide (MPAAm).** A sample of methylolated polyacrylamide was kindly prepared by Allied Colloids, Ltd., Bradford, UK. The intrinsic viscosity given by the manufacturer was 12.5 dL/g in deionized water at 25°C.

**Polymethacrylamide (PMAAm).** A product from Polyscience Inc. was used. The intrinsic viscosity was determined to be 0.8 dL/g in deionized water at 25°C.

**Poly(vinyl Alcohol) (PVA).** Five commercial products kindly supplied from Kuraray Co., Ltd., were used. Some of their properties are listed in Table I.

TABLE I  
Some Properties of PVAs Used

Grade	Degree of hydrolysis <sup>1</sup> (mol %)	Degree of <sup>a</sup> polymerization	Molecular <sup>b</sup> weight
PVA 124	98-99	2400-2500	110,000
PVA 204	87-89	350-450	20,000
PVA 217	87-89	1900-1800	86,000
PVA 224	87-89	2400-2500	120,000
PVA 420	78-81	2000-2150	110,000

<sup>a</sup> Data given by the manufacturer.

<sup>b</sup> Approximate molecular weights as calculated from the degree of hydrolysis and the degree of polymerization.

**Poly(vinyl Methyl Ether) (PVME).** A commercial product, Lutonal M40, was kindly supplied by Badische Anilline & Soda Fabrik. The intrinsic viscosity in 2-butanone at 30°C was 0.32 dL/g, which corresponds to a molecular weight of 24,300.<sup>6</sup>

**Poly(vinyl Pyrrolidone) (PVP).** A commercial product, PVP K90 from General Anilline and Film Corp. was used. The approximate molecular weight was given by the manufacturer as 360,000.

Stock solutions of all of these polymers were prepared at a concentration of 1000 ppm. To ensure complete dissolution, they were stirred for at least 24 h on a magnetic stirrer and then filtered through a sintered glass filter with medium porosity.

## METHODS

In a typical adsorption experiment, 4 g of the wet pulp (~1 g dry pulp) and a calculated amount of distilled and deionized water (total amount of liquid phase ≈100 mL) were weighed into a 250-mL round-bottomed glass flask. This glass flask was then placed in a thermostated bath and stirred with a screw-type glass stirrer (370 rpm) during the adsorption experiment. After thermal equilibration a given amount of a polymer solution was added to the pulp slurry with a pipette.

After a given time, the glass flask was taken from the water bath and the contents were filtered on a sintered medium porosity glass filter. In order to check whether the polymer was adsorbed onto the glass filter during the filtration, all polymers were separately filtered on these glass filters and the difference in concentration was determined. However, no reduction in concentration was detected within the precision limit of the measurements.

A more important factor is that a small amount of organic substance is released from the pulp fibers during the adsorption experiments. Therefore, blank tests with no polymer addition were run simultaneously with the adsorption experiments, and the increase in refractive index of the water phase was recorded. The amount of such disturbing material depended upon the kind of pulp used, and sometimes the influence of this factor on the concentration measurements could not be neglected. In these cases the refractive index of the polymer solution was corrected by subtracting the refractive index obtained in the blank tests.

The filtrate was recovered and the polymer concentration measured by determining the refractive index of the solution in a Water Associates Refractometer, Model R401, thermostated to  $\pm 0.005^\circ\text{C}$ . The calibration measurements showed that the concentration could be determined with a precision better than 1 ppm.

The pulp fibers remaining on the glass filter were oven-dried at 105°C overnight and then weighed. The pulp weight was determined by subtracting the amount of the adsorbed polymers on the pulp from the weight of the dried pulp fibers.

## RESULTS AND DISCUSSION

**Rate of Adsorption.** Prior to the examination of the adsorptivity of the different polymers onto the different pulps, it was necessary to obtain an idea

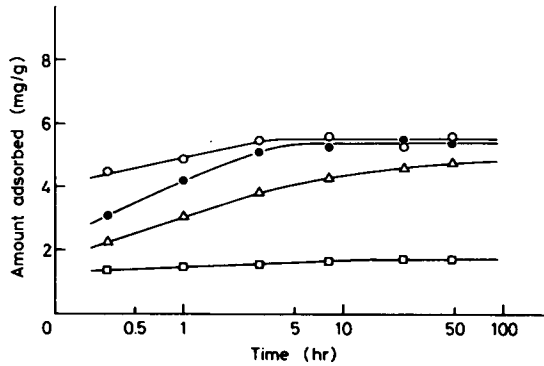


Fig. 1(a). The amount of polymer adsorbed onto an unbleached kraft pulp (UK) vs. time. Added amount of polymer: 0.5%; pulp concn = 10 g/L. PVA 224 = hydrolyzed poly(vinyl acetate) (degree of hydrolysis = 87–89%); HPC = hydroxypropyl cellulose; PMAAm = polymethacrylamide. PVA 224 on UK at (O) 40°C and (●) 25°C; (Δ) HPC on UK at 40°C; (□) PMAAm on UK at 40°C.

of how long a time was required to approach adsorption equilibrium. The results from these experiments are given in Figures 1(a) and 1(b). All the adsorption rate curves show that, except in the case of hydroxypropylcellulose (HPC), equilibrium adsorption is reached within an adsorption time of 10 h.

In spite of the fact that approximately 10 h are required to approach equilibrium, a 4-h adsorption time was selected in the subsequent experiments.

This time was chosen because some water-soluble material is extracted from the pulp during the adsorption period. This extracted material not only disturbs the measurements of the polymer concentration, but presumably also interacts with the polymer in solution and changes its interaction with the fibers. Since the release of material from the dispersed fibers increases linearly with time, the experimental error in the determination of the polymer concentration also increases with increasing adsorption time, although the concentration values are corrected for this disturbing material. It is therefore desirable to make the adsorption period as short as possible.

An adsorption period of 4 h was chosen as the best compromise, since most

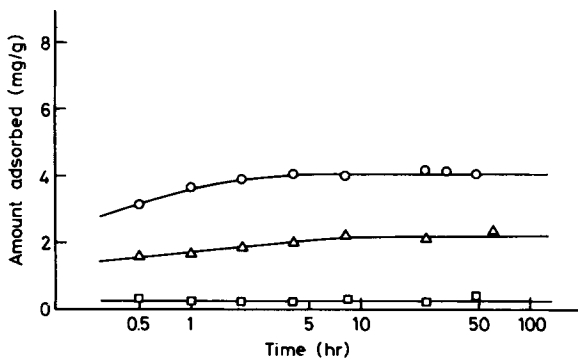


Fig. 1(b). The amount of PVP [poly(vinyl pyrrolidone)] adsorbed onto different pulps vs. time. Added amount of polymer: 0.5%; pulp concn = 10 g/L;  $T = 40^\circ\text{C}$ . (O) UK = unbleached kraft, (□) BK = bleached kraft; (Δ) MP = mechanical pulp.

TABLE II  
Adsorption of Water-Soluble, Nonionic Polymers from Aqueous Solution onto Different Kinds of Soft Wood Pulp<sup>a</sup>

Polymer	Bleached kraft (BK)		Unbleached kraft (UK)		Mechanical pulp (MP)	
	A	C	A	C	A	C
	(mg/g)	(ppm)	(mg/g)	(ppm)	(mg/g)	(ppm)
Methyl cellulose (MC)	2.2	23	3.6	8	0.7	44
Hydroxypropylcellulose (HPC)	0.7	40	3.9	7	1.3	37
Polygalactomannan (PGM)	3.0	21	2.0	22	0.9	37
Polyglycidol (PGD)	-0.1	50	0.1	49	-0.1	51
Polyacrylamide (PAAm)	-0.1	49	-0.2	50	0.3	44
Methylolated polyacrylamide (MPAAm)	-0.1	51	-0.2	52	-0.1	51
Polymethacrylamide (PMAAm)	2.2	28	2.5	24	0.3	46
Poly(vinyl alcohol) (PVA 124)	-0.1	51	0.3	47	0.0	50
Hydrolyzed poly(vinyl acetate) (PVA 224)	-0.1	51	4.1	0.4	1.0	41
Hydrolyzed poly(vinyl acetate) (PVA 420)	0.1	49	4.9	3	1.8	31
Poly(vinyl methyl ether) (PVME)	-0.1	50	5.1	1	0.7	47
Poly(vinyl pyrrolidone) (PVP)	0.2	45	3.7	17	2.0	30

<sup>a</sup> Experimental conditions: adsorption period 4 h; initial polymer concentration ~50 ppm; pulp consistency 8–12 g/L; temperature 40°C except PVME (25°C). The figures given are the averages of triplicate measurements. A: Amount adsorbed; C: concentration after adsorption.

of the adsorption takes place within this period. Figure 1(a) shows the adsorption of PVA 224 at two temperatures (25°C and 40°C). The initial rate of adsorption is apparently much higher at 40°C than at 25°C, but the time to reach equilibrium at 40°C is not very different from that at 25°C.

At the present stage of the experiments it is not possible to discern the rate-determining step in the adsorption experiments. The substrate is a swollen cellulosic fiber with a complex pore structure, and it is known that polymer sorption is slow on such substrates.<sup>7</sup> Polymer migration in the pore structure, partitioning, and displacement adsorption are examples of complex factors which must be considered in this context.

**Differences in Adsorptivity onto Different Pulps.** The adsorption of 12 different polymers onto bleached kraft (BK), unbleached kraft (UK), and a

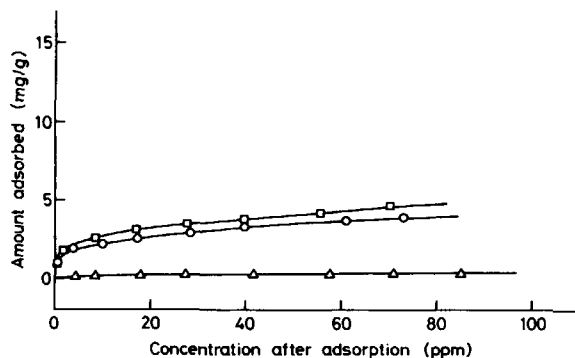


Fig. 2(a). Adsorption isotherms of polygalactomannan (PGM) on (○) UK, (△) MP, and (□) BK at 40°C.

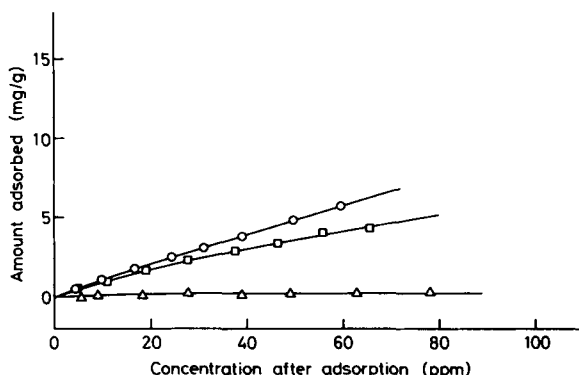


Fig. 2(b). Adsorption isotherms of polymethacrylamide (PMMAm) on (O) UK, ( $\Delta$ ) MP, and ( $\square$ ) BK at 40°C.

mechanical pulp (MP) was examined, and the results are summarized in Table II. The measurements were performed at 40°C except in the case of poly(vinyl methyl ether) (PVME), which was studied at 25°C, owing to the fact that the cloud point of PVME used was at about 35°C.

Figures 2(a)–2(e) show the adsorption isotherms of polygalactomannan (PGM), polymethacrylamide (PMAAm), hydrolyzed poly(vinyl acetate) (PVA 224), PVME, and poly(vinyl pyrrolidone) (PVP) on UK, BK, and MP.

All the isotherms except that for PMMAM show a general form in which the adsorption increases steeply at low concentrations and then rises more slowly at higher concentrations. The adsorption does not, however, reach the saturation level within the range of concentrations studied for these polymers.

A further analysis of the shape of the adsorption isotherms is not relevant, since the shape of the isotherm is probably related to the polydispersity of the polymer, as discussed by Stuart.<sup>8</sup>

The different polymers may conveniently be divided into different groups with regard to their adsorption behavior. The first group (PVA 224, PVA 420, PVME,

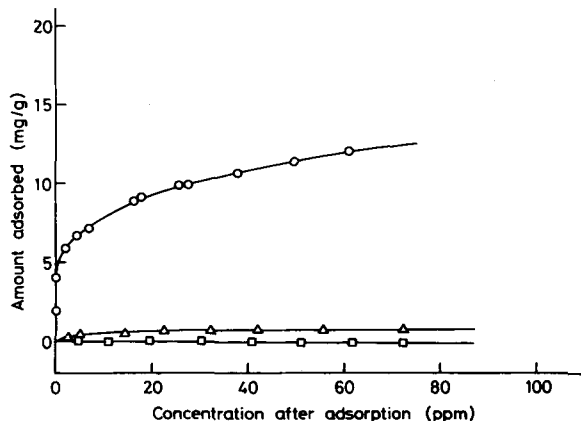


Fig. 2(c). Adsorption isotherms of hydrolyzed poly(vinyl acetate) (PVA 224) on (O) UK, ( $\Delta$ ) MP, and ( $\square$ ) BK at 40°C.

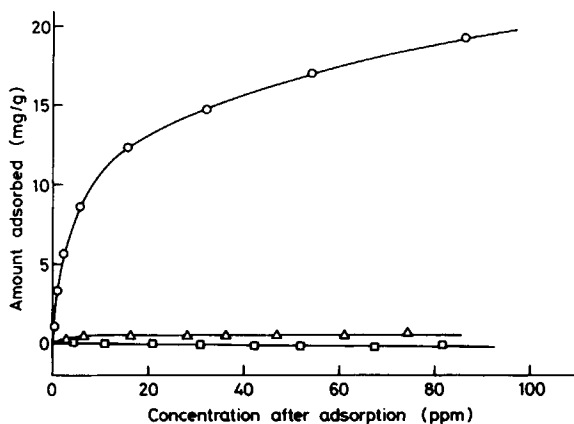
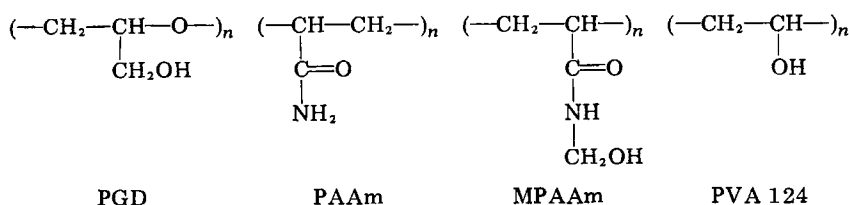


Fig. 2(d). Adsorption isotherms of poly(vinyl methyl ether) (PVME) on (O) UK, ( $\Delta$ ) MP, and ( $\square$ ) BK at 25°C.

and PVP) is strongly adsorbed onto unbleached kraft pulp, weakly adsorbed onto MP, and not adsorbed or only slightly adsorbed onto BK. The second group of polymers are adsorbed to a similar extent onto UK and BK, but are more weakly adsorbed onto MP. This group includes methylcellulose (MC), polygalactomannan (PGM), and polymethacrylamide (PMMAM). The third group is intermediate between the first and the second group and only includes HPC.

Finally there is a group of polymers which are not adsorbed or show only very weak adsorption onto all pulps. Polyglycidol (PGD), polyacrylamide (PAAm), methylolated polyacrylamide (MPAAm), and poly(vinyl alcohol) (PVA 124) belong to this group. All the polymers in the latter group are able to act as both proton donors and acceptors, as indicated in the chemical structures of these polymers shown below:



For example, PGD has alcoholic hydroxyl groups in the side chain and ether oxygens in the backbone chain. It is also well known<sup>9</sup> that alcoholic hydroxyl groups possess the nature of both a proton donor and a proton acceptor, and the ether oxygen acts as a proton acceptor. These polymers may therefore form intramolecular hydrogen bonds. In fact, Vandenberg<sup>10</sup> has suggested that the intramolecular hydrogen bonds are formed between hydrogen atoms and the ether oxygens in a PGD molecule via six- or five-membered rings.

Shiraishi<sup>11</sup> pointed out that the intrinsic viscosity (aqueous solution) of a completely hydrolyzed PVA was much lower than that of a partially hydrolyzed PVA having the same degree of polymerization as the completely hydrolyzed PVA. This was attributed to a greater abundance of intramolecular hydrogen



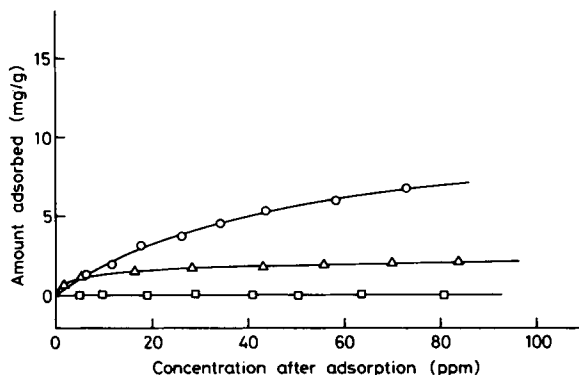


Fig. 2(e). Adsorption isotherms of poly(vinyl pyrrolidone) (PVP) on (○) UK, (△) MP, and (□) BK at 40°C.

bonds in the completely hydrolyzed PVA than in the partially hydrolyzed PVA. It is also well known<sup>9</sup> that amide groups form hydrogen bonds with each other, as a result of the proton donor and proton acceptor properties of this group.

The formation of intramolecular hydrogen bonds in a polymer molecule blocks the ability of the functional groups to be adsorbed onto a substrate. In addition, a polymer showing both proton-donor and proton-acceptor properties will interact strongly with water molecules if it does not exhibit a strong intramolecular interaction, and both of these factors will tend to reduce the polymer-substrate interaction.

The second group of polymers (MC, PGM, PMAAm) was adsorbed in a similar manner onto both UK and BK and much less on MP. It is relevant to note that the cellulose content of the pulps increases in the order MP < UK < BK owing to the removal of lignin and hemicellulose during cooking and bleaching and that the hydrodynamic specific surface determined by permeability measurements is 1.85 m<sup>2</sup>/g (MP), 1.42 m<sup>2</sup>/g (UK), and 0.99 m<sup>2</sup>/g (BK). Although the hydrodynamic specific surface area does not directly correspond to the surface area available for polymer adsorption, these two facts suggest that the second group of polymers may have a stronger affinity to cellulose than to lignin and hemicellulose.

If the adsorption of PMAAm in the second group is compared with the adsorption of PAAm in the fourth group, it is evident that the introduction of the methyl group into the polymer backbone enhances the affinity of the polymer to the pulps. The simplest explanation of this behavior is that the introduction of the methyl group decreases the polymer-solvent interaction, thereby increasing the adsorptive properties of the polymer. However, this modification increases the affinity of the polymer toward the BK but not toward the MP, which may be considered to have a hydrophobic surface character. Thus specific hydrophobic interactions are apparently less important in this case.

In the first group, the polymers (PVA 224, PVA 420, PVP, PVME) exhibit a strong adsorption onto UK, much less onto MP, and virtually no adsorption onto BK. This indicates that in this group the polymers interact preferentially with the lignin or hemicellulose and not with the cellulose. One possibility is that the adsorption of these polymers is induced by a hydrophobic interaction between

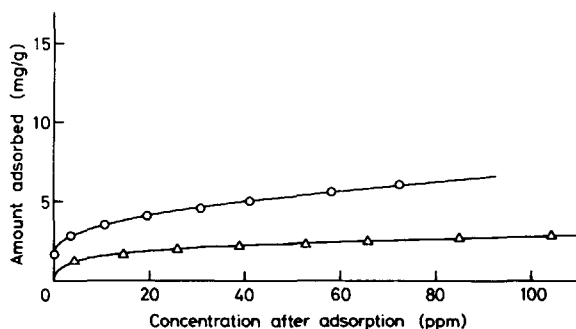


Fig. 3(a). The effect of temperature on the adsorption of hydroxypropylcellulose (HPC) on UK. (○) 40°C; (△) 25°C.

the polymer backbone chain and hydrophobic sites on the pulps. Both MP and UK contain lignin, which is considered to be a more hydrophobic material than cellulose or hemicellulose. However, since the adsorption of group 1 polymers is much stronger onto UK than onto MP and since the specific surface area of MP is larger than of UK, it is difficult to explain the adsorption behavior solely by hydrophobic interactions.

It is very likely that the kraft lignin remaining in the fibers after kraft cooking has a character considerably different from that of the lignin in the fibers after mechanical grinding.

For instance, it has been found<sup>12</sup> that an isolated kraft lignin (pine) sample contains 72 phenolic groups per 100 C<sub>6</sub>-C<sub>3</sub> units, whereas there are only six phenolic groups in samples of cell corner middle lamellae of black spruce tracheids.<sup>13</sup> It is also known that a considerable amount of catechol groups (12 catechol hydroxyls per 100 C<sub>6</sub>-C<sub>3</sub> units) are formed during kraft cooking whereas no catechol groups are found in isolated milled wood lignin samples.<sup>12</sup> Lindström and Glad-Nordmark<sup>2</sup> found that polyethyleneoxide (PEO) is adsorbed onto unbleached kraft pulp and unbleached sulfite pulps but not onto bleached kraft or stone groundwood pulp. It was suggested that the adsorption of PEO on the former pulps was caused by hydrogen bonds between the phenolic and/or catecholic protons and the ether oxygens in the PEO chain. Hence PEO acts as a proton acceptor, and it can also be noted that in the present study all the polymers belonging to the first group are proton acceptors. PVME and PVP are pure proton acceptors whereas the hydrolyzed PVA also contains proton-donating hydroxyl groups. Thus it may be suggested that the adsorption of the group 1 polymers is caused mainly by hydrogen bonds between these proton acceptors and the phenolic and/or catecholic protons in the residual lignin moieties in the pulp.

**The Effect of Temperature on Adsorption.** The effect of temperature (25°C and 40°C) on the adsorption of HPC, PVA 224, and PVP on UK was also investigated. These three polymers were chosen because their solubilities in water change in different ways with temperature. The solubility of HPC in aqueous solutions decreases with increasing temperature and precipitation takes place at 41°C.<sup>14</sup> The solubilities of PVA 224 and PVP, on the other hand, increase with increasing temperature. Water at 25°C is nearly a  $\theta$ -solvent for PVP.<sup>15</sup>

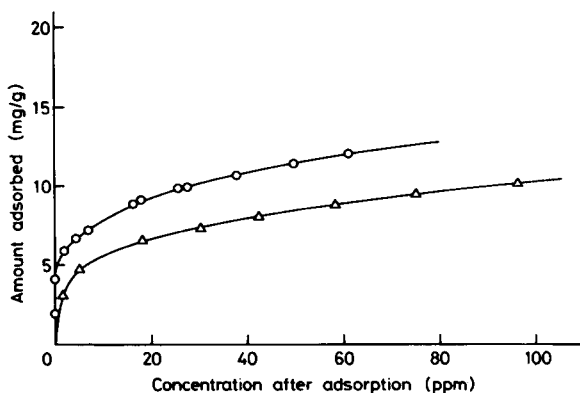


Fig. 3(b). The effect of temperature on the adsorption of hydrolyzed poly(vinyl acetate) (PVA 224) on UK. (O) 40°C; (Δ) 25°C.

Besides affecting the solubility of the polymer, the temperature also affects the conformation of the polymer in the adsorbed layer, and the competition between the solvent and the polymer for the adsorption sites. It is well known, for instance, that the adsorbed amount of polymer is usually higher from a poorer solvent.<sup>7,15</sup> It may thus be expected that the adsorption of HPC would increase and that the adsorption of PVP and PVA would decrease with increasing temperature.

The results in Figures 3(a)–3(c) show, however, that the adsorption increases with increasing temperature for all three polymers. This suggests that the favorable change with temperature in the competition between the solvent and the polymer for the adsorption sites predominates over the effect of temperature on the solubility of the polymers. It may, therefore, be concluded that, in the range of temperatures studied here, the competitive power of the solvent decreases strongly with increasing temperature. Consequently, polymer adsorption increases even when the solubility of the polymer is increased by increasing the temperature. This is not an unexpected result since water has a strong swelling power on the pulps used, which implies a strong affinity for water molecules. This is probably the main factor responsible for the low adsorption of most nonionic polymers on pure cellulose surfaces.

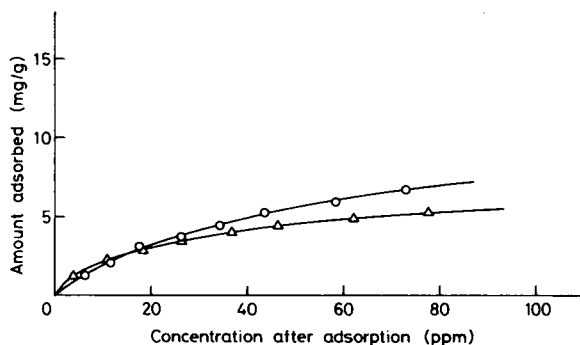


Fig. 3(c). The effect of temperature on the adsorption of poly(vinylpyrrolidone) (PVP) on UK. (O) 40°C; (Δ) 25°C.

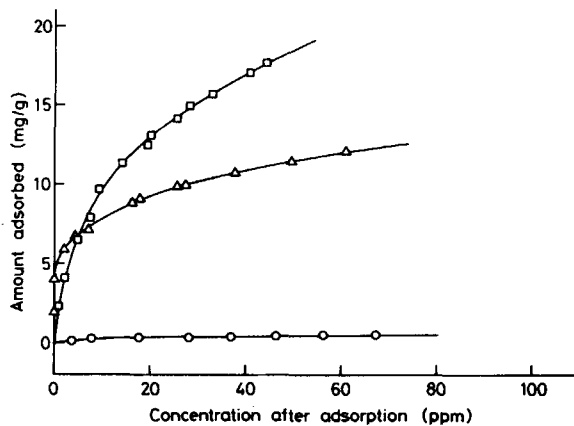


Fig. 4(a). The effect of their degree of hydrolysis on the adsorption of PVAs on UK at 40°C. Mol % of hydrolysis of each PVA is: (O) PVA 124: 98–99; ( $\Delta$ ) PVA 224: 87–89; ( $\square$ ) PVA 420: 78–81.

**The Effect of the Degree of Hydrolysis of PVA.** To study the effect of the degree of hydrolysis of poly(vinyl acetate) (PVA) on the adsorption, three different commercially available PVAs were selected. The acetyl group content increased from 1–2 mol % for PVA 124 to 11–13 mol % for PVA 224 and to 19–22 mol % for PVA 420.

Figures 4(a) and 4(b) show the adsorption isotherms of the different PVAs on UK and MP at 40°C. PVA 124 is not adsorbed onto the pulps, but the adsorption onto both pulps increases with the number of acetate groups. This large difference in adsorptivity is not an effect of a difference in the degree of polymerization or molecular weight between the samples. The molecular weights of the samples are almost the same as shown in Table I. Therefore, this factor can be neglected in the following discussion (see also the next section).

The acetyl groups in the polymer backbone can only act as proton acceptors and cannot form hydrogen bonds with each other. It is therefore likely that the extent of intramolecular hydrogen bonding in the PVAs decreases as the acetyl group content increases. As mentioned earlier, Shiraishi<sup>11</sup> suggested this from the large difference in intrinsic viscosity between completely and partially hy-

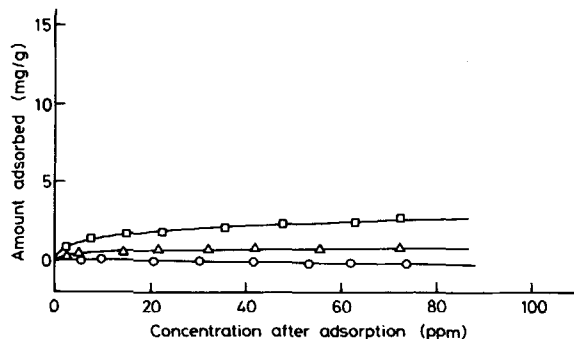


Fig. 4(b). The effect of their degree of hydrolysis on the adsorption of PVAs on MP at 40°C. (O) PVA 124; ( $\Delta$ ) PVA 224; ( $\square$ ) PVA 420.

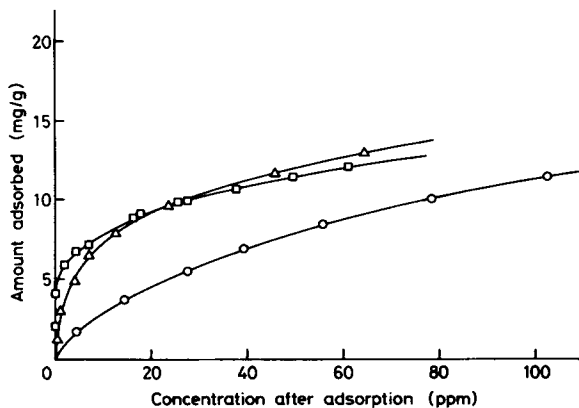


Fig. 5. The effect of molecular weight on the adsorption of medium hydrolysis type of PVA on UK at 40°C. Approximate molecular weights: (○) PVA 204: 20,000; (△) PVA 217: 86,000; (□) PVA 224: 120,000.

drolized PVA. It is therefore tempting to suggest that one of the factors responsible for the increased adsorption is the breakup of internal hydrogen bonds when the acetyl group content is increased.

Poly(vinyl alcohol) (PVA 124) is more soluble at high temperatures, whereas the solubility of a medium hydrolyzed PVA (e.g. PVA 224) is less dependent on temperature, and the less hydrolyzed type of PVA (e.g., PVA 420) is more soluble in cold water and precipitates at a temperature above 40°C.<sup>16</sup> Thus the high adsorptivity of PVA 420 onto both pulps may be explained by its low solubility at the temperature adopted here (40°C) and the previously mentioned interruption of the internal hydrogen bonds.

The acetyl groups in the PVA 420 give the polymer a more hydrophobic character. Therefore, it cannot be excluded that the adsorption of PVA 420 onto the pulps is caused partially by a hydrophobic interaction between the acetyl groups and the lignin, although there is no reason to consider the surface of UK to be more hydrophobic than the surface of a MP. This is primarily indicated by the fact that the adsorption isotherm of PVA 420 on UK rises less steeply than that of PVA 224 at low concentrations, suggesting a lower energy of interaction between PVA 420 and the pulp than between PVA 224 and the pulp. The energy of interaction is expected to be lower for a hydrophobic interaction than for an interaction mediated by a hydrogen bond.

**The Effect of Molecular Weight of PVA.** The effect of molecular weight on the adsorption of medium hydrolyzed PVAs on UK is shown in Figure 5. The molecular weight of these samples varied from approximately  $2 \times 10^4$  to  $1.2 \times 10^5$ , i.e., they are sufficiently small to enter a part of the internal voids in the swollen fibers.<sup>17</sup> It is generally recognized that an increase in the molecular weight of the polymer increases the amount adsorbed on smooth surfaces, whereas the reverse behavior is often found on porous substrates.<sup>7</sup>

Figure 5 shows that the adsorption increases with increasing molecular weight at low polymer concentrations, whereas the reverse is true at higher polymer concentrations, at least if PVA 217 and PVA 224 are considered. This immediately suggests that it is the low molecular weight tail of the polymer which is

TABLE III  
Effect of Acetylation of Pulps on the Adsorption of Nonionic Polymers on Soft Wood Pulps<sup>a</sup>

Polymer	BK		ABK		UK		AUK	
	A (mg/g)	C (ppm)	A (mg/g)	C (ppm)	A (mg/g)	C (ppm)	A (mg/g)	C (ppm)
MC	2.2	23	1.8	31	3.6	8	2.0	32
HPC	0.7	40	1.7	33	3.9	7	2.8	22
PGM	3.0	21	1.0	39	2.0	22	0.4	46
PMAAm	2.2	28	1.8	33	2.5	24	2.0	30
PVA 124	0.1	51	0.1	50	0.3	47	0.0	50
PVA 224	0.1	51	0.5	45	4.1	0.4	2.8	27
PVA 420	0.1	49	2.2	30	4.9	3	4.5	8
PVME	0.1	50	0.4	46	5.1	1	3.7	15
PVP	0.2	45	0.2	48	3.7	12	1.6	35

<sup>a</sup> Experimental conditions: adsorption period 4 h; initial concentration about 50 ppm; pulp consistency 8–12 g/L; temperature 40°C except PVME (25°C). The figures in this table are average values of three trials with nonacetylated pulps and of two trials with the acetylated pulps.

predominantly adsorbed in the small surface voids of the swollen fiber at higher polymer concentrations.

It has often been observed that the adsorption isotherm becomes steeper with increasing molecular weight (e.g., Refs. 18 and 19). This implies a higher affinity of a polymer with a higher molecular weight, and this is easily understood from the fact that a high molecular weight polymer has more segments attached to the surface than a low molecular weight polymer.

**The Effect of Acetylation of the Pulps on the Adsorption.** In order to gain further information on the adsorption mechanism, the surface characteristics of the two kraft pulps were changed by means of acetylation.

In this study, nine of the polymers were selected and the results of these experiments are summarized in Table III. The full adsorption isotherm of the different PVAs on the acetylated unbleached kraft pulp (AUK) and on the acetylated bleached kraft pulp (ABK) are given in Figures 6(a) and 6(b). The

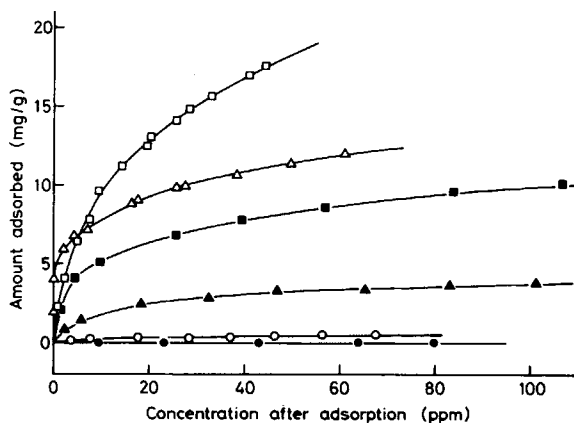


Fig. 6(a). Adsorption isotherms of different PVAs on acetylated (AUK) and nonacetylated unbleached kraft pulp (UK),  $T = 40^\circ\text{C}$ . UK: (○) PVA 124, (△) PVA 224, (□) PVA 420; AUK: (●) PVA 124, (▲) PVA 224, (■) PVA 420.

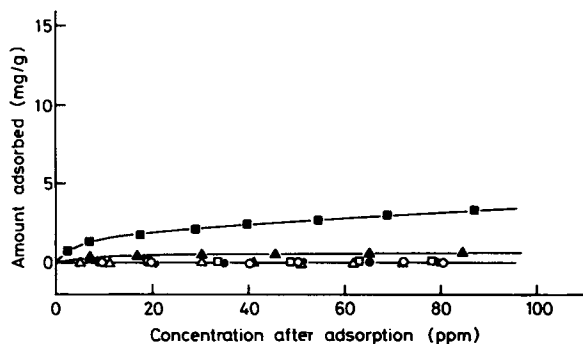


Fig. 6(b). Adsorption isotherms of different PVAs on acetylated (ABK) and nonacetylated bleached kraft pulp (BK),  $T = 40^\circ\text{C}$ . BK: (○) PVA 124, (△) PVA 224, (□) PVA 420; ABK: (●) PVA 124, (▲) PVA 224, (■) PVA 420.

results show that for all the polymers studied the adsorption decreases when the unbleached kraft pulp is acetylated.

For the first (PVP, PVME, PVA 224, PVA 420) and third group (HPC) of polymers, the adsorption increases when the bleached kraft pulp is acetylated, although the increase in adsorption among the first group of polymers is only significant in the case of PVA 420. The adsorption of group 2 polymer (MC, PGM, PMAAm) decreases when ABK is used instead of BK and PVA 124 (group 4) is not adsorbed to any of the pulps.

The introduction of acetyl groups into the pulps means first that the pulp has new proton-accepting sites and second that the fiber surface has become slightly more hydrophobic. At the same time, proton-donating phenolic and catecholic sites on the lignin have been blocked. It may therefore be concluded that a large part of the adsorptive interaction between group 1 polymers (except PVA 420) and UK is caused by hydrogen bonds between the proton acceptor in their functional groups and protons in the phenolic and/or catecholic hydroxyl groups in the lignin in the UK, as was suggested earlier. It was previously shown<sup>2</sup> that acetylation of UK decreased the adsorption of PEO onto the pulp to zero. In this particular case, it was not necessary to consider other adsorptive interactions than that mentioned above.

The polymers in group 1 do not interact with the hydrogen bonds in the cellulose, as these polymers are not adsorbed onto the bleached kraft pulp. Interaction with cellulose by hydrogen bonding must, however, be taken into account in the interpretation of the adsorption of group 2 polymers (MC, PGM, and PMAAm) onto the pulp. The decreased adsorption onto both the AUK and ABK may be explained by a decreased hydrogen bond interaction.

This does not, however, mean that hydrophobic interactions can be neglected for all the polymers used, although this is usually not considered to be the dominant adsorptive interaction. The increased adsorption of HPC after acetylation of the BK may be considered as a hydrophobic interaction between the hydroxypropyl residues and the acetyl groups. Likewise the adsorption of polymers having a hydrophobic group on the backbone (HPC; propyl group/PMAAm; methyl group) is not strongly decreased by the acetylation, and their adsorption on ABK is relatively high compared with that of the other polymers.

An examination of Figures 6(a) and 6(b) reveals that the decrease in adsorption when acetyl groups are introduced into the UK is less accentuated for the PVA 420 than for PVA 224. Since PVA 420 has a higher content of acetyl groups than PVA 224, it can be suggested that in this particular case hydrophobic interactions are probably the dominating cause of the affinity of the polymer to the fiber surface. This hypothesis is further substantiated by the fact that the adsorption of PVA 420 is raised from 0.1 to 2.2 mg/g after acetylation of the BK.

## CONCLUSIONS

1. Some polymers (PGD, PAAM, MPAAm, and PVA 124) having an ability to both accept and donate protons are not adsorbed onto any of the pulps used (UK, BK, and MP). This is attributed mainly to the intramolecular hydrogen bonds in the polymers.

2. Some polymers (PVA 224, PVME, and PVP) are strongly adsorbed onto UK, but not at all onto BK. In this case it is suggested that the major part of the interaction between the polymers and the fiber surface is caused by an interaction between phenolic and/or catecholic groups in the lignin in the UK and proton-accepting groups in the polymers.

3. Some polymers (MC, PGM, and PMAAm) show a similar adsorption on BK and UK. For these polymers it is suggested that hydrogen bonding interactions with cellulose are important for the affinity toward the fibers.

4. For some polymers (HPC, PMAAm, and PVA 420) having hydrophobic groups, it is suggested that hydrophobic interactions play a role for their adsorption behavior.

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