

Donnan Effect and Distribution of the $[\text{Si}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{6-}$ Anion in Pulp Suspension

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The Donnan distribution of a Keggin-type polyoxometalate (POM) anion, $[\text{Si}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{6-}$, in a suspension of bleached softwood kraft pulp was studied. In addition to experimental work, computerized modelling was carried out. In suspensions of low ionic strength of potassium chloride, POM was found to follow fairly well the predictions given by the Donnan model. In suspensions that had high potassium concentrations, POM showed behaviour that deviated from a typical Donnan distribution. In high potassium concentrations or when cationic polyelectrolyte was added to the suspension, POM showed an affinity to the fibre. The possible mechanisms that cause the attraction as well as their influence on the catalyzing ability of POM are discussed.

La distribution de Donnan de l'anion de polyoxométalate (POM) de type Keggin $[\text{Si}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{6-}$ dans une suspension de pâte kraft blanchie de résineux a été étudiée. En plus des essais, nous avons effectué une modélisation par ordinateur. Dans les suspensions de chlorure de potassium à faible force ionique, le POM s'est sensiblement conformé aux prévisions du modèle Donnan. Dans les suspensions à forte teneur en potassium, le comportement du POM s'écartait du modèle de distribution Donnan typique. Lorsque la teneur en potassium était élevée ou lorsque du polyélectrolyte cationique était ajouté à la suspension, le POM a montré une affinité avec la fibre. Les mécanismes pouvant causer l'attraction ainsi que leur influence sur la capacité de catalisation du POM font l'objet de discussion.

INTRODUCTION

Recently, several papers have been published on the possible use of polyoxometalates (POMs) as agents in novel effluent- and chlorine-free oxygen bleaching processes for chemical softwood and hardwood pulps [1–10]. The POM bleaching is based on the reaction



where POM_{ox} , POM_{red} , and Lignin^* represent oxidized POM, reduced POM, and an oxidized lignin structure, respectively. The reduced POM is oxidized with molecular oxygen in a subsequent reaction, after which it can further oxidize lignin structures. Therefore, theoretically, the final degradation products of lignin in POM bleaching are exclusively carbon dioxide and water.

So far, POM bleaching has not been applied in the pulping industry. One reason for this is probably that the processes presented are

too inefficient to be economically feasible. The inefficiency may be due to the Donnan effect, especially when POM is used in catalytic amounts, resulting in low ionic strength in pulp suspensions [4–7, 10]. To clarify this point, a short introduction to Donnan theory is presented.

The phenomenon that today is called the Donnan effect was studied first by Donnan and Harris in a system where ionic species were distributed unequally on each side of a semipermeable membrane because of their different sizes [11]. Later, the theory was applied also to describe the distribution of ions in suspensions of cellulose fibres [12, 13]. In pulp suspensions, the

ionizable groups attached to fibres cause the unequal distribution of ions (Fig. 1).

When the ion-distribution phenomena taking place in a pulp suspension are ap-

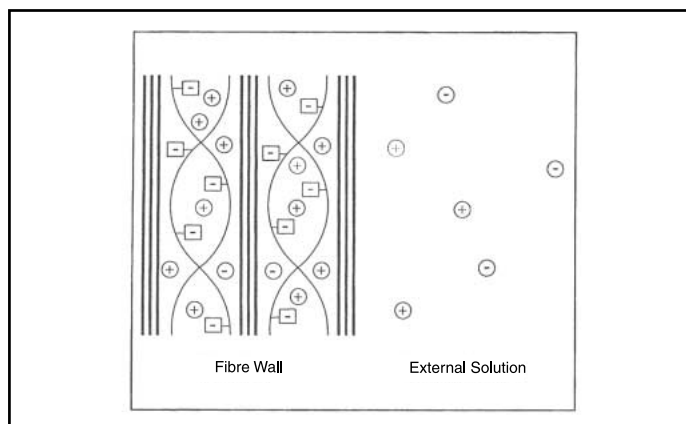


Fig. 1. The Donnan effect: a water-swollen fibre wall in an electrolyte solution. When fibre-bound functional groups (e.g. carboxylic acids) dissociate, they create a negative electric charge on the fibre. This causes a higher concentration of mobile cations in the solution within the fibre wall, while mobile anions are repelled. The figure shows only monovalent ions for simplicity [14].

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proached using the Donnan theory, the solution is thought to comprise two phases; namely, the fibre phase and the external phase [12,13]. The fibre phase is the small volume of liquid contained within the water-swollen fibre wall, and the external phase is the larger liquid volume surrounding the fibre. According to the theory, the distribution of different mobile anions and cations between the two phases is described by a single factor, the distribution constant λ :

$$\begin{aligned}\lambda &= \frac{[H^+]_f}{[H^+]_s} = \frac{[M^+]_f}{[M^+]_s} \\ &= \sqrt{\frac{[M^{2+}]_f}{[M^{2+}]_s}} = \frac{[I^-]_s}{[I^-]_f} \\ &= \sqrt{\frac{[I^{2-}]_s}{[I^{2-}]_f}} = \sqrt[3]{\frac{[I^{3-}]_s}{[I^{3-}]_f}}\end{aligned}\quad (2)$$

where H represents a hydrogen ion, M denotes a cation and I an anion; the indices *s* and *f* denote the external phase and the fibre phase, respectively. In a more general form, we can write:

$$\lambda^z = \frac{[M^{z+}]_f}{[M^{z+}]_s} = \frac{[I^{z-}]_s}{[I^{z-}]_f}\quad (3)$$

where *z* expresses the absolute value of the valence of the ion. It should be noted that, for anions, the concentration in the fibre phase is the denominator whereas, for cations, the denominator is the concentration in the external phase [11,13,15].

The constant λ depends on many factors. Naturally, its value depends on the values of the fibre and external phase volumes. These volumes are affected by pH and ionic strength [13]. The ionizable groups of the fibre dissociate at pK_a values specific to their structure and the chemical environment, leading to an increase in the negative charge of the fibre as pH increases. High concentrations of ionic species screen some of the dissociated groups, diminishing the effect of the negative charge. Considering these facts, it can be said that, as a rule, the highest values for λ are obtained when the ionic strength is low and the pH is high. According to one Donnan model [16], under these conditions λ may reach values as high as 3 or 4.

As seen in Eq. (3), the concentration of a certain ion in the fibre phase is strongly dependent on λ and on the valence of the ion. For example, for an anion that has a valence of -6 , the following equation applies:

$$[I^{6-}]_f = \frac{[I^{6-}]_s}{\lambda^6}\quad (4)$$

Equation (4) shows clearly that, when λ is large, even high external concentrations of a strongly negative anion accompany negligible concentrations of the same anion in the fibre. Being anions that characteristically have a very high negative charge, POMs may be affected

dramatically by the Donnan phenomenon. This is an important point concerning the POM bleaching processes, because POM anions need to get into contact with lignin molecules in the fibre wall for the oxidation reactions to take place.

Based on the Donnan theory, models can be developed for predicting the distribution of ionic species in pulp suspensions under varying conditions if certain basic data are known (e.g. fibre properties). In addition to the model already mentioned [16], other Donnan models have also been composed [14, 17, 18]. Since it is strongly believed that, until now, no experiments on the behaviour of POM anion in pulp suspension have been carried out, the distribution of the $[SiV^{IV}W_{11}O_{40}]^{6-}$ anion was investigated by both Donnan modelling and laboratory experiments.

EXPERIMENTAL The Experimental Plan

In this work, the aim was to prove, with simple laboratory and modelling experiments, that the Donnan effect should be considered when POM bleaching is performed, especially if catalytic amounts (less than 2 mmol dm⁻³) of POM are used. In the experiments, the emphasis was on trying to rationalize the effect that changes in the ionic strength and the pH of the pulp suspension, along with the fibre charge, have on the distribution of POM. These properties were chosen as experimental variables because they are the most important factors influencing the intensity of the Donnan effect.

Fully bleached and washed pulp was chosen for the experiments instead of unbleached pulp. This was done because unbleached pulps are rich in dissolved compounds and chemical structures that can make modelling and interpretation of the results difficult. For the same reason, instead of the reactive oxidized form of POM, the more inert reduced form was used. When designing the experiments, it was assumed that the ion distribution phenomena taking place in a suspension containing reduced POM and fully bleached pulp are essentially the same as in the case of unbleached pulp and oxidized POM.

To make the results more reliable, experiments using two techniques were planned. The most important results were to be obtained by measuring the POM concentration in filtrates of pulp suspensions. In addition, experiments to approximate the amount of POM sorbed by the fibre with direct measurements were planned. This was done to assure that the changes in the absorbance of the filtrates are caused by sorption of POM into the pulp and are not due to, for example, changes in the absorptivity of POM caused by experimental conditions (e.g. high ionic strength or low pH).

Materials

A fully bleached, never-dried softwood kraft pulp obtained from a Finnish kraft pulp mill was used in the experiments. Before sample preparation, the pulp was treated in the following way [14].

— To remove the natural cations, the pulp was

diluted to 3% consistency and the pH was adjusted to 1.7 with HCl. The suspension was mixed for 20 min, dewatered and washed several times with deionized water. The acidification followed by washing was repeated.

— To convert the acidic groups to the sodium form, the hydrogen-form pulp, as prepared above, was again set to 3% consistency, and then adjusted to pH 10 with NaOH. The pulp was washed with deionized water.

After the treatment, the pulp was stored in a refrigerator (5°C) at ~20% consistency.

$K_6[SiV^{IV}W_{11}O_{40}] \cdot 2 H_2O$ was used as POM (henceforth, by the abbreviation POM, the $[SiV^{IV}W_{11}O_{40}]^{6-}$ anion is meant, unless otherwise indicated). The POM was synthesized in the Forest Products Laboratory in Madison, WI, USA [19]. In reduced form, the POM absorbs strongly visible light and forms a dark purple solution when dissolved in water. The absorption maximum of the solution is at 496 nm.

Fibre Properties

To determine the fibre charge and the dissociation constants of the fibre's acidic groups, a modification of a potentiometric titration method was used [16]. Titration was carried out using the dynamic endpoint method and a Metrohm (Herisau, Switzerland) 751 GPD Titrimo autotitrator equipped with a combined Ag/AgCl-pH electrode. Before titration, the pulp fibres were converted to the acidic form by adjusting the pH to 1.7, mixing for 20 min, washing several times, and finally dewatering in a Büchner funnel. The pulp (0.5 g) was suspended in 0.100 dm³ of 0.5 mol dm⁻³ NaCl. An amount of 10 cm³ of 0.1 mol dm⁻³ HCl was added and the suspension was titrated with 0.05 mol dm⁻³ NaOH in 0.5 mol dm⁻³ NaCl under an argon atmosphere at 25°C.

The total sodium content of the pulp was determined according to SCAN-P 83:00 [20]. A Teflon vessel, 65% HNO₃, and a microwave oven were used for dissolving the pulp. The sodium concentration was determined by atomic absorption spectroscopy (AAS) using the flame atomization technique (Varian 600, Varian Inc., Palo Alto, CA, USA, equipment with air-acetylene flame).

To estimate the volume of fibre-bound water, the water retention value (WRV) of the fibre was determined by a modification of SCAN-C 62:00 [21]. In the method used, the WRVs were measured at a different consistency, pHs and electrolyte concentrations (9.1%, 2–7, and 0.006–1.000 mol dm⁻³ of KCl, respectively) from those suggested in the standard method.

Sample Preparation

The samples were prepared in disposable polyethylene vessels. All samples contained 1 g of pulp (o.d.) and the total liquid volume was always 10 cm³. The ionic strength of the suspension was adjusted by adding KCl and the pH was adjusted with HCl. POM was always added as an aqueous solution (concen-

tration $10.0 \text{ mmol dm}^{-3}$) right before the samples were mixed for 30 min with a mechanical shaker. The POM concentration of the samples was $1.00 \text{ mmol dm}^{-3}$ (10 mmol kg^{-1} of fibre).

When cationic polyelectrolyte (Polybrene, Sigma-Aldrich Co., St. Louis, MO, USA, molecular weight ~ 8000) was used in sample preparation, the suspension was mixed for 30 min with the mechanical shaker to allow the polyelectrolyte to be distributed evenly and adsorbed onto the fibres before adding the POM. This was done to minimize the possibility of complex formation between POM and the free polyelectrolyte in the solution phases of the suspension.

Samples prepared for the determination of $[\text{POM}]_s$ (i.e. POM concentration of the external phase) were filtered with suction in a Büchner funnel after mixing. The pH of the filtrate was measured immediately after filtration. The fibres, which remained in the Büchner funnel, were dried to constant weight at 105°C and weighed.

The parallel samples that were prepared for direct determination of POM content in the fibre, were, instead of filtering, centrifuged as described in SCAN-C 62:00. After centrifuging, the supernatant was discarded, and the pulp pads formed on the wire mesh of the sample holders were weighed first and then dried at standard temperature and humidity. After optical measurements, the pulp pads were further dried at 105°C and weighed to determine the weight of the fibre phase.

Absorbance Measurements

The $[\text{POM}]_s$ values were determined by measuring the absorbance spectra of the filtrates from 350–700 nm. Disposable polystyrene cuvettes were used. Because it was suspected that the filtrates contained light-scattering particles, they were filtered with a membrane filter (Gelman Acrodisc, Pall Corp., East Hills, NY, USA, with $0.2 \mu\text{m}$ GHP membrane) before measuring the absorbance spectrum. The spectra were measured using a Unicam 5625 UV/VIS Spectrometer, Thermo Electron Corp., Waltham, MA, USA.

To avoid the problems caused by baseline variation, the value of $A_{496 \text{ nm}} - A_{650 \text{ nm}}$ was used as a reference for POM concentration. Values for $[\text{POM}]_s$ were determined by comparing the absorbance of the filtrates to a series of absorbance values of standard samples that contained known concentrations of POM.

When the POM content of the pulp pads was determined, the reflectance spectra of the pads prepared by centrifuging were measured with an Elrepho 2000 instrument, Datacolor Corp., Lawrenceville, NJ, USA. From the spectra, the computer program of the equipment calculated the colour coordinates of the CIELAB system (L^* , a^* and b^*). An approximation of the POM content in the pad was obtained by calculating the value of colour difference (ΔE) for each sample and comparing it to the respective values of standard samples. As standard samples, pulp pads that contained a known amount of POM were used.

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Modelling

To verify whether the distribution of POM in a pulp suspension followed the predictions given by the Donnan theory, a computerized version of a model created by Räsänen et al. [16] was used. The computer program requires the values of total liquid volume, fibre phase volume (e.g. WRV of the fibre), the amount of fibre in the suspension, fibre charge, pK_a values of the acidic groups in the fibre, and the total concentrations of mobile ions and acid in the system. Based on the input values, the values of λ for the system, the pH of the fibre and external phases, and the concentrations of ions in each phase are obtained.

RESULTS AND DISCUSSION Fibre Properties

In the analysis of the titration data for the fibre, it was assumed that the fibres contained acidic groups with two different dissociation constants. When the titration data were compared mathematically with the theoretical hydrogen ion binding isotherm, the content and the pK_a values of the acidic groups in the fibre were obtained (Table I). The AAS analysis supported these results; the total sodium content of the fibre, which had its acidic groups in sodium form, was 0.763 mg g^{-1} ($33.1 \text{ mmol kg}^{-1}$).

For the fibre phase volume, a value of $1.5 \text{ cm}^3 \text{ g}^{-1}$ was used. This value was roughly the average of the water content of the pulp pads after centrifuging to determine WRV. It should be mentioned, however, that the value de-

termined for the pulp pads is technically not the WRV of the pulp. The suspensions, which were centrifuged, were prepared in a different way

TABLE I
FIBRE PROPERTIES USED IN MODELLING

Property	Value
Fibre weight (o.d.)	1 g
Total liquid volume	10 cm^3
Fibre phase volume	1.5 cm^3
Total sodium content	35 mmol kg^{-1} *
Content of acid group 1 (pK_{a1})	$27.3 \text{ mmol kg}^{-1}$ (2.90)
Content of acid group 2 (pK_{a2})	$7.70 \text{ mmol kg}^{-1}$ (5.19)

* A value that corresponds to the acid group content of the fibre was used instead of the experimentally determined sodium content ($33.1 \text{ mmol kg}^{-1}$).

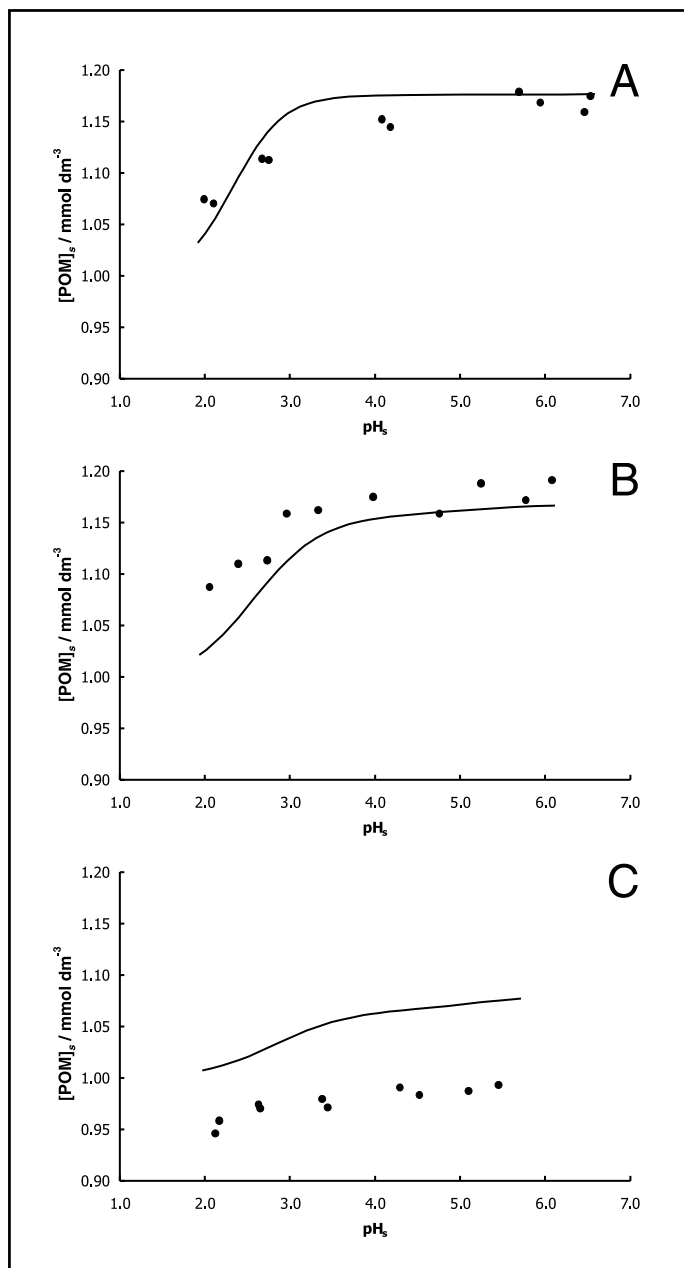


Fig. 2. Theoretical curve (—) and experimental data (•) for $[\text{POM}]_s$ as a function of pH_s at varying potassium ion concentrations: (A) 6.00 , (B) 20.0 and (C) 100 mmol dm^{-3} .

from that presented in the standard method and contained added ionic species (H^+ , Na^+ , K^+ and Cl^-). Added ionic species, as well as the pH of the suspension, affect the amount of water retained by a pulp [13]. Because of this, determining the actual value for the fibre phase volume under different conditions is a challenging task and therefore the approximation made for the fibre phase volume is justified.

Donnan Modelling

In Donnan modelling, the values used for fibre properties were essentially the ones obtained in the tests mentioned above (Table I).

In modelling, as in the empirical experiments, the total POM concentration was always kept at $1.00 \text{ mmol dm}^{-3}$ ($10.0 \text{ mmol kg}^{-1}$ of fibre). The sodium contained by the fibre was assumed to be present as mobile ions in the solution. Therefore, a sodium concentration of 3.5 mmol dm^{-3} for the suspension was used in modelling. The concentration of potassium was varied. The values for $[POM]_s$ given by the model were compared with the results of the experiments carried out under the same conditions.

Effect of Changing pH and Potassium Concentration on the Distribution of POM

Samples were prepared and the modelling carried out at three different potassium concentrations: 6.00, 20.0 and 100 mmol dm^{-3} . Because each POM anion possessed six potassium counter ions and the POM concentration of the samples was $1.00 \text{ mmol dm}^{-3}$, the minimum concentration for potassium was $6.00 \text{ mmol dm}^{-3}$. In addition, sodium from the fibre also was present as mobile cations in the pulp suspension.

In experimental work, it was supposed that the concentration of POM in the filtrate equalled the equilibrium concentration of the external Donnan phase, $[POM]_s$. According to the Donnan theory, the highest possible value for $[POM]_s$ can be calculated by assuming that all of the POM added to the system occupies the external Donnan phase when the equilibrium conditions are achieved. In our system, this calculation gives:

$$\begin{aligned}
 [POM]_s &= \frac{[POM]_{tot} V_{tot}}{V_s} \\
 &= \frac{1 \text{ mmol dm}^{-3} \times 10 \text{ cm}^3}{10 \text{ cm}^3 - 1.5 \text{ cm}^3} \\
 &\approx 1.18 \text{ mmol dm}^{-3} \quad (5)
 \end{aligned}$$

Some experimental results exceeded the value presented in Eq. (5). This was believed to be caused by the fact that the actual fibre phase

volume varied due to changes in pH and ionic strength and therefore differed from the value used (1.50 cm^3). Moreover, the model used in this paper assumed that the fibre phase had the same volume despite changes in conditions, which undoubtedly creates some deviation between the theoretical and experimental values.

The theoretical and experimental results for $[POM]_s$ at different pH values and potassium concentrations are presented in Fig. 2.

The theoretical curves presented are characteristic for a Donnan model. As stated earlier, when the pH of the suspension is greater than the pK_a values of the fibre's acid groups, the value of λ is high. This means that the POM anion is repelled by the negatively charged fibre, which causes the $[POM]_s$ to rise. When the pH is smaller than the pK_a values of the acid groups, the value of λ decreases and the Donnan effect becomes weaker. At the point where λ reaches unity, the Donnan effect no longer exists, and the values of $[POM]_s$ and $[POM]_f$ are equal (see Eq. 2). In our system, this means that, according to the Donnan theory, the smallest value for $[POM]_s$ and the highest value of $[POM]_f$ are both equal to $1.00 \text{ mmol dm}^{-3}$.

The biggest changes in the slopes of the theoretical curves are associated with the pH region between 2 and 4, which is due to the fact that, in modelling, the pK_a value of the most abundant acidic group was set at 2.90 (see Table I). Moreover, the effect of ionic strength on the value of λ can be seen in the theoretical curves; the difference between the maximum and minimum values of $[POM]_s$ decreases as the ionic strength of the suspension increases, i.e. the Donnan effect becomes weaker due to increasing electrolyte concentration. This is well in accordance with the principles of the Donnan theory presented earlier.

In the experiments where the potassium concentration was 6.00 and $20.0 \text{ mmol dm}^{-3}$, there is a fairly good correlation between experimental and theoretical values of $[POM]_s$ (Fig. 2A,2B). At low pH, the Donnan model predicted lower values for $[POM]_s$ than the experimentally determined ones. The deviation may be caused at least partly by the large size of POM compared to simple anions. The typical diameter of a Keggin structure is 1.1 nm [1], which may restrict its ability to pen-

etrate into the smallest pores of the cellulosic fibre.

The Donnan effect also influenced the distribution of POM in suspensions where the potassium concentration was 100 mmol dm^{-3} . Experimental values of $[POM]_s$ follow the theoretical curve calculated with the model (Fig. 2C). However, all the experimental points for $[POM]_s$ are lower than the lowest possible values predicted by the Donnan model ($1.00 \text{ mmol dm}^{-3}$). This indicates that increased potassium concentrations may cause the distribution of POM to deviate from a typical Donnan distribution.

The theoretical values of $[POM]_s$ presented in Fig. 2 were obtained when the valence of the POM anion was assumed to be -6 . However, due to the low charge density of the anion and its ability to form ion pairs with alkali metal cations [22], it is unlikely that the distribution of the POM anion would follow ideally the Donnan theory. Because of this, values other than -6 also were tested for the valence. While changing the valence improved the correlation between certain theoretical and experimental test points, correlation between other test points of the same series was decreased.

Because of the deviation from the theoretical values (Fig. 2C), the effect of increasing potassium concentration on the distribution of POM was tested further in experiments where the potassium concentration of pulp suspensions was changed but the pH value was not adjusted with HCl. The pH of the filtrates was between 5.7 (for highest ionic strength) and 7.0 (lowest ionic strength). The results of the experiments are given in Fig. 3.

The results presented in Fig. 3 show that the deviation between the theoretical and experimental values of $[POM]_s$ becomes larger as the potassium concentration of the suspensions increases. It becomes clear from the results that

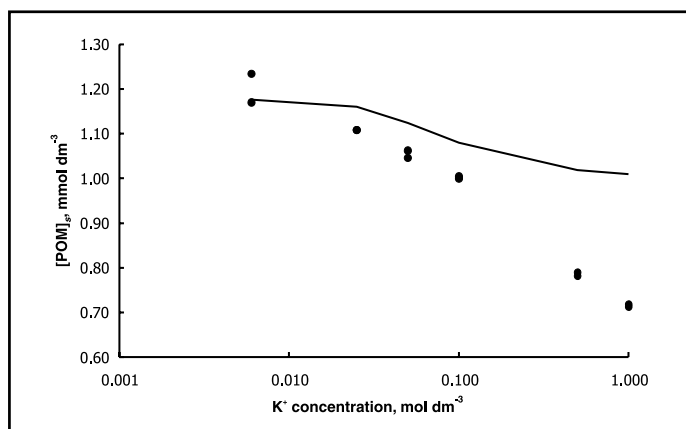


Fig. 3. Theoretical curve (–) and experimental data (•) for $[POM]_s$ as a function of potassium concentration. Note the logarithmic scale of the x axis. In modelling, POM was assumed to have a valence of -6 .

Equation 6

$$[POM]_f = \frac{[POM]_{tot} V_{tot} - [POM]_s V_s}{V_f} = \frac{1 \text{ mmol dm}^{-3} \times 10 \text{ cm}^3 - 0.71 \text{ mmol dm}^{-3} \times 8.5 \text{ cm}^3}{1.5 \text{ cm}^3} \approx 2.64 \text{ mmol dm}^{-3}$$

the Donnan model [15] can be used to describe the distribution of the POM anion in pulp suspensions only when the potassium ion concentration is low. The lowest value observed for $[POM]_s$ was $0.71 \text{ mmol dm}^{-3}$ at a potassium ion concentration of $1.000 \text{ mol dm}^{-3}$. This value is less than three quarters of the lowest possible value for $[POM]_s$ according to the Donnan theory ($1.00 \text{ mmol dm}^{-3}$). To make the deviation from the Donnan theory appear even more striking, we can calculate the corresponding value of $[POM]_f$ (POM concentration in the fibre phase) at a potassium concentration of $1.000 \text{ mol dm}^{-3}$ (Eq. 6).

Equation 6 shows that, at this test point, the POM concentration in the fibre phase is more than twice the theoretical maximum of $[POM]_f$. Indeed, the POM concentration exceeds the value predicted by the Donnan theory by $1.64 \text{ mmol dm}^{-3}$.

To make the experimental results more reliable, two parallel tests were carried out at each potassium concentration. It can be seen that the deviation between the parallel tests was very small for the tests run at high potassium concentrations (Fig. 3). Furthermore, measurements of the POM content in the pulp pads with reflectance spectroscopy qualitatively supported the values of $[POM]_s$ presented in Figs. 2 and 3. Based on these facts, it is a strong feeling of the authors that the Donnan effect is not the only phenomenon that influences the distribution of POM in pulp suspensions.

One possible mechanism, in addition to the Donnan effect, that can be used to explain the results presented in Fig. 3 is the bonding of POM with carbohydrate molecules of the cellulosic fibre. When a pulp suspension has a high ionic strength, the negative charge of the fibre is screened by the high concentration of metal cations. On the other hand, the negative charge of POM is decreased by ion pairing. This probably leads to a situation where POM anions are no longer repelled very strongly by the fibre and may form bonds with carbohydrate molecules. So far, no evidence of such bonds exists. However, it is well known that some transition metal oxides, e.g. molybdates and tungstates, form bonds with hydroxyl groups of polyhydroxycompounds, including certain carbohydrates [23–28].

Effect of Cationic Polyelectrolyte on the Distribution of POM

Samples where Polybrene was sorbed into the fibre before adding POM to the suspension were prepared to test whether the influence of fibre charge on the distribution of POM could be eliminated by the addition of a cationic polyelectrolyte. Polybrene (molecular weight ~8000) was chosen as the polyelectrolyte because it has a molecular size small enough to penetrate into cellulosic fibres. For each sample, a theoretical ratio of charges was calculated by dividing the positive charge of the total Polybrene added by the negative charge of the fibre in the suspension (the values used in the calculations were specific charge of Polybrene = 5.35 meq g^{-1} and fibre charge = 35.0 meq kg^{-1}).

Figure 4 shows experimental $[POM]_s$ values as a function of the added polyelectrolyte. Addition of Polybrene to a pulp suspension has a dramatic effect on the distribution of POM; the POM concentration in the filtrate decreases significantly as the amount of Polybrene is increased. When an excess of polyelectrolyte is used, only a negligible amount of POM remains in the filtrate.

The results were qualitatively supported by the experiments where the POM content of pulp pads prepared under similar conditions was determined.

In addition to Polybrene, high potassium concentrations decrease the amount of POM in the filtrates (Fig. 3). Although the effect is similar, the mechanisms in the two cases are probably different. To clarify the interaction between the POM and Polybrene, aqueous solutions of the two compounds were mixed. The experiment led to an immediate formation of an insoluble precipitate. Therefore, it is probable that, in a pulp suspension, Polybrene does not only bind with the cellulosic fibre thus neutralizing its charge, but also complexes with the POM anion. This makes the suspension a very complex system that cannot be treated with a Donnan model. Because of this, only experimental results are shown in Fig. 4.

CONCLUSIONS

Results presented in this paper show that the Donnan effect greatly hinders the sorption of POM into the fibre in pulp suspensions that have low ionic strengths and near-neutral pH values. Because of this, it is probable that the efficiency of delignification in POM bleaching could be increased if the process were carried out at acidic pH and/or increased ionic strength. Indeed, the results in this paper indicate that, in pulp suspensions which have high potassium concentrations, an attraction is created between the fibre and the POM anion. The mechanism for this attraction is unknown yet, and also unknown is its effect on the reactivity of POM.

The cationic polyelectrolyte (Polybrene) added to a pulp suspension increases the amount of POM attached to the fibre. However, since POM and Polybrene form complexes, the Donnan theory alone cannot be applied in the modelling of systems containing cellulosic fibre, Polybrene and POM. Nevertheless, the formation of complexes between these three components may increase the amount of POM that comes into contact with the fibre and, thus, enhance delignification in POM bleaching.

Because of these facts, research is needed on the effect that increased ionic strength has on the rate of delignification in

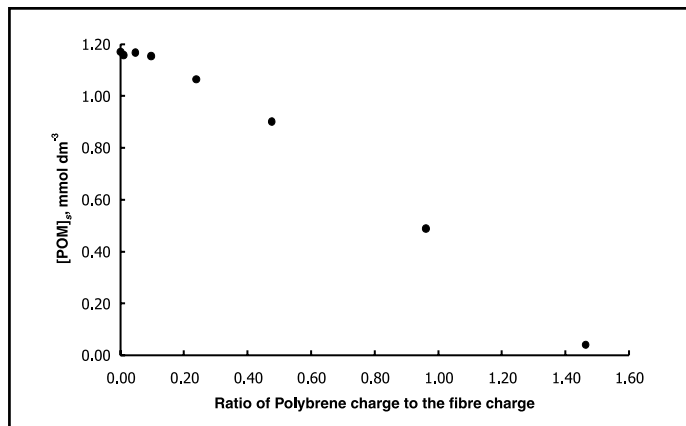


Fig. 4. Effect of added cationic polyelectrolyte on $[POM]_s$ in a pulp suspension. The x axis shows the calculated ratio of the positive charge of added Polybrene divided by the negative charge of the fibre.

POM bleaching. Furthermore, the nature of the attractive force between POM and the fibre detected in this work has to be rationalized, since it is reasonable to assume that the catalytic properties of POM are altered if it complexes with carbohydrates or other components present in pulp suspensions. It may also be argued that POM-carbohydrate complexes might impede chemical recovery after a POM bleaching stage. However, as shown in this paper, at low ionic strength, POM distribution follows the Donnan theory and, because of that, washing POM from the fibre should not be problematic.

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