Donnan Effect and Catalytic Bleaching

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Donnan Effect

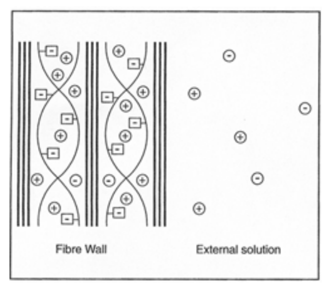
- Uneven distribution of mobile ionic species in a system that contains ionisable immobile chemical structures
- Introduced by Donnan and Harris in 1911
- Thereafter applied to systems containing cellulosic fibres
- Important in bleaching and papermaking
  - Donnan theory is applied to understand the distribution of ions in pulp suspensions

Donnan Theory

- When placed in an aqueous solution, a cellulosic fibre swells because part of the bulk solution is sorbed into the fibre wall
- Cellulosic fibre contains several immobile ionisable functional groups that have different pK_a values, i.e. dissociate at different pH

Functional group	**pK_a**
Carboxylic acid	3.1 – 3.3 (carbohydrate origin) 5 – 6 (lignin origin)
Phenol	7.3 – 10.3

Donnan Theory



(Towers & Scallan 1996)

- Dissociated acidic groups create a negative charge on the fibre
- Mobile ions are distributed unevenly (cations attracted, anions repelled by the fibre)

Donnan Theory

- In pulp suspension the solution is thought to comprise two phases
  - Fibre phase (*f*)
  - External solution phase (*s*)
- The distribution constant λ describes the distribution of ions between the two phases:

$$\lambda = \frac{[H^+]_f}{[H^+]_s} = \frac{[M^+]_f}{[M^+]_s} = \sqrt{\frac{[M^{2+}]_f}{[M^{2+}]_s}} = \frac{[I^-]_s}{[I^-]_f} = \sqrt{\frac{[I^{2-}]_s}{[I^{2-}]_f}} \quad (1)$$

where H^+ denotes a hydrogen ion, *M* a cation and *I* an anion

Donnan Theory

- In a more general form we can write

$$\lambda = \left(\frac{[X^z]_f}{[X^z]_s} \right)^{\frac{1}{z}}$$

where *X* represents any ion with charge *z*
- After λ is determined, the distribution of any ion between the two phases can be calculated under the given conditions
- Factors that affect the value of λ:
  - Volumes of the *s* and *f* phases (WRV of the pulp)
  - Contents of ionisable groups in the fibre and their pK_a values
  - Added acid or base (pH of the suspension)
  - Ionic strength of the suspension

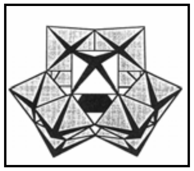
Application

- Closure of water circulation at bleach plants
  - Reduction of effluent (desired effect)
  - Accumulation of "non-process" elements
    - e.g. K, Ca, Mg, Mn, Fe, Al, Si, Cl
  - "Non-process" elements cause problems
    - Formation of scales
    - Corrosion
    - Deterioration of cellulose
    - Increased consumption of chemicals
- The Donnan effect e.g. increases the sorption of metal cations into the fibers

  ⇒Knowledge of the Donnan theory is important in understanding the bleaching process

POM bleaching

- Polyoxometalates (POMs) are transition metal oxygen anion clusters able to catalyse redox reactions, e.g. $[SiVW_{11}O_{40}]^{5-}$



(Weinstock *et al.* 1998)

- Bleaching based on reactions:

  lignin + POM_{ox} → oxidized lignin + POM_{red} + $2H^+$ (I)

  POM_{red} + ½O_2 + $2H^+$ → POM_{ox} + H_2O (II)
- POM can be reused in the process, i.e. can function as a catalyst

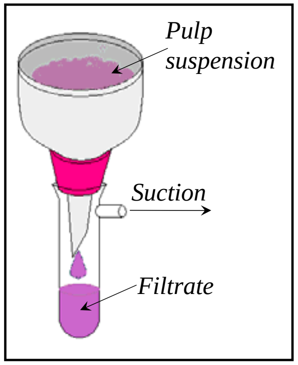
POM bleaching

- In POM bleaching processes presented so far, POM concentrations up to 0.5 M are needed
  - Molecular weight of $K_5[SiVW_{11}O_{40}]$ ≈ 3 000 g/mol
    - ⇒ 0.5 M corresponds to ca. 1 500 g/L!!
- Our goal is to reduce the POM conc. to <1 mM
- POM anions possess high negative charges
  - ⇒If distribution of POM follows the Donnan theory:

$$[POM^{5-}]_f = \frac{[POM^{5-}]_s}{\lambda^5}$$

  - ⇒When λ is large (e.g. 5), even high $[POM^{5-}]_s$ leads to negligible $[POM^{5-}]_f$ (5^5 = 3 125)
  - ⇒Delignification reactions greatly hindered

Distribution of POM in a pulp suspension, experimental



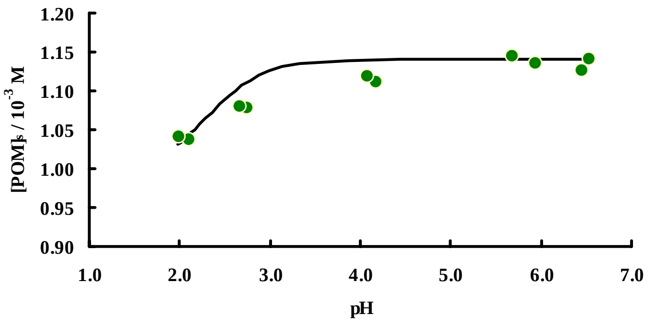
- Pulp: fully bleached softwood kraft in Na form
- Samples were prepared at medium consistency (ca. 9 %)
- $K_6[SiVW_{11}O_{40}]$ was used as the POM
- pH was adjusted with HCl, ionic strength with KCl
- Initial POM concentration was always 1.0 * 10^{-3} M
- $[POM]_s$ was determined by measuring $A_{496\ nm} - A_{650\ nm}$

Distribution of POM in a pulp suspension, modelling

- Theoretical distribution of POM was calculated with a computerized Donnan model (Räsänen *et al.*, 2001)
- The model calculated λ and theoretical $[POM]_s$ for the values of pH, ionic strength, and fibre properties entered to the program
  - experimental values for fibre charge, sodium content, water retention value (WRV), and dissociation constants of the acidic groups were used

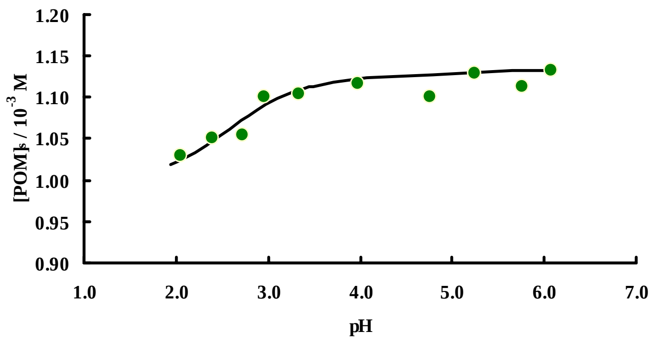
Results: 1. Low ionic strength

K^+ 0.006 M, pH 2.0 – 6.5



Results: 2. Higher ionic strength

K^+ 0.020 M, pH 2.1 – 6.1



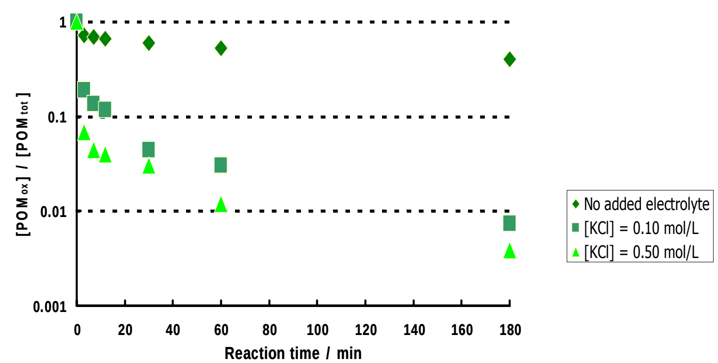
Conclusions

- Distribution of $[SiVW_{11}O_{40}]^{6-}$ anion follows the Donnan theory
- Effect on reactivity of the POM?
  - ⇒Experiments with POM_{ox} ($[SiVW_{11}O_{40}]^{5-}$) and pulp

Reactivity of POM_{ox} at varying K^+ concentrations, experimental

- Reaction conditions:
  - KCl additions of 0, 0.1 and 0.5 mol/L
  - Room temperature
  - 5 % consistency (unbleached sofwood kraft pulp)
  - Nitrogen atmosphere
  - Initial $[POM_{ox}]$ = 1 mmol/L
  - Near-neutral pH
- After the desired reaction time, pulp suspensions were filtered on suction
- POM_{ox} and POM_{red} concentrations of the filtrates were determined spectrophotometrically

Results: 5. Reactivity of POM_{ox} at varying conditions



Reactivity of POM_{ox} at varying conditions

Conclusions

- Ionic strength has a very strong influence on the reactivity of POM_{ox}:
  - More than 99 % of the POM_{ox} reacts during 180 minutes in the samples where KCl was added – the respective value for the sample without electrolyte addition is ca. 60 %
  - In the electrolyte-containing samples, significantly more POM_{ox} reacts during the first three minutes than in 180 minutes in the sample without electrolyte addition
- Reasons for increased reactivity
  - Elimination of the Donnan effect
  - Other mechanisms?