# Adsorption, Structure, and Rheology of Cellulose Nanocrystals at the Air-Water Interface

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### ABSTRACT

Cellulose nanocrystals (CNCs) are a promising biological alternative for the stabilization Pickering of foams and emulsions. Despite interest great and numerous successful applications in recent vears, the underlying mechanisms of adsorption were long unclear. Here, we provide an overview of our recent findings on the adsorption kinetics, adsorption isotherms, interfacial layer structure, and rheology of CNCs at the A/W interface

### **INTRODUCTION**

The stabilization of fluid interfaces by solid particles, called Pickering, is a common practice in colloid and interface science. The use of biological particles has recently emerged as an alternative for the production biocompatible of materials. Cellulose nanocrystals (CNCs) extracted from wood pulp are charged, anisotropic nanoparticles which adsorb at the air-water (A/W) or oil-(O/W) interface, allowing water the stabilization of foams and emulsions.1 CNC stabilized colloids are extraordinarily stable,<sup>2</sup> and their biocompatible nature qualifies them for biomedical. cosmetic. and food applications.<sup>3</sup> Despite successful the application of CNCs in foams and emulsions. the underlying mechanisms of adsorption were long unclear, mainly due to the inability to form controlled interfacial layers. Here, we summarize our findings on the adsorption, structure, and rheology of CNCs at the A/W interface.4,5

# EXPERIMENTAL

CNCs were kindly provided by CelluForce (Montreal, Canada). They are rod-like 80x5x5 nm crystalline particles.<sup>4</sup> Negatively charged sulfate ester residues are distributed on the CNC surface at a linear charge density of 0.67 nm<sup>-1</sup>, enabling to control the interactions within CNCs from repulsive to attractive by salt-induced charge screening.<sup>6</sup>

For CNC adsorption experiments, a paper Wilhelmy-plate was attached to a balance (KSV Nima) and immersed in CNC dispersion in a home-made Teflon trough with a surface area of 86 cm<sup>2</sup>. Dilatational rheology experiments were performed by sinusoidal area oscillation cycles induced by two movable Teflon barriers. The seup is schematically illustrated in Fig. 1. Experiments were performed at 22 °C.



Figure 1. Schematic of the Wilhelmy-plate setup with immersed paper plate and movable barriers employed for CNC adsorption and dilatational rheology experiments.

Interfacial shear rheological experiments were performed with an Anton Paar MCR702 equipped with a bicone geometry at 20°C.

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Atomic force microscopy (AFM) images were taken from CNC adsorption layers which were transferred by an adapted Langmuir-Schaefer technique.<sup>7</sup> Using (3aminopropyl)-triethoxysilane, the charge of freshly cleaved mica was inversed to positive to allow displacement of negatively charged CNC adsorption layers. The mica was dipped horizontally on equilibrated CNC layers, washed with Milli-Q and dried with pressurized air. AFM height images were taken with a Bruker Dimension FastScan in tapping mode.

# **RESULTS & DISCUSSION**

# <u>CNC Adsorption and Layer Structure at the</u> <u>A/W Interface</u>

The adsorption of CNCs at the A/W interface can be monitored by changes in surface tension, commonly expressed by the surface pressure  $\prod$ :

$$\prod = \gamma_0 - \gamma_t \tag{1}$$

which describes the decrease in surface tension  $\gamma$  over time t relative to the clean A/W interface with  $\gamma_0 = 72.4$  mN/m. Fig. 2A depicts  $\prod$  as a function of time during CNC adsorption. The adsorption of CNCs is characterized by a diffusion limited lagphase (see inset) followed by steady adsorption within  $\approx 15$  hours. The adsorption was accelerated and higher final surface pressures  $\prod_{max}$  were reached at increasing CNC concentration. No changes were observed at CNC concentrations above 0.5 wt%, indicating that maximum coverage is attained. However, the lag-phase was further reduced and CNC adsorption accelerated by NaCl-induced charge screening, as illustrated in Fig. 2B. The NaCl concentration required to accelerate CNC adsorption corresponds to  $\approx$  10 mM, which is the critical salt concentration required for sufficient charge screening to allow for CNC attractive interactions.<sup>6</sup>

This adsorption behaviour suggests that CNC adsorption is a two-step process, limited by (i) diffusion to the interface and (ii) a kinetic adsorption barrier, as commonly observed for non-surface active nanoparticles.<sup>8</sup> The same applies for the comparably slow adsorption at the time-scale of hours, which however does not impede adsorption during foaming or emulsification where high shear strains are at play. Thus, CNCs must be considered nonsurface active nanoparticles that stabilize fluid interfaces by a Pickering mechanism, the energetic unfavourable preventing contact of the two subphases. Hence, not CNC amphiphilicity, but wettability by both subphases is crucial for CNC adsorption. This further suggests that the decrease in surface tension is not induced by CNC amphiphilic properties. Adsorbed nanoparticles may decrease the surface tension by capillary forces induced by contact line distortions in the nano-range. This effect is enhanced in case of anisotropic nanoparticles like CNCs.9

The salt-induced charge screening may decrease the kinetic adsorption barrier in two possible ways. First, the charge screening reduces the electrostatic repulsion of particles in the bulk and particles already adsorbed at the A/W interface. Second, there is increasing theoretical and experimental evidence that fluid interfaces are also charged. This opposes adsorption of charged species, whether the interactions are attractive or repulsive in nature.<sup>10</sup>

The  $\prod_{max}$  attained in Fig. 2A and B were compiled into CNC adsorption isotherms, as depicted in Fig. 1C. The isotherms are well described by asymptotic fits with increasing  $\prod_{max}$  at higher CNC concentrations and a plateau at  $\approx 0.5$  wt%. This suggests a monolayer saturation with limited adsorption sites available for CNCs. The higher  $\prod_{max}$  at increasing NaCl concentration further indicates that CNC coverage is increased upon charge screening. The structure of



Figure 2. Adsorption of CNCs at the A/W interface de function of time for (A) increasing CNC concentration NaCl concentration. (C) CNC adsorption isotherms at ( interfacial CNC layer formed at image of a displace experiments were p formed by the Wilhelmy-plate te

(0.75 wt% and 20 mM saturated CNC laye tigated by NaCl) was inv neutron reflectometry, ch confirmed the W formation of a discontinuous monolayer with a surface coverage of 17%. The layer roughness was equal to layer thickness, indicating that CNCs orient in the interfacial plane. The scattering length density profile suggests that CNCs adsorb at an adsorption angle  $> 90^{\circ}$  and are preferably wetted by the aqueous phase.<sup>4</sup> Adsorbed CNC layers were displaced and imaged by AFM (Fig. 1D)<sup>4</sup>, revealing a monolayer with a surface coverage of 21%, in good agreement with



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where A is the interfacial area occupied by one particle approximated by a rectangle of 400 nm<sup>2</sup> from AFM images. This results in an adsorption energy of  $-4.5 \times 10^3$  k<sub>B</sub>T for a single CNC in absence of salt and  $-6.1 \times 10^3$ 



Figure 3. (A) Interfacial dilatational rheology of adsorbed CNC layers performed at an oscillation frequency of 10 mHz and 5% area deformation at 22 °C. (B) Interfacial shear amplitude sweeps performed at an angular frequency of 1 rad/s and 20 °C.

 $k_BT$  at 20 mM NaCl. However, as this approach neglects CNC interactions, the adsorption promoting effect of NaCl is probably underestimated.

# Interfacial Rheology of CNC Adsorption Layers

The mechanical properties of high surfaceto-volume systems like foams and emulsions are ultimately affected by the rheology of the underlying fluid interfaces.<sup>12</sup> Interfacial dilatational and shear rheology aim at measuring the stress-strain response of adsorbed interfacial layers under oscillating area and shear, respectively. Fig 3A depicts the interfacial dilatational storage modulus E' of layers adsorbed at different CNC and NaCl concentrations. At low NaCl concentrations, a negligible elasticity around 1 mPa·m was observed for all CNC layers. From 10 mM NaCl, E' steadily increased. This is in good agreement with critical NaCl concentrations that enhance CNC adsorption and allow for CNC attractive interactions.<sup>6</sup> Although at 0.1 wt% CNC, E' did not increase. Hence, both a sufficient surface coverage and salt-induced CNC interactions are required to form viscoelastic CNC interfacial layers. Dilatational amplitude sweeps showed an increasingly nonlinear response at increasing CNC and NaCl concentrations.<sup>5</sup> Lissajous-plots revealed that this derives from a strain-hardening in compression.

Fig. 3B depicts oscillatory shear rheological amplitude sweeps for layers formed at increasing CNC concentration and 25 mM. CNCs form viscoelastic interfacial layers with high critical strains  $\gamma_{crit}$ , probably because of the comparably low surface coverage of CNCs < 20% and their anisotropic shape which may facilitate alignment in the flow field. At lower CNC surface coverage or salt concentrations, the adsorbed layers have viscous character and are not measurable with interfacial shear rheology.<sup>4</sup>

Hence, CNCs form interfacial layers with primarily viscous character when electrostatic repulsion is dominant. Upon salt-induced charge screening, CNC layers are increasingly elastic in dilatation and shear. CNCs form viscoelastic interfacial layers at comparably low surface coverage, probably due to their shape anisotropy, as previously for reported micron-sized ellipsoids.<sup>13</sup> This interfacial behaviour may explain certain features of CNC-stabilized colloids. The viscoelasticity of CNC layers despite low surface coverage could be the reason for the high steric stability observed in O/W emulsions.<sup>2</sup> Further, the increase in elasticity upon charge screening may explain the strong gelling of CNC-stabilized interfaces at high ionic strength, which provides emulsion stability even under gastric conditions.<sup>14</sup>

### CONCLUSIONS

CNCs adsorb at the A/W interface within hours and decrease the surface tension by induced capillary forces. The driving force is a Pickering mechanism determined by particle wettability. The adsorbed layer is a discontinuous monolayer with particles oriented in the interfacial plane at a surface coverage of  $\approx 20\%$ . Despite the rather low surface coverage, CNC layers show a viscoelastic response in dilatation and shear due to their shape anisotropy. However, sufficient charge screening is required to form viscoelastic layer, underlining the importance of CNC attractive interactions for interfacial viscoelasticity.

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# NOTES

This transaction summarizes our recent findings on CNC adsorption, structure, and rheology at the A/W interface, as published in detail in Ref. 4 and 5. Figures are reprinted with permission of the American Chemical Society, Copyright 2018 and 2019, respectively.

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