Electronic Supplementary Information

for

Influence of adsorbed polyelectrolytes on pore size

distribution of a water-swollen biomaterial

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Electronic supplementary information includes Size exclusion chromatography (SEC) data for the cationic polymers used (S1), calculation of the effect cryoscopic effect of the salt (S2), adsorption isotherms for poly(diallyl dimethyl ammonium chloride) (PDADMAC) samples (S3) and the differential scanning calorimeter (DSC) data as the cumulative pore volume with error limits and the DSC data converted to volume and pore diameter size. (S4)

S1 Size exclusion chromatography data for the cationic polymers used



Figure S1. The SEC data for the cationic polymers used. The fractionated PDADMAC and polybrene had no overlap while the unfractionated PDADMAC had a part of the distribution in the polybrene MW range.

S2 Calculation of the cryoscopic effect of the salt

This calculation intends to show that the cryoscopic effect of the salt is minimal to our samples and does not affect the samples during DSC analysis. The cryoscopic effect (freezing-point depression) can be calculated from the well-known equation:

$$\Delta T_F = K_F \cdot b \cdot i, \tag{S1}$$

where ΔT_F is the freezing point depression, K_F the cryoscopic constant (for water ~1.9 K·kg/mol), *b* the molality of the solvent, *i* is the van't Hoff factor (in our case just 2 since we assume simple monovalent ions to be dissolved *i.e.* NaCl.) Our samples (fibres dispersed in water) exhibited conductivity of <5 μ S/cm before analysis (typical value was 3.2 μ S/cm). From a tabulated reference we obtain conductivity of roughly 10⁻⁴ molality.^{S1} Several other methods can be used: For NaCl, either by solving the concentration using Kohlrausch's law:

$$\kappa = \Lambda_{m}^{0} \cdot \mathbf{c} \cdot \mathbf{K} \cdot \mathbf{c}^{1.5}, \tag{S2}$$

where κ is the conductivity, Λ^0_m the limiting molar conductivity, *c* the concentration and *K* Kohlrausch constant) with 126.5 S cm²/mol as limiting molar conductivity (of NaCl) and *ca*. -2100 S·cm^{3.5}·mol^{-1.5} as the Kohlrausch constant (for water-NaCl system) or simply by measuring the conductivity of a series of NaCl solutions (10⁻³-10⁻⁵ M) and comparing the sample conductivity with the series. With this we obtain molarity between 10⁻⁴-10⁻⁵ M and thus maximum molality of ~10⁻⁴ mol/kg. Using these values in equation (S1) yields a freezing point depression of ~0.00038 K (1.9 K·kg/mol·10⁻⁴ mol/kg·2 K), a value small enough to consider its influence insignificant.

S3 Adsorption isotherms for unfractionated and fractionated PDADMAC samples



Figure S2. Adsorption isotherms for unfractionated (\bullet) and fractionated (O) PDADMAC samples. The adsorbed amounts were weight-percentage per unit mass of fibre. Equilibrium concentration was the unadsorbed PDADMAC in the solution after 30 mins. Ionic strength was 1 mM (NaHCO₃) and pH ~9. The fractionated sample had a constant adsorption of about 0.15% while the unfractionated sample had increasing adsorption due to the adsorption of the low molecular weight (MW) part of the MW distribution of the unfractionated PDADMAC.

S4 Cumulative pore volume data with error limits and the pore size distribution data from the DSC measurements.

We have added the actual data from the DSC measurements to exemplify the measurement details (Figure S3). The cumulative pore size distribution is the most common way to describe the pore size distribution obtained from differential scanning calorimeter (DSC) data with step-melting (Figure S4-6) and is therefore added here as a reference. The basis for this work was laid in the fundamental efforts of Maloney to employ DSC to study the pore size diameters found in the wet-state of the cellulosic fibres. For the equations and a method how to convert the DSC data to pore size distribution, see the main article and the references therein. The measurement error in cumulative pore size distribution is composed of the cumulative error of 13 independent measurements which have been added together. This produces error that is much larger than each individual measurement alone. In addition, the difficulties in homogenising the samples, *i.e.*, when the fibres are treated with less than equilibrium adsorption some fibres may obtain more and some less than the optimal amounts. In these cases the measurements were increased to obtain better results.



Figure S3. Example data from DSC measurement for illustrative purpose. The graph indicates the endothermic melting at different times. The indicated temperatures correspond to the isothermal steps. The non-freezing water (NFW) is calculated from the melted and refrozen sample and the peak is shown in the figure on the right. Grey line is for the control reference and black line for fibres adsorbed with 2.0% of polybrene.



Figure S4. (a) Cumulative pore size distributions for never-dried fibre samples adsorbed with indicated amounts of polybrene (weight percentage). (b) The pore size distributions for the same samples as in (a).



Figure S5. (a) Cumulative pore size distributions for never-dried fibre samples adsorbed with PDADMACs of different origin. (b) The pore size distributions for the same samples as in (a).



Figure S6. (a) Cumulative pore size distributions for dried fibre samples adsorbed with indicated amounts of polybrene (weight percentage). (b) The pore size distributions for the same samples as in (a).



Figure S7. Cumulative pore size distributions for dried fibre samples adsorbed with PDADMACs of different origin. (b) The pore size distributions for the same samples as in (a).



Figure S8. The effect of drying on pore size distribution of the polyelectrolyte treated fibres (control reference for dried fibres is set to zero). Error bars for the samples polybrene 0.5% and unfractionated PDADMAC 0.22%.



Figure S9. The non-freezing water (NFW) with error limits for all never-dried samples. Average NFW was 0.307±0.015 mL/g.

References:

^{S1} R. B. McCleskey, J. Chem. Eng. Data, 2011, 56, 317–327