

Salt sorption on regenerated cellulosic fibers: electrokinetic measurements

Avinash P. Manian  · Adisak Jaturapiree · Thomas Bechtold 

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Abstract Streaming potential measurements were conducted on lyocell and viscose fibers, to determine the relative order in sorption extents of salt cations and anions. The sorption of K^+ was greater than Na^+ ions, and the sorption extents of the anions, Cl^- and Br^- , were similar. Previously, we had examined accessibility of the same ions in the fibers, and found them to follow the order: $K^+ < Na^+$ and $Cl^- < Br^-$. From these two contrasting results, we find that the mode of salt interaction with cellulose, from aqueous solutions, changes with the salt concentration. At low concentrations, the interaction is governed by ion-exchange processes with the cellulose carboxyl groups and the Donnan equilibrium; but at higher concentrations, the interaction is a function of the mobility (or diffusivity) of the ions. Thus, sorption and accessibility of cellulose fibers as measured with salts may not apply for other solutes, and conversely, similar studies with other probe molecules may not be relevant for salts.

Keywords Lyocell · Viscose · Salt sorption · Accessibility

A. P. Manian (✉) · T. Bechtold
Research Institute of Textile Chemistry/Physics,
University of Innsbruck, Hoehchsterstrasse 73,
6850 Dornbirn, Austria
e-mail: avinash.manian@uibk.ac.at

A. Jaturapiree
Faculty of Industrial Technology, Phranakorn Rajabhat
University, Bangkok 10220, Thailand

Introduction

The accessibility of fibers to reagents and catalysts influences the uniformity and extent of chemical reactions, in treatments intended to improve their performance. Nearly all textile treatments of cellulosic fibers are performed with aqueous solutions, and cellulose swells in water. Thus, it becomes useful to measure fiber accessibility in aqueous media, where the effect of fiber swelling is accounted for; rather than in non-swelling media, such as for example when accessibility is determined by vapor or gas sorption. With this in mind, we previously investigated the accessibility of two regenerated cellulosic fibers, viscose (CV) and lyocell (CLY), by measuring the sorption of salts from aqueous solutions of salt–alkali mixtures. Salts were chosen as probe molecules since they do not exhibit chemical affinity for the polymer, and alkalis were added because fiber treatments are often performed in alkaline solutions, and the alkalinity influences fiber swelling.

Both CV and CLY are composed of cellulose, and derived from wood pulp through dissolution and re-precipitation (coagulation). In the viscose process, the pulp is first derivatized to sodium cellulose xanthate, dissolved in NaOH, and then re-precipitated in an acid solution. In the lyocell process, the pulp is directly dissolved in *N*-methylmorpholine *N*-oxide (NMMO), and re-precipitated in a water bath (Woodings 2001). Generally, CV fibers have a lower degree of

polymerization, lower degree of crystallinity, higher swelling degree in water, and exhibit higher moisture regain as compared to CLY fibers (Bredereck and Hermanutz 2005).

In the previous work, 0.5 g fiber specimens were immersed in 50 ml solutions of the following combinations: NaOH with NaCl or NaBr, and KOH with KCl or KBr (Jaturapiree et al. 2006). The salt concentrations were always 0.02 mol/l, and the alkali concentration ranged from 0 to 8 mol/l. There were no differences of salt accessibility between the fibers. However, in both fibers, there were differences of accessibility between the salts. Regardless of the alkali content in solutions, the salt accessibility increased in the order: KCl < NaCl < KBr < NaBr; i.e. the Br⁻ salts exhibited greater accessibility than the corresponding Cl⁻ salts, and the Na⁺ salts exhibited greater accessibility as compared to the corresponding K⁺ salts.

Among the ions that were studied, the charge density increases in the order: Br⁻ < Cl⁻, and K⁺ < Na⁺. Cellulosic fibers develop a negative surface charge in aqueous solutions (Stana-Kleinschek et al. 2002; Trotman 1984), and electrostatic forces will influence fiber-salt interactions. As the strength of such forces is proportional to the charge densities on the ions, it was concluded that the observed results could be explained by the greater attraction between the negatively charged cellulose and Na⁺ as compared to K⁺, and a greater repulsion of the Cl⁻ as compared to Br⁻. The order also suggested that the salt accessibility was dictated more by the repulsion of anions than attraction of the cations. We explored these findings further with electrokinetic measurements, and the results are presented here.

Materials and methods

Materials

Two fibers were used in this investigation: lyocell (CLY) and viscose (CV), both of 38 mm length and 1.3 dtex linear density. They were kindly donated by Lenzing AG, Austria, and used as supplied. The salts and alkalis were of analytical grade and purchased from Sigma-Aldrich; and deionized water was used in the preparation of solutions.

Textile fibers do not exhibit a uniform diameter along their length. But a nominal diameter may be estimated from their linear density (dtex = mass in g per 10,000 m length), the density of cellulose (1.5 g/cc) (Hearle 2001), and with the geometric formula for the volume of a right circular cylinder ($\pi r^2 L$, where r is the radius and L , the length or height). In this manner, the diameter of the fibers is estimated to be ca. 10.5 μm .

Methods

The streaming solutions were aqueous solutions of salt–salt and salt–alkali mixtures as shown in Table 1. The salt–salt mixtures contained either a common cation or a common anion. The total salt concentration was always 1×10^{-3} mol/l, but the mole fraction of each salt varied between 0 to 1. The salt–alkali mixtures contained a common cation at 1×10^{-3} mol/l, but the mole fraction of salt and alkali varied between 0 to 1. Separate solutions were prepared for each combination of mole fractions, and fresh fibers were used with each solution.

There is a reduction of zeta potential magnitudes with increase in ionic strength of the streaming solutions (Delgado et al. 2005; Mikhailov et al. 2017). It is because of an acceleration in the decay of potential as function of distance from the solid surface, which is also referred to as a decrease in thickness or suppression of the electrical double layer. Hence, to promote sensitivity in measurements, the amount of electrolyte in streaming solutions is kept low (10^{-4} to 10^{-3} mol/l electrolyte). To avoid any influence of changing ionic strengths on the results, it was decided to maintain the concentration of cations and anions at the same level in all mixtures (i.e. 1×10^{-3} mol/l), but to vary relative proportions of the components.

The streaming potentials were measured on an electrokinetic Analyzer from Anton Paar GmbH, Austria. The measurements were performed on a 2.50 g fiber plug packed in a volume of 31 cm³, in a cylindrical measurement cell with platinum electrodes. The fibers were previously soaked for 12–14 h in the streaming solution. During measurements, the solution was streamed along both left-to-right and right-to-left directions with flow pressures of 15–40 kPa (150–400 mbar). The asymmetric

Table 1 The salt–salt and salt–alkali mixtures in streaming solutions

Mixture	Components	Notes
Salt-Salt	KCl + KBr	Mixtures with a common cation Total salt concentration = 1×10^{-3} mol/l
	NaCl + NaBr	
	NaCl + KCl	Mixtures with a common anion Total salt concentration = 1×10^{-3} mol/l
	NaBr + KBr	
Salt-Alkali	KCl + KOH	Common cation = K^+ Total cation concentration = 1×10^{-3} mol/l
	KBr + KOH	
	NaCl + NaOH	Common cation = Na^+ Total cation concentration = 1×10^{-3} mol/l
	NaBr + NaOH	

potential in all measurements was in the range of ± 3 mV. At the end, the cell with fiber plug was flushed with 0.1 mol/l KCl, and the electrical resistance of the fiber plug and the solution conductance were re-measured.

The apparent zeta potentials were calculated from the streaming potentials with the Helmholtz–Smoluchowski equation (Eq. 1). The Fairbrother–Mastin method was applied to more accurately estimate the length and cross-sectional area of the fiber plug (Eq. 2) (Delgado et al. 2005; Jacobasch et al. 1985).

$$\zeta_{app} = \frac{dU}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \kappa_L \quad (1)$$

$$\zeta_{corr} = \frac{dU}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{R_S^C \times \kappa_L^C}{R_s} \quad (2)$$

where ζ_{app} = apparent zeta potential (V), ζ_{corr} = zeta potential corrected with more accurate estimate fiber plug length and cross-sectional area (V), dU/dp = slope of change in streaming potential with flow pressure (V/Pa), η = streaming solution viscosity (Pa.s), ε = dielectric constant of the streaming solution, ε_0 = permittivity of free space (F/m), κ_L = bulk conductivity of streaming solution (S/m), R_S = electrical resistance of fiber plug flushed with streaming solution (Ω), R_S^C = electrical resistance of fiber plug flushed with 0.1 mol/l KCl (Ω), κ_L^C = bulk conductivity of 0.1 mol/l KCl (S/m).

The zeta potential plots show the average of four repetitive determinations per fiber plug, and the error bars show the standard deviation. All comparisons were assessed with Analysis of Variance (ANOVA) and Bonferroni tests at a 0.05 level of significance, with SPSS[®] (IBM Software, USA).

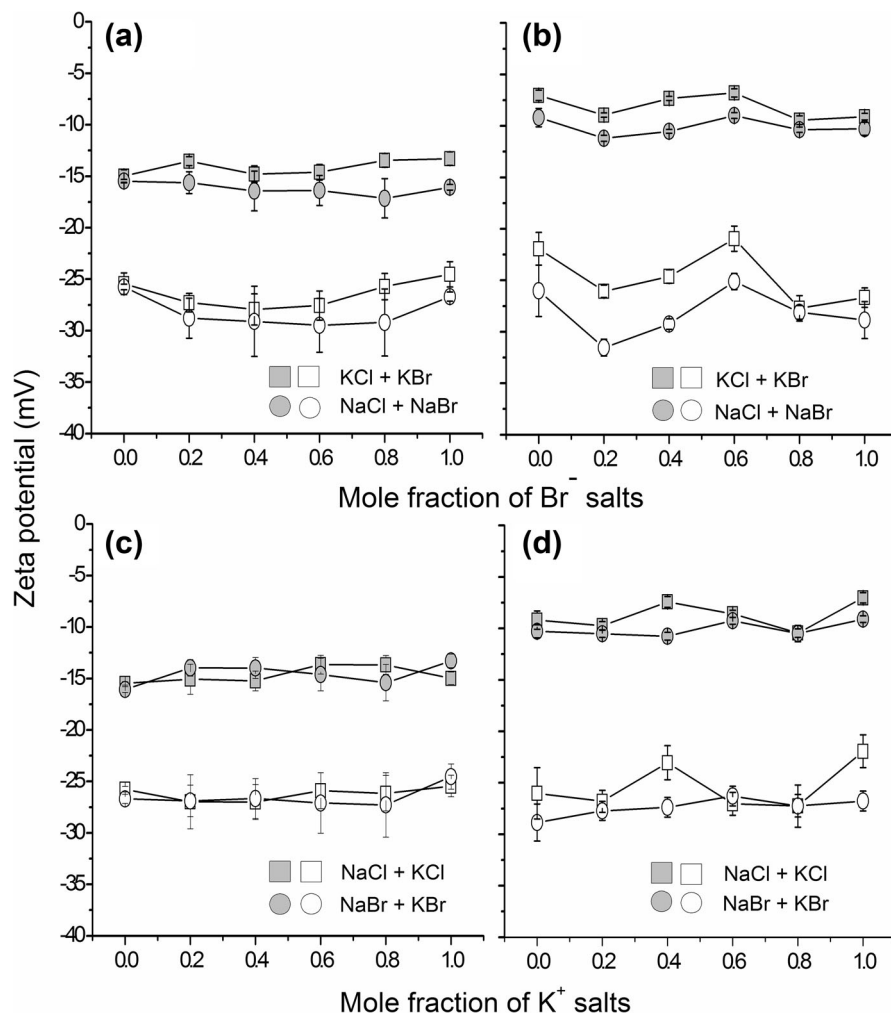
Results

Zeta potential

Figures 1 and 2 show the apparent zeta potentials (ζ_{app}), and the same values corrected for fiber plug dimensions (ζ_{corr}). Negative values were obtained in all measurements, and in the discussions that follow, we refer only to their magnitudes.

The results with mixtures of KCl + KBr and NaCl + NaBr are shown in Fig. 1a, b. The magnitudes of ζ_{app} and ζ_{corr} with K^+ salts were generally lower than the corresponding values with Na^+ salts, and the differences persisted regardless of the relative proportions of Cl^- and Br^- in the mixtures. The results with the mixtures of NaCl + KCl and NaBr + KBr are shown in Fig. 1c, d. Generally, the ζ_{app} and ζ_{corr} values with Br^- were similar to the corresponding values with Cl^- salts, and the similarities persisted regardless of the relative proportions of K^+ and Na^+ in the mixtures. In all results shown in Fig. 1, the ζ_{app}

Fig. 1 The zeta potentials of the fibers with salt–salt mixtures. In parts **a**, **b**, the values are plotted against mole fractions of bromide salts in the mixtures; and in parts **c**, **d**, the values are plotted against mole fractions of the potassium salts in mixtures. The gray symbols show the apparent values (ζ_{app}), and the white symbols show the values after the Fairbrother–Mastin correction (ζ_{corr})



magnitudes of CV were lower than CLY, but the ζ_{corr} magnitudes of both fibers were similar.

The results with mixtures of KCl and KBr with KOH, and of NaCl and NaBr with NaOH, are shown in Fig. 2a, b. The zeta potential magnitudes increased with rising mole fraction of alkali in the mixtures, but in all cases, the magnitudes with Cl⁻ containing mixtures were similar to those with Br⁻ containing mixtures. As above, for the most part, the ζ_{app} magnitudes of CV were lower than CLY, but the ζ_{corr} magnitudes of both fibers were similar.

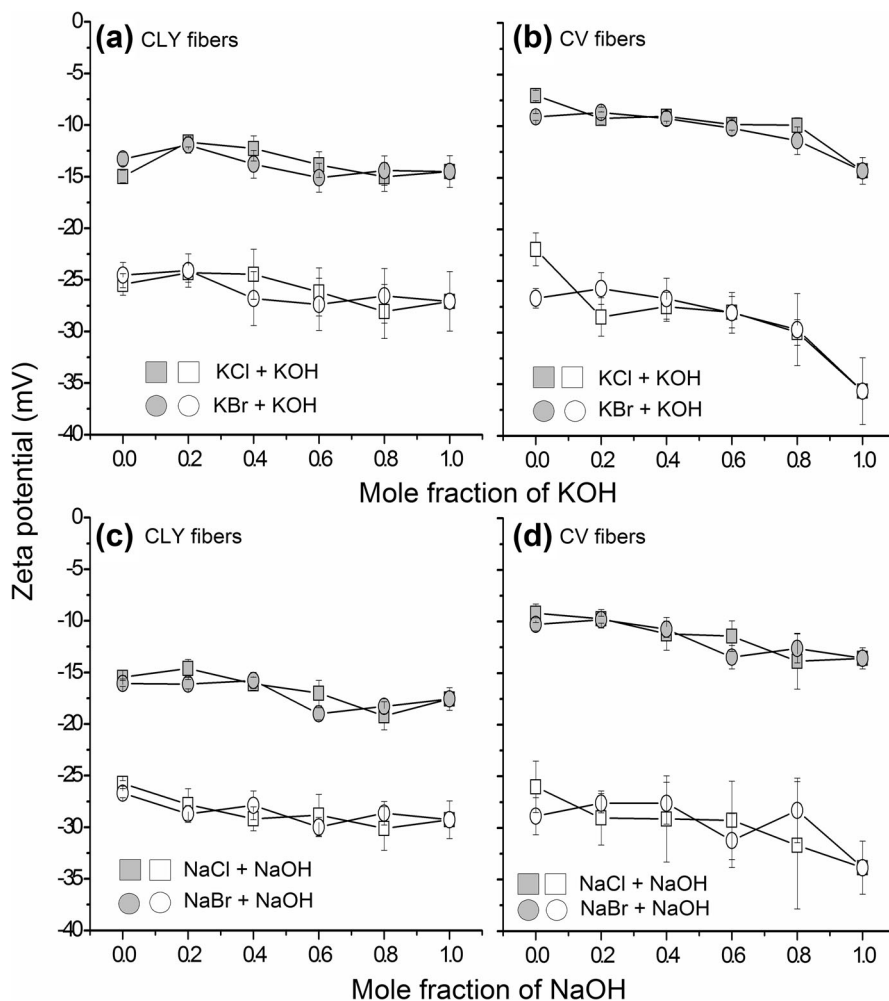
Fiber surface conductance

A rigorous determination of surface conductance in substrates is possible only for simple and regular packing geometries and this is not the case when plugs

of randomly oriented fibers are packed in measurement cells. A pragmatic alternative is to determine the conductivity of the streaming solution within the fiber plug (Lyklema 1995; Briggs 1928). This is done by determining the cell constant of the plug when it is flushed with the solution of concentrated electrolyte (in our case 0.1 mol/l KCl), and then using the value to determine plug conductivity during the regular measurements (i.e. with the salt–salt and salt–alkali mixtures). When the bulk conductivity of the streaming solution is subtracted from the plug conductivity determined in this manner, we obtain the conductivity of the streaming solution within the fiber plug (K_S). The results are plotted in Fig. 3.

The K_S was generally higher with the mixtures of K⁺ salts as compared to the Na⁺ salts (Fig. 3a), while the values with Cl⁻ and Br⁻ salts were generally

Fig. 2 The zeta potentials of the fibers with salt–alkali mixtures. In parts **a, b**, the values are plotted against mole fractions of potassium hydroxide in the mixtures; and in parts **c, d**, the values are plotted against mole fractions of sodium hydroxide in the mixtures. The gray symbols show the apparent values (ζ_{app}), and the white symbols show the values after the Fairbrother–Mastin correction (ζ_{corr})



similar (Fig. 3b). In the salt–alkali mixtures (Fig. 3c, d), the K_S did not vary significantly with change in the proportion of salt versus alkali, but the values were generally higher with KOH–salt mixtures as compared to the NaOH–salt mixtures. In all measurements, the K_S with CV fibers were higher than with the CLY fibers.

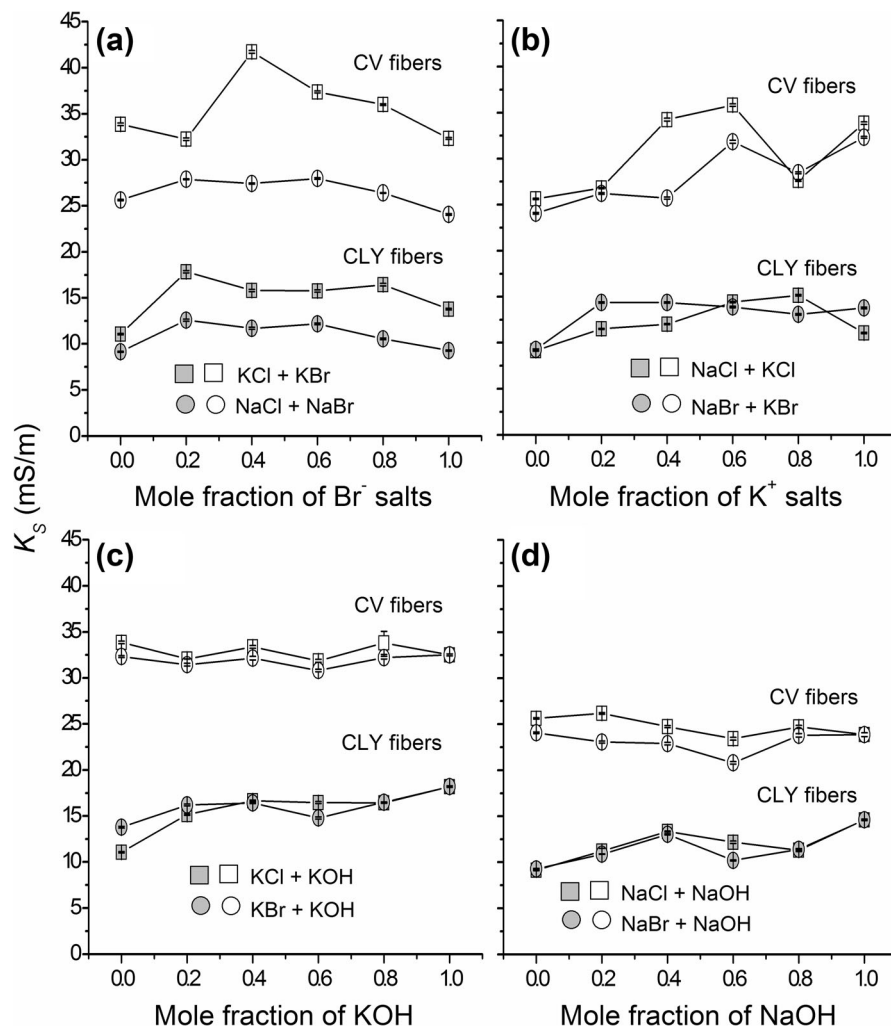
Discussion

The negative zeta potentials are attributed to the dissociation of carboxyl and hydroxyl functional groups present on the cellulosic fibers, and thus the zeta potential magnitudes vary with the degree of functional group dissociation, and with the degree of sorption of ionic species (Pothan et al. 2002; Ribitsch

et al. 1996, 2001; Stana-Kleinschek et al. 2001; Stana-Kleinschek and Ribitsch 1998). The sorption of counter-ions reduces zeta potential magnitudes and the sorption of co-ions increases them.

The literature reported pK_a of cellulosic carboxyl and hydroxyl groups are in the regions of 3–4 and 9–10 respectively (Farrar and Neale 1952; Räsänen et al. 2001; Bygrave and Englezos 1998; Saric and Schofield 1946; Bagrovskaya et al. 2002; Shet and Yabani 1982; Fras et al. 2004). The pH of all salt–salt streaming solutions was in the range of 5–6. Thus, in the measurements, it is expected that all available cellulosic carboxyl groups were fully dissociated and there was not a significant dissociation of the hydroxyl groups. Therefore, the zeta potential magnitudes did not change with the concentration of any individual salt in the mixtures. In the salt–alkali streaming

Fig. 3 The conductivity of streaming solutions within the fiber plugs (K_s). The values for CLY fibers are shown by the gray symbols, and the values for CV fibers by the white symbols



solutions, the pH varied changed from 5 to 11 with rising proportion of the alkali. Thus, in addition to the carboxyl group dissociation, it is expected that the degree of hydroxyl group dissociation became significant, and it continued to rise with increase in the proportion of alkali. There will also be sorption of OH^- ions. Therefore, the zeta potential magnitudes increased with rise in the alkali proportion of mixtures.

The lower zeta potential magnitudes obtained with the K^+ as compared to Na^+ salt mixtures indicates that the sorption of K^+ ions was greater. This is opposite to the results of our previous study (Jaturapiree et al. 2006), where the Na^+ ions exhibited greater accessibility than K^+ ions. We had concluded that salt accessibility in cellulose is governed by electrostatic repulsion and attraction, but that is not tenable in light

of the zeta potential results. In membrane separation processes with cellulose-related polymers such as cellulose acetate that are relatively uncharged, it is found that at low salt concentrations, the interaction with salts first proceed through cation exchange with ionized groups (e.g. carboxyl groups), and is governed by the Donnan equilibrium. But when the salt amount exceeds the available ionized groups and all charges are neutralized, the salt uptake is directly correlated with the mobility (or diffusivity) of the ions—which follows the order: $\text{Na}^+ > \text{K}^+$ and $\text{Br}^- > \text{Cl}^-$ (Geise et al. 2014; Ohya et al. 2001a, b). This was the order of accessibility in our previous work (Jaturapiree et al. 2006), where the salt ion content in the 50 ml solutions (1 mol) was far in excess of carboxyl groups in the 0.5 g of fiber specimens (7–9 μmol).

The results from electrokinetic measurements reflect the ion-exchange propensities of the salt cations. The greater selectivity in ion-exchange reactions for K^+ as compared to Na^+ , is attributed to the greater polarizing power of K^+ ions, which stems from its smaller radius of hydration and weaker energy of hydration (Heymann and McKillop 1941; Braithwaite and Smith 1999). Ehrlich et al. (Ehrlich et al. 1989), suggest that the greater sorption of K^+ on cellulose is due to selective sorption at crown-ether like arrangements of carbonyl groups. The lack of difference between the zeta potential magnitudes with Cl^- and Br^- salts indicates that both anions exhibited similar sorption extents. The anions are not expected to exhibit significant ion-exchange interactions with the negatively charged cellulose, and it appears that their sorption levels were limited to the amounts required to maintain charge neutrality.

The K_S was always higher with CV as compared to CLY, and that may be attributed to the greater carboxyl content of the CV (Rabinov and Heymann 1943; Frascos et al. 2004). As a result, almost always, the ζ_{app} magnitudes of CV were lower than those of CLY, but their ζ_{corr} magnitudes were similar. Lower ζ_{app} magnitudes of CV as compared to CLY have been attributed to a greater swelling of the CV (Ribitsch et al. 2001). However, we observed significant differences of K_S between the two fiber types, which precludes comparisons of the ζ_{app} . The similarity of ζ_{corr} magnitudes between the two fiber types indicates there were no differences in their interactions with the salt and alkali ions.

A greater sorption of an ion implies that the ion is present in larger amounts in the electrical double layer at the fiber surface, and thus a larger K_S is expected. That was observed in our measurements with both fiber types: the K_S was greater with the K^+ salts as compared to the Na^+ salts.

Conclusions

The results of this and our previous work (Jaturapiree et al. 2006), suggest that the mode of salt sorption and accessibility in cellulose fibers from aqueous changes with the salt concentration. At low concentrations, the salt sorption occurs through ion-exchange, and thus the relative affinities of the cations are dictated by their polarizing powers. The anion sorption extents are

limited only to the extents required to maintain charge neutrality of the cellulose. At higher salt concentrations, i.e. when the salt amount exceeds that of available carboxyl groups and all charges are neutralized, the salt accessibility in cellulose is dictated by the mobility or diffusivity of both the cations and anions, which in turn are inversely proportional to their hydration sizes. Thus, the fiber accessibility as measured with salts may not apply for other solutes, and conversely, accessibility studies with other probe molecules may not be relevant for salts. As pointed out by a reviewer, it will be of interest to conduct similar studies with salts containing multivalent ions (e.g. Mg^{2+} , Al^{3+} , SO_4^{2-} , PO_4^{3-} , etc.).

The presence of carboxyl groups on cellulose fibers increase the ion concentration at and around the fiber surface and significantly increase the conductivity within the fiber plug, and may lead to an underestimation of the zeta potential. Thus, in streaming potential measurements, it may be more prudent to calculate the zeta potentials with a correction term for the length and cross-sectional area of the fiber plugs.

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