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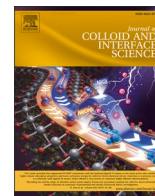
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## Specific ion effects on lignin adsorption and transport through cellulose confinements

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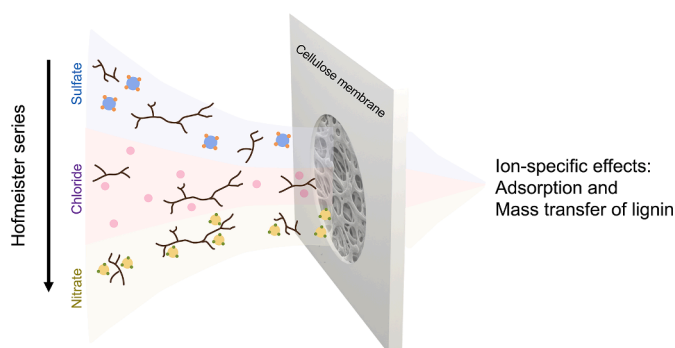
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### GRAPHICAL ABSTRACT



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### ABSTRACT

The presence of ions in a solution is anticipated to induce distinct effects on macromolecules. Consequently, the tuning of adsorption and mass transfer of lignin molecules can be achieved by incorporating ions with chaotropic or kosmotropic characteristics. This study examines the adsorption and mass transfer behavior of lignin molecules across model cellulose membranes in presence of ions from the Hofmeister series. Experimental investigations encompassed the use of diffusion cells to quantify lignin's mass transfer through the membranes, and quartz crystal microbalance with dissipation (QCM-D) monitoring was used for adsorption studies. Notably, at high ion concentrations, the mass transport rate of lignin was observed to be lower in the presence of highly hydrated (kosmotropic) sulfate ions, conforming to the Hofmeister series. Intriguingly, this relationship was not apparent at lower ion concentrations. Furthermore, QCM-D experiments indicated that lignin displayed higher adsorption onto the cellulose surface when exposed to less hydrated (chaotropic) nitrate anions. This behavior can be rationalized by considering the system's increased entropy gain, facilitated by the release of adsorbed ions and water molecules from the cellulose surface upon lignin adsorption. This study highlights the complexity of ion-specific effects on mass transfer and adsorption processes and their dependency on ion concentrations.

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## 1. Introduction

In recent years, there has been a growing emphasis on discovering renewable and more environmentally friendly substitutes for current fossil-based products[1]. One of the challenges associated with utilizing wood as a raw material for various products is the inefficient separation of its primary components: cellulose, hemicelluloses, and lignin[2]. Separation of wood components can be achieved through several methods, including various mechanical or chemical pulping methods, as well as enzymatic hydrolysis[3]. During chemical pulping, reactive chemicals are employed to separate wood components. Among the chemical pulping methods, kraft pulping is the most commonly used, accounting for over 80% of global pulp production[2]. During the kraft process, wood chips are processed at high pressure and temperature with a mixture of chemicals, known as white liquor, which contains active chemicals such as sodium sulfide and sodium hydroxide[4]. This kraft cooking process induces partial degradation of lignin, which in turn generates new functional groups. It is desirable for lignin to undergo ionization, thereby improving its aqueous solubility, a crucial prerequisite for the effective extraction of lignin via boiling and washing procedures[5].

Despite the pulping process being widely used and extensively studied, our current understanding of the mass transport events occurring during kraft pulping remains limited. Mass transport events are relevant to several steps in the kraft pulping process[6]. The first mass transport event involves penetration of cooking chemicals into the wood structure to reach the reaction sites[7]. The pathway from which the cooking chemicals need to be transported in wood chips is an intricate arrangement where fibers and fiber cell walls are arranged differently depending on the type of wood used[8]. As the lignin and hemicellulose react and dissolve, a second mass transport event can occur: diffusion of dissolved lignin molecules from the wood chip through the fibers to the surrounding liquor. This process creates new pores and surfaces where lignin may interact with. The driving force for the diffusion of lignin is the lignin concentration gradient between the inside of the wood chip and the surrounding liquor[9].

To produce high-quality pulp with excellent strength and better printability, removing lignin from the fibers is crucial[10]. Like many other researchers, we have dedicated our efforts to studying the complex and multifaceted transport process of lignin[11–15]. Our particular focus has been to investigate one of the subprocesses within this complex mass transport phenomenon: the diffusion of dissolved lignin in the presence of different sodium salts concentrations in an alkaline solution via a model system approach. We utilized diffusion cells and cellulose membranes with defined pore sizes, relevant for lignin transport in the wood cell wall as model for wood cell wall. These diffusion cells contain a donor, an acceptor chamber, and the membrane, over which a well-defined lignin concentration gradient acts as the driving force for the lignin mass transport. Contrary to various membrane filtration studies, where external pressure is applied to force substances through a membrane[16,17], here we have relied on the concentration gradient between two sides of the membrane as the driving force.

Our earlier findings from the diffusion cell experiments revealed that several factors significantly influence the diffusion of dissolved lignin molecules through cellulose membranes. Notably, mass transport decreased when: i) the pore size was reduced, ii) the alkalinity of the solution decreased (leading to the aggregation of lignin molecules to particles), and iii) the molecular weight of lignin decreased[18,19], where high molecular weight lignin can act as colloids[20].

Previous research has investigated pulping with different salt concentrations and types in the cooking liquor, revealing effects on lignin diffusion[21]. The addition of salts potentially influences factors such as lignin's solubility[13], interactions between lignin and cellulose surfaces, and the swelling of cellulose structures[22]. Yet, more profound studies are needed to fully grasp these impacts.

The influence of ions on various systems has been a focus of research

since Hofmeister studied protein aggregation of egg proteins in presence of different salts[23]. The effect of ions in these systems was not solely dependent on their valency but also on the type of the ion[24]. Hofmeister ordered the ions after their protein precipitation efficiency[24], which was later named the Hofmeister series. Classically, in the Hofmeister series ions are divided into two categories depending on their interactions with water: the ions that could order the water molecules were called kosmotropes (after the Greek word for order), and the ones that disturbed the water structure chaotropes (after the Greek word for disorder)[25]. Later it was found that the ions could not influence the bulk water, but the density of their first hydration shell was larger[26]. Nevertheless, the names kosmotropes and chaotropes have remained and are commonly used in the literature. Gregory *et al.* have suggested using the terms “charge diffuse ion” and “charge dense ion” rather than chaotrope and kosmotrope[27], but a change to these terms has not yet been successfully implemented in the scientific community. The importance of ion-specific effects has been seen in various systems[23]. Extensive research has been done on, for example, ion-specific effects on proteins and biological systems[25,28,29], in various polymers[30], surface tension of electrolytes[31], and stability of latex particles[32].

Despite the ubiquity of ion-specific effects and their importance, there is limited research on the ion-specific effects on lignin. For example, Sundin and Halter explored the interaction of lignin molecules with different cations, including both monovalent and divalent[5]. At pH 9, all examined cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$ ) precipitated lignin, however, at pH 11–13, only calcium and magnesium ions precipitated lignin to a significant extent. Swering and co-workers have studied specific ion effects in the presence of high salt concentrations, and they found that the colloid stability of lignin changed with the identity of the salt and NaCl addition precipitated lignin, whereas  $\text{Na}_2\text{SO}_4$  did not[33]. In addition, Norgren *et al.* have also studied the aggregation of lignin in the presence of different salts[34]. Interestingly, their results show that lignin aggregation is specific to the presence of both cations and anions. They observed that lignin solutions were stable over time in the presence of sodium nitrate, whereas in the presence of sodium chloride, the suspensions exhibited increased turbidity within ten minutes of preparation. Similarly, the presence of potassium cations was found to stabilize the lignin solution, whereas the presence of sodium ions and cesium ions facilitated the aggregation of lignin[20]. Since lignin is a negatively charged hydrocolloid, the presence of cations is expected to have a significant impact on its solution properties. According to classical mean-field theories, anions are expected to be expelled from the vicinity of negatively charged hydrocolloids, resulting in less effect on their physicochemical properties. However, experimental observations suggest that they do have a significant effect on the physicochemical properties of polymers[27,35], affecting processes such as ionization[36], adsorption[37], gelation[38], and phase transitions[30]. Recently, Arumughan *et al.* have shown that the presence of less hydrated co-anions in the solutions facilitates the adsorption of carboxymethylcellulose on cellulose[37].

The colloid stability of lignin in presence of specific ions is paramount in biorefinery processes where one aims to produce pure lignin via precipitation, e.g., in the LignoBoost process. In the delignification process, on the contrary, it is of the utmost importance that the lignification does not precipitate to enable good mass transport. Considering kraft pulping complexity, a robust understanding of specific ion effects on lignin mass transport and adsorption is critical for optimizing the processes and producing high-quality pulp. Therefore, in this model study, the effect of sodium nitrate ( $\text{NaNO}_3$ ), sodium chloride ( $\text{NaCl}$ ), and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) salts on the mass transport of solubilized lignin molecules through model cellulose membranes were investigated using a simple diffusion cell setup. Furthermore, the conformation of lignin molecules in the salt solutions was characterized by intrinsic viscosity measurements, and the adsorption to cellulose model surfaces of lignin molecules in the presence of the salts was investigated using a quartz crystal microbalance. This study will hopefully guide further

development of the delignification process of pulp.

## 2. Materials and methods

The kraft lignin (softwood with an average molecular weight of 4 kDa [18] and see ref. 18 for more characteristics of the lignin) used in this study was isolated from black liquor by the LignoBoost process at the Bäckhammar mill in Sweden. NaOH, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich, Germany), and NaCl (Thermo Fisher Scientific, Sweden) were dissolved in deionized water to produce salt solutions with the desired concentrations. The diffusion experiments were carried out utilizing a diffusion cell setup where regenerated cellulose (RC) membranes (Spectrum™ Labs Spectra/Por™, Germany) were used as membranes, the weight cut-off (MWCO) of the used membranes was 50 kDa. For water permeation measurements, 5 mCi (185 MBq) tritium-labeled water from PerkinElmer (USA) was used. Ultima Gold from Perkin-Elmer (USA) was added to the samples prior to measurements in the scintillator. Trimethylsilyl cellulose (TMSC), was sourced from TITK (Thuringian Institute of Textile and Plastic Research, Germany), with a molecular weight of 185,000 g/mol and a degree of substitution (DS) of 2.8. TMSC was used to create RC (regenerated cellulose) surfaces on gold quartz crystal microbalance with dissipation monitoring (QCM-D) sensors (QuartzPRO, Gothenburg, Sweden). Toluene (Sigma Aldrich, Germany) was used to dissolve the TMSC prior to spin coating.

### 2.1. Intrinsic viscosity measurements

An automated Ubbelohde viscometer (Schott-Geräte, Germany) was used to measure intrinsic viscosity. The capillary (531 01a, with 0.005 K constant) was placed in a 25 °C water bath to avoid temperature fluctuations. The relative and specific viscosities ( $\eta_{rel}$  and  $\eta_{spec}$ , respectively) were calculated by measuring the average flow-through time for both the salt solutions and different concentrations of lignin-containing salt solutions using the following equations:

$$\eta_{rel} = \frac{t}{t_{solvent}} \quad (1)$$

$$\eta_{spec} = \eta_{rel} - 1 \quad (2)$$

where  $t$  is the flow-through time for lignin-containing solutions, and  $t_{solvent}$  is the flow-through time for the solutions without lignin. The intrinsic viscosity [ $\eta$ ] (ml/mg) was calculated by the following equation:

$$[\eta] = \lim_{C \rightarrow 0} \left( \frac{\eta_{spec}}{C} \right) \quad (3)$$

where  $C$  (mg/ml) is the concentration of lignin in the solution. The value of [ $\eta$ ] was obtained by plotting  $\frac{\eta_{spec}}{C}$  vs  $C$  and extrapolating the line to  $C = 0$ . The kraft lignin solutions were prepared in 45 mg/mL concentration, the solutions were stirred for 2 h and were allowed to stand for 30 min to ensure complete dissolution. The dilution series was prepared directly in the capillary, and the flow-through times for each concentration were measured at least three times.

### 2.2. Setup and procedure for diffusion cell experiments

Diffusion experiments, in the presence of various anions and ionic strengths, were performed using custom-made Teflon diffusion cells, as previously described [18,19]. Briefly, the diffusion cells comprised two compartments, each containing five chambers with a volume of 15 mL. RC membranes, which were used as model membranes for the diffusion of kraft lignin, were placed between the half-cells over their lateral openings. To prevent any potential leakage, rubber O-rings were utilized to seal the openings, and the compartments were securely fastened together using screw rods. Donor solutions containing lignin (0.4 g/L) were prepared at various sodium concentrations (0.2, 0.5, and 1 M) in

0.1 M NaOH and the cation concentration was adjusted by the addition of different salts (NaCl, NaNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub>). Since the counter ion (Na<sup>+</sup>) concentration may significantly affect the double layer around lignin, it was kept constant between the various salts. Blank solutions of the same ionic strengths (no lignin) were used as acceptor solutions.

In each diffusion chamber, equal volumes (15 mL) of the donor and acceptor solutions were simultaneously introduced. The entire experiment was conducted in triplicate to ensure reliable results. To maintain uniformity of solutions throughout the experiments, the samples were placed on an orbital shaker (PSU-20i, LabTeamet, Grant Instruments, Cambridge, United Kingdom) set at 100 rpm for the entire duration of the experiment. Every 24 h, 1 mL samples were withdrawn from the acceptor chamber and replaced with a blank solution to keep the volume constant. The lignin concentrations in the withdrawn samples were determined using a Cary60 UV-Vis spectrophotometer (Agilent Technologies, Inc., CA, USA) by measuring the UV/Vis absorbance. The kraft lignin concentration was quantified by utilizing the absorbance at 280 nm, based on calibration curves specific to kraft lignin in the respective solutions. The calculation of the water and lignin mass transport rate through the membrane was performed using the following equation (4), derived by Van den Mooter *et al.* [39].

$$2 \left( \frac{DS}{hV} \right) t = - \ln \left\{ \frac{C_0 - 2C_{acc}}{C_0} \right\} \quad (4)$$

Let  $D$  (m<sup>2</sup>/s) denote the efficient diffusion coefficient,  $S$  (m<sup>2</sup>) denote the surface area of the membrane where diffusion occurs, and the volumes of the solution in the donor and acceptor chambers are denoted by  $V$  (m<sup>3</sup>). The thickness of the membrane is represented by  $h$  (m). The concentrations of the donor solution at time zero is shown as  $C_0$  (g/m<sup>3</sup>(-|-)) and  $C_{acc}$  (g/m<sup>3</sup>(-|-)) is the concentration in the acceptor solution at time  $t$ .

### 2.3. Water permeation through RC membranes in various alkalinities

Water diffusion through 50 kDa membranes in various salt solutions was measured according to a previously published method [18]. In brief, the membranes were placed between the two half-cells of the diffusion cells. 15 mL of solution was added simultaneously to each donor and acceptor chamber. To the donor chamber at the start, 10  $\mu$ L of tritium-labeled water was added. 0.5 mL samples were withdrawn at specific time intervals from the acceptor chamber and instantly replaced with 0.5 mL of the corresponding solution. The diffusion cells were placed at room temperature on an orbital shaker set at 75 rpm. 3 mL of Ultima Gold was added to the samples that were collected, and then were analyzed using a liquid scintillation analyzer (Tri-Carb B2810TR, Perkin-Elmer, USA). The experiments were repeated three times. Equation (4) was used for calculations of the water diffusion coefficients similar to the lignin diffusion coefficient measurements.

### 2.4. Preparation and characterization of RC films on QCM-D sensors

Gold QCM-D sensors were used as substrates for film preparation. For the preparation of the spin coating solutions, TMSC was dissolved overnight in 10 %wt toluene and centrifuged at 5000 rpm for 15 min. The supernatant was separated, diluted to 50% concentration, and used for spin coating. 150  $\mu$ L of the respective solution was deposited on the QCM sensors and spin-coated at 3000 rpm with 2100 rpm/s acceleration for 60 s. The sensors were then exposed to HCl vapor for 20 min for regeneration. The RC on the surfaces was then characterized by Fourier-transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) imaging, see supplementary information for more details.

### 2.5. Adsorption studies using QCM-D

Model adsorption experiments were conducted using QCM-D (Biolin

Scientific, Gothenburg, Sweden) to evaluate lignin adsorption in the presence of various anions. 0.8 g/L kraft lignin solutions containing 0.01 M NaOH and 0.1 M of various salts (NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>) were injected into the flow cells at 25 °C at a flow rate of 100 μL/min. Prior to the introduction of the kraft lignin solutions, the RC surfaces were equilibrated with the corresponding salt solutions. Accounting for density changes, this procedure normalizes the QCM-D (Quartz Crystal Microbalance with Dissipation) responses and ensures reliable and comparable analysis of data obtained from various salt solutions. To calculate the adsorbed mass from the frequency shifts, a model developed by Johannsmann *et al.* was used, which related the shift in complex frequency to the crystal's resonance frequency in solution[40]. A simplified version of the calculations can be found in the literature[41]. The calculated mass through Johannsmann *et al.*'s model includes the mass of bound water to the adsorbed layer, therefore, the dry mass of the adsorbed kraft lignin is lower than the calculated mass.

### 3. Results and discussion

#### 3.1. Lignin molecules in the presence of salts in the solution

As mentioned in the introduction, the lignin transport through cellulose membranes is complex and multifaceted. One of the main factors that can affect mass transport is the solution characteristics of lignin. Depending on the solvent conditions, the lignin molecules can adopt different conformations that influence their transport through the membranes. Since lignin is a negatively charged hydrocolloid, the presence of salt can influence its solution characteristics. To investigate it further, the intrinsic viscosity  $[\eta]$  of the lignin solutions was evaluated in the presence of different salts. A polymer's intrinsic viscosity is its ability to affect the viscosity of a solution without interacting with its neighbors. This is proportional to the hydrodynamic size of the polymer in the solution and is thus dependent on the solvent quality[42]. Fig. 1 shows a Huggin's plot, constructed to determine the intrinsic viscosity values measured for lignin in the different solutions using Ubbelohde viscosity measurements. The salt concentration was maintained at 0.1 M of NaOH and 0.4 M of equivalent added cations (Na<sup>+</sup>). The y-intercept of the plots corresponds to the intrinsic viscosity of lignin in the corresponding salt environment. It was observed that the intrinsic viscosity of lignin was higher in the presence of Na<sub>2</sub>SO<sub>4</sub> (0.0035 mL/mg) than in NaCl or NaNO<sub>3</sub> solutions (0.0013 and 0.0012 mL/mg, respectively), which indicates that lignin molecules adopt a more extended conformation in the presence of Na<sub>2</sub>SO<sub>4</sub> compared to NaCl or NaNO<sub>3</sub>.

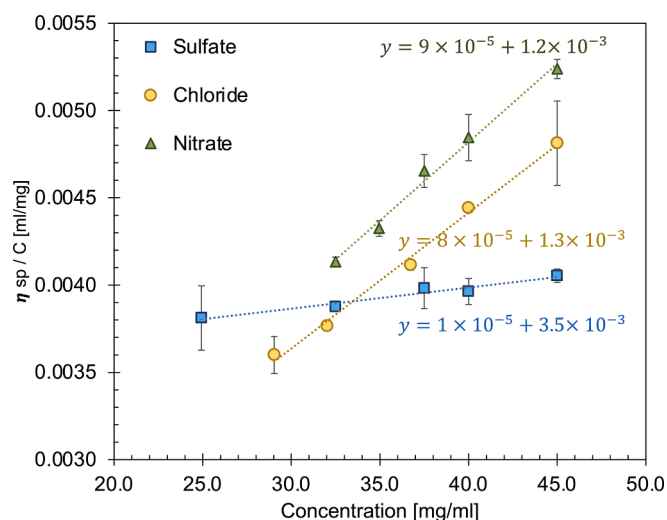


Fig. 1. Huggins plot constructed for determination of intrinsic viscosity of lignin in 0.1 M NaOH and 0.4 M cation equivalent of sodium salts.

According to the Hoffmeister series, sulfate ions belong to the salting out type of anions, which typically reduce solvent quality. However, the concentration of salt also plays a role in determining the specific ionic effect on the physical properties of hydrocolloid systems[43,44].

The concept of ion pairing can be employed to explain the effect of the sulfate ions on the intrinsic viscosity of the lignin solution. Experimental and theoretical investigations suggest that Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> tend to form ion pairs in solution[45–47]. According to Simonsson *et al.*, the ion pairing in solution decreases the effective concentration of cations that can be associated with the negatively charged colloid surface[38]. In the case of lignin, this could lead to increased charge density, thereby increasing polymer–solvent interactions and resulting in higher intrinsic viscosity. The higher intrinsic viscosity of the lignin solution could alter the mass transport rates as the extended lignin molecules transport differently through the confined pores[19]. During pulping, the ion concentrations are often high, therefore, it is important to investigate how lignin would behave in solutions with high concentrations of salts. The intrinsic viscosity at higher salt concentrations was impossible to measure due to the low solubility of lignin molecules, especially in sulfate containing solutions.

The solubility limit of lignin molecules in the different salt solutions is given in Table 1. The solubility limit is reduced with increasing the salt concentration, ascribed to charge screening effects of the ions. At low salt concentrations, the solubility of lignin in the presence of all salts was similar, with a slightly higher value in the presence of Na<sub>2</sub>SO<sub>4</sub> at 0.1 M cation concentration. However, when the cation concentration was increased to 0.9 M, the trend was reversed, and the lignin solubility was the lowest in the solution containing Na<sub>2</sub>SO<sub>4</sub> and almost 3-fold higher in the solution containing nitrate. This trend of reverse Hoffmeister series at lower salt concentrations and direct Hoffmeister series at higher salt concentrations has been reported previously in the literature[48]. The observed ion-specificity in lignin solubility is in agreement with observations from Norgren *et al.*, who observed that nitrate ions facilitated the improved solubility of lignin in alkaline solutions[34].

The influence of ion identity on the solubility and phase behaviour of macromolecules has been investigated for a long time, especially in the case of proteins and polymers such as poly(*N*-isopropylacrylamide) (PNIPAM)[30], polyethylene oxide (PEO)[49], and different polyelectrolyte brushes[50,51]. Although lignin does not strictly conform to the classical polymer definition, it should still be possible to leverage the current understanding of specific ion effects on other macromolecules to gain insights into lignin solubility. According to Cremer *et al.*, the Hoffmeister effects on macromolecule solubility could be explained by the interaction of ions with macromolecules and their first hydration shell. Strongly hydrated ionic species (kosmotropes), such as sulfate, do not readily shed their innermost hydration shell to interact with macromolecules. They facilitate hydrophobic interactions causing aggregation. In contrast, the weakly hydrated chaotropic ions, such as nitrate, tend to directly interact with the surface of the macromolecules and facilitate their solubilization by increasing hydrophilicity[44,52].

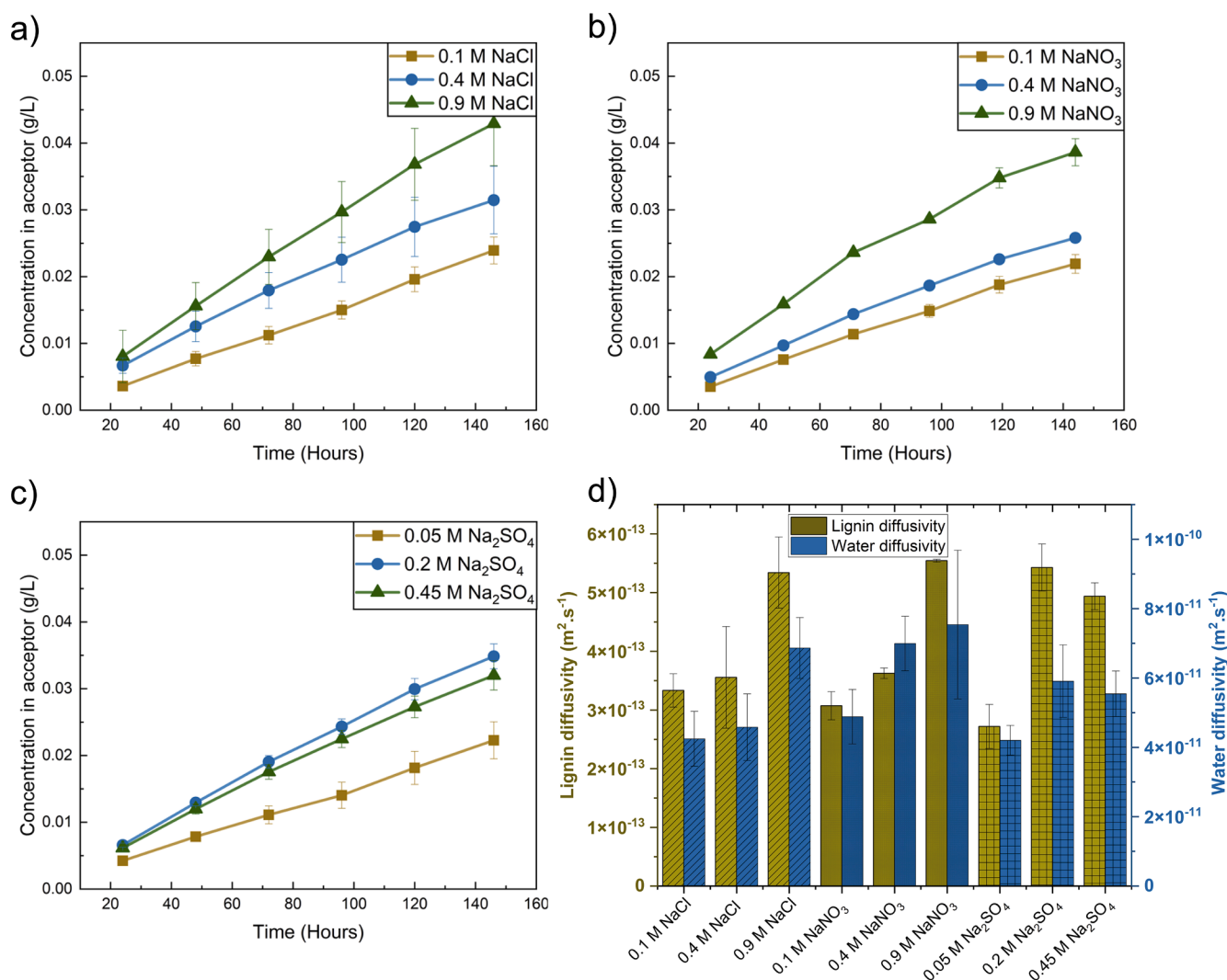
#### 3.2. Lignin transport through cellulose membranes in the presence of different salts

The transport of lignin molecules through the small pores of an RC membrane was studied using a diffusion cell setup. Fig. 2 shows the concentration of transported molecules (acceptor samples) versus time in the presence of different concentrations of salts. The transport of molecules through the membrane follows a linear trend. This confirms the stability of the membranes during the experiments. By increasing the concentration of NaNO<sub>3</sub> and NaCl, the transport of lignin through the membrane becomes faster. In the case of Na<sub>2</sub>SO<sub>4</sub>, the transport of lignin is increased by raising the concentration from 0.05 M to 0.2 M of salt. However, when further increasing the Na<sub>2</sub>SO<sub>4</sub> concentration to 0.45 M, the transport of lignin through the membrane slightly decreased.

**Table 1**

Summary of the measured viscosity of solutions, the intrinsic viscosity of lignin, the solubility limit of lignin, and the diffusivity of water and lignin in the solutions.

Solution	Viscosity of the solution (cP)	Intrinsic viscosity of lignin (mL/mg)	Solubility limit of lignin (mg/mL)	Water diffusivity (m <sup>2</sup> /s)	Lignin diffusivity (m <sup>2</sup> /s)
0.1 M NaCl + 0.1 M NaOH	0.87	1.3 × 10 <sup>-3</sup>	54.0	4.2 × 10 <sup>-11</sup>	3.3 × 10 <sup>-13</sup>
0.4 M NaCl + 0.1 M NaOH	0.88		44.3	4.6 × 10 <sup>-11</sup>	3.6 × 10 <sup>-13</sup>
0.9 M NaCl + 0.1 M NaOH	0.91		17.4	6.8 × 10 <sup>-11</sup>	5.3 × 10 <sup>-13</sup>
0.1 M NaNO <sub>3</sub> + 0.1 M NaOH	0.84	1.2 × 10 <sup>-3</sup>	53.6	4.9 × 10 <sup>-11</sup>	3.1 × 10 <sup>-13</sup>
0.4 M NaNO <sub>3</sub> + 0.1 M NaOH	0.84		45.6	7.0 × 10 <sup>-11</sup>	3.6 × 10 <sup>-13</sup>
0.9 M NaNO <sub>3</sub> + 0.1 M NaOH	0.88		39.2	7.5 × 10 <sup>-11</sup>	5.5 × 10 <sup>-13</sup>
0.05 M Na <sub>2</sub> SO <sub>4</sub> + 0.1 M NaOH	0.88	3.5 × 10 <sup>-3</sup>	59.5	4.2 × 10 <sup>-11</sup>	2.7 × 10 <sup>-13</sup>
0.2 M Na <sub>2</sub> SO <sub>4</sub> + 0.1 M NaOH	0.93		47.3	5.9 × 10 <sup>-11</sup>	5.4 × 10 <sup>-13</sup>
0.45 M Na <sub>2</sub> SO <sub>4</sub> + 0.1 M NaOH	0.99		14.2	5.5 × 10 <sup>-11</sup>	4.9 × 10 <sup>-13</sup>



**Fig. 2.** Graph showing the measured concentration of lignin in the acceptor chamber over time in a solution of 0.1 M NaOH and various concentrations of a) NaCl, b) NaNO<sub>3</sub>, and c) Na<sub>2</sub>SO<sub>4</sub>. UV/VIS absorbance of the solutions was used to determine the concentrations of kraft softwood lignin according to a previously constructed standard curve; d) Comparison of lignin diffusion coefficients in various solutions with water diffusivity values measured during diffusion experiments using diffusion cells.

In the case of NaNO<sub>3</sub>, increasing the concentration of the salt resulted in some deviation from linearity after 80 h. This shows that mass transport has, to some extent, slowed down over time. The decrease in

transport rate could indicate a clogging of the pores, possibly due to the adsorption of lignin molecules on the walls of the pores in the presence of NaNO<sub>3</sub>. This has been investigated and will be discussed in the next

section. A similar trend was not observed for the other two salts.

When comparing the lignin diffusivity rates at the intermediate concentrations in Table 1 (0.4 M for NaCl and NaNO<sub>3</sub>, 0.2 M for Na<sub>2</sub>SO<sub>4</sub>), the lignin diffusivity in the Na<sub>2</sub>SO<sub>4</sub> sample was higher than the other two salts. The lignin solubility in all salts at the aforementioned concentration was similar, however, the intrinsic viscosity of the Na<sub>2</sub>SO<sub>4</sub> sample was higher than the other two. As mentioned earlier, this indicates a more expanded conformation in 0.2 M Na<sub>2</sub>SO<sub>4</sub>. However, at higher concentrations of Na<sub>2</sub>SO<sub>4</sub>, the lignin diffusivity was lower compared to that at higher concentrations of NaNO<sub>3</sub> and NaCl, indicating ion specificity in diffusion, which could be due to altered colloidal stability and aggregation of lignin in the presence of sulfate ions at high concentrations.

There are various ways in which salts could affect lignin transport through cellulose membranes: i) The presence of ions in the solution can affect the swelling of the RC membrane, changing the sizes of the pores and the thickness of the membrane; ii) Lignin molecules are prone to adsorption on the surface of the membrane, which is affected by ion-specific effects and in turn influences the transport through the membrane differently in the presence of each ion; iii) The self-aggregation of lignin is also affected by the presence of ions in the solution, which could, in part, be responsible for the difference in transport rate through the membrane. Subsequently, we have investigated each of these scenarios in more detail using techniques such as diffusion of tritium-labeled water through the cellulose membrane and QCM-D measurements.

### 3.3. The membrane stability in the presence of ions

The RC membranes used in this study were stable in alkaline conditions, i.e., they did not lose their structural integrity during the experiment. However, when exposed to high alkalinity and various salts, the membranes may experience swelling [22], changing their pore sizes and thickness. These phenomena are important in our setup since thickness and pore size changes are expected to affect lignin transport through the membrane [19]. In this context, investigation of the diffusion of water through the RC membrane in various salt solutions at high alkalinity can improve the understanding of ion-specific effects on the membrane and elucidate eventual membrane effects on the mass transport of lignin.

The water diffusivity results were compared to lignin diffusivity in the diffusion cell setup (Fig. 2d). Both water diffusivity and lignin diffusivity followed the same trend in various solutions. While lignin diffusivity could be affected by lignin self-association, lignin adsorption on the membrane surface, changes in solution characteristics, and changes membrane thickness and pore sizes due to swelling. On the other hand, the water diffusivity is mostly affected by changes in the membrane and the solution characteristics. Ions could affect the viscosity of the solution, which, in turn, changes the mobility of the water molecules within the solution. The measured viscosity values for the salt solutions showed that the addition of Na<sub>2</sub>SO<sub>4</sub> can significantly increase the viscosity of the solution (Table 1), which is in agreement with the literature [53–55]. In contrast, NaNO<sub>3</sub> decreased the viscosity of the solution at low concentrations of the salt. Since the viscosity of the Na<sub>2</sub>SO<sub>4</sub>-containing solutions was higher, it was expected that the water diffusivity through the membrane in these solutions would be lower.

The similarity in the trends of water diffusivity and lignin diffusivity implies that any modifications in the cellulose membrane can substantially impact the mass transport of lignin through the membrane. The swelling of the cellulose membrane can be influenced by salts, resulting in the creation of tortuous and longer pathways for lignin to diffuse through and a potential decrease in available spaces. On the other hand, swelling can also lead to an increase in the surface area of cellulose for lignin to adsorb onto.

### 3.4. Adsorption of lignin on the cellulose surface

Adsorption of dissolved lignin onto the cellulose surface significantly impacts the diffusion. To investigate the effect of anions on the adsorption of kraft lignin on the cellulose surface, QCM-D experiments were performed with lignin solution in different sodium salts. Ultrathin films of RC were prepared on a gold QCM-D sensor for the adsorption experiments. Characterization of the RC films is described in the supplementary information. FTIR spectra showed that regeneration of the surface was successful, and the AFM images of the films revealed a uniform surface with an average root mean square roughness of 0.94 nm (Figure SI 1).

Fig. 3a shows the frequency and dissipation responses associated with the adsorption of kraft lignin on regenerated surfaces. Dissipation is a measure of energy loss and can provide information about the viscoelastic nature of the adsorbed layer. Although Fig. 3a shows that the dissipation increased with the adsorption of lignin, which usually indicates softness of the lignin films, the dissipation values were not as high as cellulose derivatives and other polymers, therefore, the adsorbed lignin layer is considered to be relatively rigid [56–58]. The dissipation response was similar in all the examined cases; therefore, it can be concluded that the structure of the adsorbed layer does not depend on the type of salt used.

A decrease in frequency indicates an increase in mass at the cellulose-liquid interface. The normalized frequency shift upon injection of kraft lignin solution followed a similar shape for all samples. However, in the case of the lignin in presence of NaNO<sub>3</sub> salt solution, the frequency shift was almost double that of the other samples, indicating that more lignin was adsorbed on the surface. Fig. 3b compares the calculated adsorbed mass in the presence of the different sodium salts and shows that NO<sub>3</sub><sup>-</sup> ions significantly affect the adsorption on the RC surface.

Adsorption of lignin molecules on cellulose surfaces can significantly affect the mass transport of lignin during pulping. The adsorbed lignin molecules can form a dense layer on the membrane surface, effectively reducing the available pore space, increasing the resistance to lignin transport, and decreasing the diffusivity. As mentioned earlier regarding Fig. 2b, after 80 h some deviation from linearity of the transport curve occurred. Since lignin molecules adsorb to a greater extent on the cellulose surface in presence of nitrate ions, they can clog the pores and decrease the transport rate, which was observed as a deviation from linearity. Furthermore, the adsorption of lignin on the cellulose membrane can alter the surface properties and charge distribution, resulting in changes in electrostatic interactions.

Adsorption of lignin onto the weakly negatively charged cellulose surface could occur through a variety of mechanisms, including van der Waals interactions, hydrogen bonding, or electrostatic interactions. In alkaline conditions, the lignin molecules are negatively charged, therefore, the main interactions between the lignin molecules and the cellulose surface are expected to be electrostatic repulsion. However, at elevated salt concentrations, this electrostatic repulsion is screened, therefore, the adsorption is instead promoted by non-electrostatic forces [59]. According to the current understanding of the adsorption of polymers on cellulose surfaces, the entropy gain due to the release of water molecules from the interface during adsorption is the major driving force for adsorption [56,60–62]. The origin of anion specificity during adsorption is suggested to stem from differences in the water organization at the interface in the presence of different salts. Arumughan *et al.* recently reported anion-specific effects in the adsorption of carboxymethyl cellulose on cellulose fiber surfaces [37]. It has been suggested that the hydration of anions is one of the decisive factors that impart ion specificity during the adsorption process. The hydration of ions dictates their arrangement near the interface. Fig. 4 is a schematic representation of how different salts arrange themselves in solution and how this arrangement can affect the adsorption.

Less hydrated ions (chaotropic ions), such as nitrate, are considered to be located in the vicinity of the cellulose-water interface, leading to an

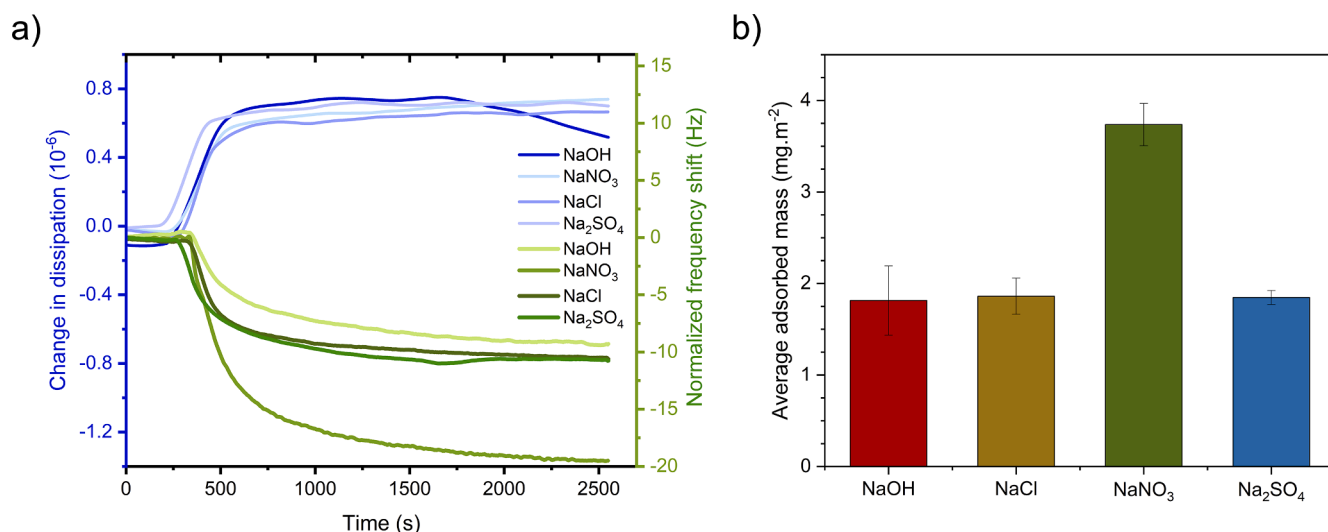


Fig. 3. A) representative changes in the dissipation and normalized frequency shifts upon injection of the lignin in various salt solutions; b) calculated average mass of the adsorbed lignin from the different salt solutions on the rc surface.

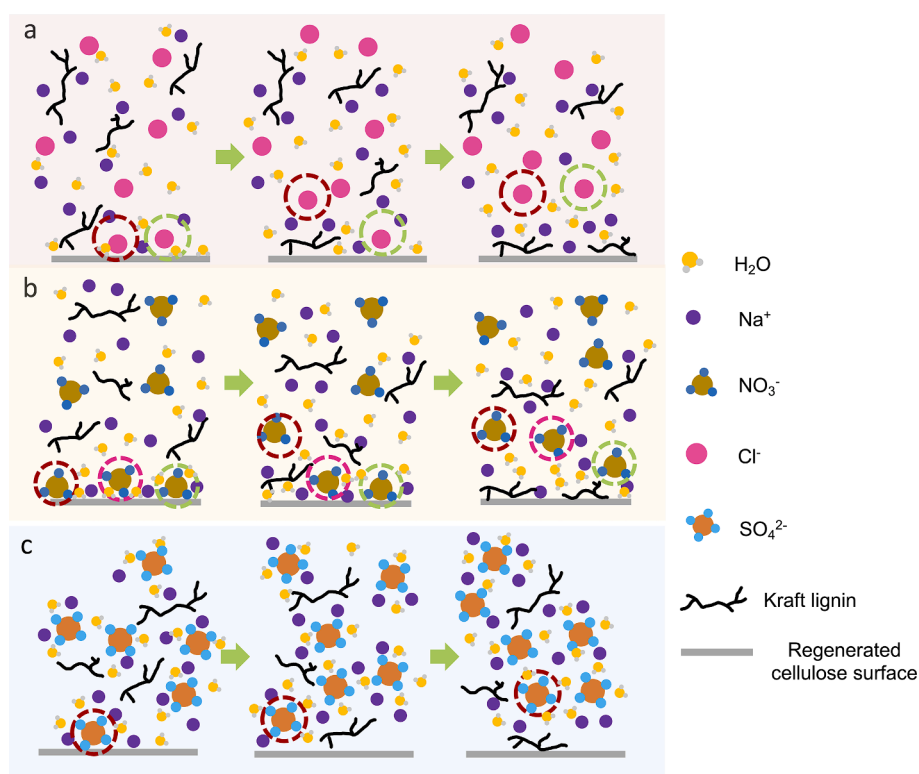


Fig. 4. Schematic representation of lignin adsorption in the presence of different salts a) NaCl, b) NaNO<sub>3</sub>, and c) Na<sub>2</sub>SO<sub>4</sub>. From left to right: ions have arranged themselves in the system, where chaotropic nitrate ions (b) tend to arrange themselves preferentially on the cellulose surface, whereas kosmotropic sulfate ions (c) are predominantly found in the bulk water. The presence of nitrate ions on the surface leads to a more structured arrangement of water molecules near the membrane. However, when lignin molecules are adsorbed onto the cellulose surface, the ions previously arranged on the surface are released into the bulk solution. This release of ions increases the entropy of the system.

energetically unfavorable organization of water molecules at the interface. In this case, the entropy gain due to the release of water molecules during adsorption would be higher, thus, the presence of chaotropic species would result in higher adsorption. However, as mentioned during the discussion of lignin solubility, strongly hydrated sulfate ions are reluctant to shed their innermost hydration shell to interact with surfaces or polymers and are thus situated in bulk [44,52].

#### 4. Conclusion

The role of ion-specific effects, particularly within the Hofmeister series, has been extensively examined in proteins and biological systems [25,28–30]. However, systematic investigations of these effects on lignin are limited. Previous studies have touched upon the influence of salts on lignin precipitation [5,34] as well as the sorption of kraft lignin on pulp [63], but a comprehensive analysis of ion-specific effects is

lacking.

In this study, we hypothesized that anions prone to ion-specific effects, could change the mass transfer and adsorption behavior of dissolved lignin molecules. This would directly impact the release of lignin from fiber cell walls during pulping. Therefore, we selected anions based on the Hofmeister series and conducted a thorough examination of lignin molecule diffusion through a model cellulose membrane in the presence of a range of sodium salts, spanning from highly hydrated kosmotropes ( $\text{Na}_2\text{SO}_4$ ) to weakly hydrated chaotropes ( $\text{NaCl}$  and  $\text{NaNO}_3$ ). We explored several factors, including adsorption, changes in membrane structure, and lignin conformation in the presence of salt solutions and their respective effects on lignin transport through cellulose pores.

While we initially anticipated lower lignin solubility in the presence of kosmotropic sulfate ions compared to chaotropic nitrate ions [34], our observations revealed a reversed Hofmeister series at low salt concentration. At higher salt concentrations, the solubility followed the expected Hofmeister series. A similar trend reversal was previously observed in the swelling and collapse of weakly charged polymers [47], suggesting that complex ion-specific effects emerge at higher salt concentrations. This indicates that the complex ion-specific effects emerge above a certain salt concentration.

Our mass transport experiments, utilizing diffusion cells and model membranes, confirmed the effect of lower lignin solubility at the highest kosmotropic salt concentration. Additionally, adsorption studies using QCM-D demonstrated that chaotropic nitrate ions enhanced lignin adsorption on cellulose surfaces due to higher entropy gain of lignin adsorption in the presence of  $\text{NaNO}_3$  [64]. This preference arises from the tendency of chaotropic ions to arrange themselves on the cellulose surface rather than in the bulk. Upon adsorption of lignin on the surface, these ions initially adsorbed at the surface are released into the bulk water. On the other hand, the less chaotropic anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) showed minimal influence on adsorption of lignin.

This study highlighted the intricate nature of ion-specific effects on mass transport and lignin adsorption. Our findings revealed that the combined effect on the transport of lignin is a result of individual effects that, to some extent, counteract each other. To uncover the full potential use of ion-specific effects on an industrial scale, further studies using combinations of various industrially relevant ions or molecular dynamic simulations can be of great importance.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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