Investigating Adsorption of Cellulose Nanocrystals at Air–Liquid and Solid–Liquid Interfaces in the Presence of Hydrotropes

Geosmin A. Turpin, Andrew Nelson, Stephen A. Holt, Luke W. Giles, Izabela Milogrodzka, Boon M. Teo, Vikram S. Raghuwanshi, Roger G. Horn, Leonie van ’t Hag,* and Rico F. Tabor*

Coating a substrate with anisotropic nanoparticles such as cellulose nanocrystals (CNCs) confers some of their desirable physicochemical properties, such as strength, wettability, and barrier properties. The formation of monolayer coatings of CNCs via dip coating is affected by the enrichment of CNCs at both air–liquid and substrate–liquid interfaces. In this work, a surfactant-free method for dip coating CNCs is presented through use of the hydrotrope tetraethylammonium chloride. Hydrotropes demonstrate a different mechanism for facilitating interfacial enrichment, adsorbing to CNCs and rendering them weakly hydrophobic, causing them to adsorb to both solid–liquid and air–liquid interfaces without affecting the surface tension of the system. This new coating mechanism may be more robust as adsorption onto the substrate from the bulk dispersion is less sensitive to the air–liquid interface. Adsorption at the solid–liquid interface showed two distinct CNC layers, with a tightly bound, close-packed CNC layer at the interface, and a loosely associated outer layer. Adsorption of both layers is shown to be fully reversible after washing with ultra pure water, highlighting the potential of hydrotropes for facilitating new coating mechanisms.

1. Introduction

The behavior of nanoparticles at interfaces is a field that has generated great interest, due to the unique physicochemical characteristics of nano-dimensional materials conferred by their size. In particular, chemically or physically anisotropic nanoparticles have captured the attention of researchers as their properties make them attractive for a variety of applications. Anisotropic shapes can pack more effectively than their spherical counterparts, requiring a lower particle concentration to cover an interface than isotropic particles because they are able to align in different orientations. This makes anisotropic nanoparticles such as rods and disks more effective at Pickering stabilization, with uses in many industries including food, medicine, and personal care products.

Introducing even small amounts of surfactant can modify the surface energy of such nanoparticles, further influencing the complex balance of forces dictating their behavior at interfaces. An advantage of using nanoparticles as Pickering stabilizers is a reduction in the amount of surfactants being used in industrial systems, motivating investigation into other molecules that may subtly influence the surface energy of nanoparticles without being surface-active themselves. Previous research has shown that hydrotropes, smaller amphiphilic solubilizing agents, offer a promising alternative to surfactants for facilitating the adsorption of anisotropic graphene oxide.
CNCs, but little previous work has been undertaken on how also been found to influence the interparticle interactions of nanosheets to the air–liquid interface,[10] hydrotropes are key stabilities of glass substrates[20] as well as enhancing the interfacial properties such as electrical and thermal conductivity,[18] and can locate at the air–liquid interface when surfactants are present.[14] Such systems can be tuned further by changing the ratio of additive to nanoparticle, with the viscoelastic modulus of the air–liquid interface containing octylamine-modified CNCs changing depending on the ratio of octylamine molecules to CNC surface charges.[15] A similar effect is seen when increasing ionic strength, highlighting the potential for manipulating interactions between interfacial layers of CNCs.[16] Hydrotropes have also been found to influence the interparticle interactions of CNCs,[27] but little previous work has been undertaken on how such additives influence their adsorption behavior.

2. Results
2.1. Tetraethylammonium Chloride Enables Surfactant-Free Dip Coating of CNCs

The first section of this work explores the effect of a model hydrotrope on the dip coating of CNCs onto a solid substrate from aqueous dispersion. It is seen that 0.5 mg mL$^{-1}$ aqueous dispersions of CNCs and 10 mM of the hydrotrope tetraethylammonium chloride (TEAC) form a monolayer coating after Langmuir–Blodgett dip coating onto a plasma treated glass substrate (Figure 1a). This aligns with previous work showing hydrotropes enabling graphene oxide nanosheets to adsorb to the air–liquid interface.[10] These rodlike CNCs appear to partially overlay due to capillarity and rearrangement during drying, causing the layers to be thicker than the height of a lone, flat crystal (see Figure S1, Supporting Information) with the nanocrystals from this specific source previously characterized as having an average length of 89.5 nm and a height of 4.1 nm as measured by atomic force microscopy (AFM).[25] The term monolayer is used to describe these coatings despite this partial overlay because it is just above the height scale of individual nanocrystals and there is no evidence of bilayer arrangement. When dip coating CNCs in the absence of a hydrotrope or surfactant, poor coverage is obtained (Figure 1d). This is the case even though the glass substrate was plasma treated in order to hydrophilize it, decreasing the contact angle to a wetting/film forming state with water.[16]

We compared the properties of these coatings to those formed by dip coating CNCs in the presence of the surfactant dodecytrimethylammonium bromide (DTAB) (Figure 1b), as well as a “gold standard” coating of pure CNCs spin coated onto glass cover slips (Figure 1c). These coatings have similar thicknesses to both surfactant-coated samples and pure CNCs spin coated at around 10 nm as confirmed by a scratch test, indicative of a monolayer of cellulose nanocrystals (Table 1). Although it is difficult to directly compare experiments using different sources of CNCs, this is consistent with previous Langmuir–Blodgett experiments with CNC and dioctadecyldimethylammonium bromide (DODAB).[27] Interestingly, those CNC–surfactant systems often required extreme compression, exhibiting full coverage only at surface pressure values of around 40 mN m$^{-1}$, whereas the present coatings could be achieved uncompressed.

CNC–TEAC coatings exhibit a water contact angle below 5°, allowing water to form a wetting film, and below the practical limit of measurement,[28,29] similar to coatings prepared by spin coating pure CNCs (Table 1). These results are distinct from CNC–DTAB coatings, which provide a higher contact angle of 15°. The hydrotrope–CNC dip coated system appears to behave more similarly to the pure CNC coating due to the lack of hydrophobic surfactant tails that are the likely reason for the higher contact angle of DTAB–CNC coatings. This difference in wettability and surface energy is important to consider when exploring future applications for hydrotrope-facilitated CNC
coatings, as having a more wetting surface may prove to be advantageous in some situations.

No notable structuring, patterning, or increase in roughness could be seen when comparing an uncompressed sample to one where the air–liquid interface was compressed to 30% of its original area before coating (see Figure S3, Supporting Information). This is interesting as anisotropic ellipsoidal particles have been shown to “flip” upon compression at packed interfaces, and a key result from our previous work enriching 2D graphene oxide nanosheets at the interface using hydrotropes was the ability to compress the air–liquid interface so as to order or pattern the resultant coating after deposition. To better understand the mechanisms behind the compression-insensitive CNC dip coating process, further investigation into the behavior of CNCs and hydrotropes at the air–liquid interface was warranted to confirm they were enriching at the air–liquid interface and if so, determine what self–assembly behaviors they were exhibiting.

2.2. TEAC Facilitates the Enrichment of CNCs to the Air–Liquid Interface

In order to confirm that TEAC was facilitating enrichment of CNCs to the air–liquid interface, surface pressure measurements were undertaken using both pendant drop tensiometry and Wilhelmy plate tensiometry measured in a Langmuir–Blodgett configuration. Mixed CNC–TEAC systems demonstrated a moderate surface pressure response when measured via pendant drop tensiometry (Figure 2), confirming that TEAC does facilitate enrichment of CNCs to the air–liquid interface, with surface pressure corresponding to the CNC-enriched interface resisting compression. It is interesting to note that the CNC–TEAC system shows a much weaker surface pressure response in a Langmuir trough, but this discrepancy is likely due to geometric effects caused by the difference in compressing a curved versus a flat interface, as well as the

![Figure 1. Atomic force microscopy images of cellulose nanocrystal coatings on plasma cleaned glass substrates (n > 3). a) Langmuir–Blodgett dip coated from 0.5 mg mL$^{-1}$ CNC dispersions in the presence of 10 mM TEAC, exhibiting monolayer coverage, b) manually dip coated from 0.5 mg mL$^{-1}$ CNC dispersions in the presence of 0.1 mM DTAB, showing monolayer coverage, c) spin coated from 3 mg mL$^{-1}$ CNC dispersions without TEAC or DTAB, showing monolayer coverage, d) a negative control Langmuir–Blodgett dip coated from 0.5 mg mL$^{-1}$ CNC dispersion without TEAC or DTAB, showing a very low level of coverage.](image-url)
increased shear experienced by the sample when producing a much larger, rectangular interface at a higher compression rate.

This result can be compared to the much stronger surface pressure response of CNC–DTAB systems in both tensiometry configurations, indicating that even if both TEAC and DTAB facilitate enrichment at the air–liquid interface, there are mechanistic differences, with DTAB either facilitating more CNCs enriching to the interface or causing them to arrange in a different way. We will return to this question in Section 3.

X-ray reflectivity (XRR) was used to develop a more direct understanding of the adsorption behavior of CNCs at the air–liquid interface in the presence of DTAB or TEAC. By analyzing reflectivity profiles of the air–liquid interface of CNC and hydrotrope dispersions, it is possible to ascertain the thickness, roughness, and coverage of CNCs at the interface.[31,32] This has been repeated at different levels of interfacial compression to see the impact that this has on packing and orientation.

XRR profiles of CNCs in the presence of 10 mM TEAC (Figure 3a) can be successfully fitted using a model with a thickness and scattering length density (SLD) consistent with a single 3–5 nm layer of cellulose nanocrystals at the air–liquid interface. This is consistent with our findings from surface pressure tensiometry; even if the surface pressure response is weak, hydrotropes are enriching CNCs to the air–liquid interface.

Figure 2. Surface pressure plots obtained from both pendant drop tensiometry (PDT) and Wilhelmy plate tensiometry measured in a Langmuir–Blodgett configuration (LB), of 0.5 mg mL\(^{-1}\) aqueous CNC dispersions in air with the hydrotrope tetraethylammonium chloride (TEAC) (10 mM) or the surfactant DTAB (0.1 mM), as well as a negative control of 0.5 mg mL\(^{-1}\) CNC with no additive present. Sample size of presented data for each system and compression level was \(n = 1\), although trends were consistent across repeated experiments.

Figure 3. a) X-ray reflectivity data of samples containing 0.5 mg mL\(^{-1}\) CNC and 10 mM TEAC at the air–liquid interface at the specified compression levels. The filled circles represent the experimental data points and the solid lines are model fits. Data have been offset by multiplication for clarity \((\times 1, \times 10, \times 100, \times 1000)\) respectively from \(A/A_0 = 1.00\) to \(A/A_0 = 0.30\). b) The corresponding scattering length density profiles for the results in (a). c) X-ray reflectivity data of samples containing 0.5 mg mL\(^{-1}\) CNC and 0.1 mM DTAB at the air–liquid interface at the specified compression levels. The filled circles represent the experimental data points and the solid lines are model fits. Data have been offset by multiplication for clarity \((\times 1, \times 10, \times 100, \times 1000)\) respectively from \(A/A_0 = 1.00\) to \(A/A_0 = 0.30\). d) The corresponding scattering length density profiles for the results in (c). Sample size for each system and compression level was \(n = 1\).
This system only shows a weak response to compression, with the thin CNC layer becoming slightly thicker and more rough. These results can be compared to the XRR profile of CNC and DTAB systems, where there was a more prominent surface pressure response (Figure 3c). The steeper XRR reflectivity profile and broader, taller SLD peaks (Figure 3d) present for the most compressed samples in the CNC–DTAB system is consistent with there being more material irreversibly adsorbed to the interface in a single layer, which is also expected from the stronger surface pressure response previously observed. These features are made more evident when comparing these SLD profiles to a theoretical, pure air–water interface (see Supporting Information).

Given the subtlety of the enrichment of CNCs to the air–liquid interface in the presence of TEAC when compared to CNC–DTAB systems, another important mechanistic question that arises is whether these moderately hydrophobic self-assemblies could be adsorbing to solid substrates from the bulk aqueous phase as well as being transferred from the air–liquid interface, and whether adsorption from the bulk may in fact be dominant. This motivates direct investigation of interactions between bulk aqueous CNCs and glass substrates using the techniques of quartz crystal microbalance (QCM) and in-liquid AFM in the presence of TEAC.

2.3. TEAC Facilitates Enrichment of CNCs to the Solid–Liquid Interface

QCM was used to determine interactions between cellulose nanocrystals and a silicon dioxide sensor as a chemical analogue for the plasma-treated glass substrates used during dip coating, in the presence and absence of TEAC and DTAB. When measured using QCM, 0.5 mg mL\(^{-1}\) CNC shows strong adsorption to a silicon dioxide sensor in the presence of 10 mM TEAC, indicated by significant and rapid changes in both dissipation and frequency after a 750 s induction period (Figure 4). This system reaches equilibrium at 3500 s, but the strong initial adsorption event suggests that this may be more reflective of the time required for the oscillation of the sensors to stabilize rather than CNCs desorbing from the sensor. The coverage of the rigid layer can be approximated from the change in frequency using the Sauerbrey equation\(^{[13]}\) with a coverage of 433 ng over the 0.7854 cm\(^2\) active area of the QCM sensor, corresponding to an estimated CNC thickness of 4 nm.

After equilibrium was reached, the system was washed with ultrapure water, exhibiting interesting desorption behavior. Of note is the shoulder at 3750 s, indicating that desorption is occurring in two distinct stages, with the initially high change in dissipation reducing by a factor of 4. This is indicative of a soft, viscoelastic outer layer being washed off first, leaving a more rigid layer underneath that is washed off subsequently. Also of note is the restoration to baseline frequency and dissipation reducing by a factor of 4. This is indicative of a complete removal of the layer, likely due to electrostatic repulsion between CNCs and the SiO\(_2\) interface in the absence of TEAC due to their negative charges, confirmed by a lack of any significant adsorption as measured via QCM (see Figure S6, Supporting Information). This behavior was reproducible in multiple separate experiments. Comparing these findings to a CNC and DTAB system highlight the mechanistic differences between the additives, as a negligible adsorption response was registered in the presence of surfactant (see Figure S5, Supporting Information).

The solid–liquid adsorption behavior of CNCs in a bulk dispersion to a glass substrate was further investigated using force–distance AFM measurements in liquid, and the results obtained corroborate the presence of CNC adsorbed in two distinct layers as determined via QCM. By measuring the force response as the AFM tip interacts with adsorbed CNCs at different distances, it is possible to deduce the likely adsorption behavior of the CNCs in the presence of TEAC (Figure 5a). Initially showing no force response (i), at ≈50 nm from the glass surface (ii), the force response starts increasing, indicating the presence of a soft layer consistent with that hypothesized to exist from the high change in dissipation during QCM measurements. There is a breakthrough event (iii) as the tip passes through the soft, loosely associated CNC layer to a more rigid underlayer, with the increased gradient indicative of a harder surface. This increased gradient could also be interpreted as being representative of indentation, however this is unlikely due to the high Young’s modulus of this crystalline material and the complementary QCM data suggesting the presence of both a tightly adsorbed layer of CNCs and a more loosely associated one.

The breakthrough position can be quantified in order to better understand the properties of the adsorbed rigid layer. A median breakthrough distance of 15 nm for position (iii)
indicates an underlying, tightly adsorbed monolayer of CNCs (Figure 5b), and the median breakthrough force of 1.1 nN (Figure 5c) indicates that this layer is easily perturbed, as this force is roughly ten times smaller than what is required to break through lipid bilayers at the same temperature and ionic strength.[34] A second breakthrough event (iv) demonstrates the tip snapping through the tightly bound monolayer to the underlying glass substrate.

After washing very gently with water by perfusion of the AFM cell and waiting for 10 min, we see a significant change in the force–distance response curve as it becomes identical to that of a clean glass substrate, having a flat baseline before a slight repulsion due to electrical double-layer repulsion, followed by a snap-to-surface event due to short-range Van der Waals forces. These findings indicate complete stripping of the CNCs, similar to what was seen during QCM measurements.

The solid–liquid adsorption behavior studied by QCM and AFM indicate the presence of a compact monolayer of CNCs at the interface with a more loosely associated layer beyond that, whereas our XRR model of CNC–TEAC at the air–liquid interface demonstrates a single adsorbed layer, with any loosely associated second layer unlikely to be resolved with XRR. Further discussion of these parallels and comparisons will be given in the following section.

2.4. Exploring the Dip Coating Mechanism for TEAC and CNC

After confirming that CNCs are adsorbing to both air–liquid and solid–liquid interfaces, the key outstanding mechanistic question provoked is: what mechanism or mechanisms drive these processes? Previous literature has indicated that electrostatic interactions dominate the interactions between pure CNCs and an SiO2 substrate during spin coating,[35] but this question becomes more complex upon introduction of agents such as hydrotropes or surfactants. Zeta potential measurements were undertaken to assess the contribution of electrostatic interactions when surfactants and TEAC facilitate dip coating.

Our data shows little change in CNC charge as a function of additive concentration, with the CNCs remaining strongly negatively charged at the concentrations used for dip coating (10 mM TEAC, 0.1 mM DTAB). Much higher concentrations of cationic surfactant were required to reverse the surface charge of CNCs, and CNCs remain negatively charged in the presence of TEAC at all concentrations where the dispersion remains stable (Figure 6). These findings are consistent with previous literature showing that CNCs remain negatively charged with tetraalkylammonium bromide hydrotrpope concentrations at and beyond the concentration selected for this work.[36]
Although the addition of salts has been previously shown to enrich CNCs to the air–water interface by induction of aggregation,[37] because TEAC does not dramatically change the surface charge of CNCs, it is unlikely to be facilitating dip coating with a similar, electrostatically dominated mechanism.

3. Discussion

In order to understand and potentially control the formation of CNC layers by dip coating, it is helpful to consider the adsorption behaviors of CNCs to air–liquid and solid–liquid interfaces in the presence of a representative cationic surfactant (DTAB) or a cationic hydrotrope (TEAC). The results presented above demonstrate that CNCs dispersed in water without additives do not adsorb to either interface; with the addition of DTAB, there is strong adsorption to the air–liquid interface but not to the solid–liquid interface (see Supporting Information); in the presence of TEAC there is weaker adsorption to the air–liquid interface and weak, reversible adsorption to the solid–liquid interface.

3.1. Adsorption Behavior of Pure CNCs

CNCs are negatively charged in water (Figure 6), as are the solid surfaces investigated here (plasma-cleaned glass slides in AFM measurements, silicon dioxide in QCM) under the utilized experimental conditions. The air–liquid interface is also known to be negatively charged in water at pH >4.[38] CNCs are therefore repelled electrostatically and do not adsorb at any of these interfaces.

3.2. Effect of DTAB on CNC Adsorption Behavior

In the presence of DTAB, there are two possible mechanisms to explain adsorption of CNCs to the air–liquid interface. First, it is likely that DTAB adsorbs to the CNC nanoparticles and renders them hydrophobic, whereupon they sequester to the air–liquid interface in a single layer.[14,39,40] Second, the DTAB molecules themselves could adsorb to form a monolayer at the interface,[41] driven by the tendency for their strongly hydrophobic tails to partition out of water and into the air phase at a 45° angle.[42] This would create a significant positive charge at the interface,[43] attracting the CNC particles, which remain negatively charged at this concentration (0.1 mM) of DTAB (see Figure 6).

At the solid–liquid interface, where the solid (plasma-cleaned glass slide for AFM and dip coating, silica-coated quartz for QCM) is negatively charged in the aqueous CNC dispersion, DTAB is likely to adsorb. However, the DTAB concentration is well below the CMC (15 mM) and probably even less than the nominal 0.1 mM, because some DTAB will have been adsorbed to CNC particles, so that the coverage would be less than a monolayer. It has been shown that it requires higher concentrations of surfactant to lower interfacial tension in the presence of CNCs, as some surfactants adsorb to CNCs rather than the interface, hydrophobizing them.[23] Cationic surfactant adsorption would partially compensate the solid’s surface charge, but the coverage would not be sufficient to cause charge reversal and the surface would remain negative. The CNCs also remain negative (Figure 6) and so they are repelled by the solid. Neither the solid nor the CNCs are sufficiently hydrophobic for hydrophobicity alone to drive adsorption.

3.3. Effect of TEAC on CNC Adsorption Behavior

We now come to the more interesting case, and more relevant for our novel dip coating result, of CNCs in the presence of the hydrotrope TEAC. There is clear evidence for some adsorption occurring to both the air–liquid interface (surface pressure in Figure 2 and XRR in Figure 3) and to the solid–liquid interface (QCM in Figure 4 and AFM in Figure 5). At the solid–liquid interface, the adsorbed structure shows both a loosely bound and soft layer sitting adjacent to a more rigid layer that has dimensions consistent with a monolayer of CNCs, whereas at the air–liquid interface only a single layer was visible via XRR. It is possible this loosely bound second layer may still be present at the air–water interface even if it was not able to be resolved with XRR, as it is reasonable to suppose that the loose layer only “sees” the rigid layer, and is blind to the nature of the interface, that is, to the material (air or solid) beyond the rigid layer. But what causes the formation of the rigid layer?

For the air–liquid case, we propose that TEAC molecules adsorb to CNC particles and render them slightly hydrophobic (but not as hydrophobic as in the presence of the long-chain surfactant DTAB) even if hydrotropes do not significantly lower the surface tension of the air–liquid interface themselves. Previous work has shown that shorter-chain surfactants favor admicelle formation on CNCs whereas longer chain surfactants are driven to form hemimicelles more quickly.[19] There could be a similar comparison made with hydrotropes if they could be seen as acting as “extremely short chain surfactants.” The mild induced hydrophobicity is enough to drive a partitioning
of decorated CNC particles to the water surface. It is more difficult to argue that the same effect drives a layer to the solid boundary, given that the solids concerned are negatively charged and hydrophilic; nevertheless, the evidence is clear that such adsorption does occur and so perhaps the same hydrophobic mechanism is operating. Such a phenomenon, purportedly of entropic origin, has been seen previously with the anionic surfactant sodium dodecyl sulfate, adsorbing to negatively charged silica particles.[44] We will discuss below that adsorption is not caused by a strong attractive binding force as might occur between oppositely charged particle–surface couples or by Van der Waals forces in the absence of electrostatic repulsion. Computational modeling may help develop a deeper understanding of these mechanisms with the more diverse and appropriate computational force fields now available for investigating the behavior of nanoparticles at interfaces.

CNC particles in the second layer appear to be loosely associated with each other and with the first layer, which suggests there is an attraction between them. This could come from a combination of Van der Waals forces, from hydrophobicity, or from electrostatic interactions, as all have been shown to affect the balance of particle–particle and particle–substrate interactions.[45,46] Weak electrostatic attraction could occur if tetraethylammonium cations partially cover CNCs and create patches of charge.[47] However, as measured by dynamic light scattering (DLS), the CNC particle dispersion remains colloidal stable in the presence of TEAC up to a concentration of 10 mM, so there is no attractive force strong enough to cause flocculation or particle aggregation in the bulk liquid.

A second notable feature of CNC adsorption created by TEAC is that it is easily reversed on dilution. This is evidence for the absence of a strong binding force to either air or solid phases. Reversibility is more readily understood if the layer formation is seen as a partitioning of particles between the bulk liquid and the surface region, with mass balance determining the relative concentrations between bulk and surface. Reducing bulk concentration by dilution (as done in the QCM and AFM experiments) also reduces concentration in the surface region, that is, the particles appear to desorb. This picture is also consistent with the low surface pressure shown in Figure 2: decreasing the surface area would simply drive particles back into the bulk. The layer structure observed by XRR also seems fairly insensitive to compression beyond the surface getting more rough and the adsorbed layer getting rougher and slightly thicker (Figure 3). This is consistent with atomic force microscopy analysis of coatings formed by dip coating after compression looking very similar to coatings formed by dip coating an uncompressed interface (see Supporting Information).

3.4. TEAC and DTAB Facilitate Dip Coating through Differing Mechanisms

As a result of the different adsorption behaviors of CNCs with the addition of DTAB or TEAC, we propose different mechanisms behind the successful dip coating observed in either case. At 0.1 mM, the surfactant DTAB adsorbs to CNCs, making them hydrophobic but leaving them still negatively charged. DTAB-decorated CNCs are thermodynamically driven to the air–liquid interface. After passing a glass substrate through the air–liquid interface, CNCs enriched to the interface are transferred to the substrate via capillary action. In the presence of 10 mM TEAC, CNCs are rendered weakly hydrophobic, and they adsorb weakly at both the air–liquid interface and the glass substrate. They form a compact layer with a much more loosely associated second layer that is visible when analyzing the solid–liquid interface, and may be possible at the air–water interface.

After passing a glass substrate through the air–liquid interface, CNCs may be coating the substrate from a combination of transfer from the air–liquid interface through capillary action, and from CNCs already adsorbed via the bulk. The presence of a loosely associated secondary layer at either interface is unlikely to significantly impact the coating mechanism as it is likely removed through the same repartitioning effect described when discussing QCM measurements. As CNCs do not act as an insoluble monolayer, at such relatively low loadings, they would redisperse back into the bulk dispersion in response to the compression they experience during the dip coating process. This repartitioning back into the bulk dispersion also explains why the final coatings are relatively insensitive to compression of the air–liquid interface (see Supporting Information). Both adsorption to the air–liquid interface and adsorption onto the solid–liquid interface from the bulk aqueous dispersion appear to play a role in the dip coating process with the hydrotrope TEAC.

4. Conclusions

This work demonstrated for the first time that monolayer CNC coatings can be formed on a glass substrate using a low-energy, surfactant-free method by dip coating CNCs after the addition of the hydrotrope TEAC. Unlike surfactants which facilitate adsorption of CNCs only at the air–liquid interface, TEAC facilitates adsorption at both solid–liquid and air–liquid interfaces. In the presence of TEAC, CNCs adsorb onto the solid–liquid interface in two distinct layers, producing a compact monolayer backed by a more loosely associated outer layer, whereas at the air–liquid interface only a single adsorbed layer could be resolved, potentially due to XRR resolution limitations. These findings demonstrate different adsorption mechanisms depending on which additive is present. Modifying the interfacial adsorption behavior of CNCs by adding a simple salt-like hydrotrope additive has advantages over other processes, as it is much easier than covalently modifying CNCs, and does not affect the interfacial tension of aqueous dispersions during processing or increase the hydrophobicity of the final coatings like surfactants. These advantages, the increased flexibility to tune the hydrophobicity of coatings, and the decreased sensitivity to the air–liquid interface will hopefully allow for surfactant-free methods for the robust and scalable formation of anisotropic nanomaterial coatings in the future.

5. Experimental Section

Materials: Cellulose nanocrystals were purchased from the University of Maine Process Development Centre (11.5–12.5% aqueous gel, 0.85% sulfur content). Agents used to enrich CNCs to the interface (TEAC
and DTAB) were purchased from Sigma and used without further purification, as were the NaCl and HCl used for pH and ionic strength correction. All dispersions/solutions were made up with ultrapure water dispensed from a Millipore Direct-Q 5 system.

**Pendant Drop Tensiometry/Contact Angle/ Surface Pressure Measurements:** Pendant drop measurements were performed inside a glass cuvette sealed with polytetrafluoroethylene tape. Samples contained 0.5 mg mL\(^{-1}\) CNC dispersions and varying amounts of aqueous hydro trope, and surfactant, and were dispensed from a 1.27 mm blunt cannula. Measurements were performed using Opendrop 1.1 (open-source software)\(^{21,22}\) with a Flea3 CMOS camera (Point Grey, Richmond, Canada) and a custom pendant drop setup attached to an Adelab syringe pump. Interfacial tension measurements were taken until interfacial tension reached a plateau. Surface pressure measurements were typically taken for 4000 s, with a droplet having an initial volume \(≈14\ \mu\)L, before being shrunk to \(≈6\ \mu\)L at \(≈1000\) s for 500 s, before being left to equilibrate for 500 s. After equilibration of the droplet, it was then grown again at \(≈2500\) s for a further 500 s until it approximated its original volume, before being left to equilibrate once more to complete the measurement. Contact angle measurements were taken by dispersing a droplet onto the coated substrate in air.

**Dip Coating:** Dip coating was performed on glass slide substrates coated with acetone, ethanol, and ultra pure water before being plasma cleaned in an air plasma (Model PDC 002, Harrick Scientific Corporation) and treated with 30 W plasma power for 7 min. Langmuir–Blodgett deposition was performed with the substrate initially submerged, being inserted in at a rate of 5 mm min\(^{-1}\). Barriers were then closed at a rate of 5 mm min\(^{-1}\) in order to achieve desired level of compression. Substrate was kept in the dispersion medium for 15 min before being retracted at a rate of 3 mm min\(^{-1}\) in a single pass. Coating process was performed at 100% and 50% of initial interfacial area, with coating performed on fresh slides each time. Slides were allowed to air-dry before being stored at room temperature in a plastic petri dish. The coating dispersion was 500 mL of 0.5 mg mL\(^{-1}\) CNCs with and without 10 mm TEAC.

Manual dip coating was performed by manually inserting into vials containing dispersions containing 20 mL of 0.5 mg mL\(^{-1}\) CNC with and without either 0.1 mm DTAB or 10 mm TEAC at a rate of \(≈60\) mm min\(^{-1}\). Samples were incubated for 90 s before being removed at a rate of \(≈60\) mm min\(^{-1}\).

**Spin Coating:** Glass slide substrates were washed with acetone, ethanol, and ultra pure water before being plasma cleaned in an air plasma (Model PDC 002, Harrick Scientific Corporation) and treated with 30 W plasma power for 7 min. Spin coating was performed by depositing a 20 µL droplet of 3 mg mL\(^{-1}\) CNCs onto a cleaned slide before spinning at 1600 rpm for 1 min.

Atomic Force Microscopy: Height profiles of dip-coated glass were taken using a JPK Nanowizard 3 in AC (alternating contact) mode in air, with Bruker Model NHVCV cantilevers, with nominal resonant frequencies of 340 kHz. Scratching experiments were performed manually by gently running a razor blade over the coating, before gently blowing N\(_2\) gas over the surface to remove any detritus. Force measurements were measured using the same instrument, with Bruker MSCT cantilevers, at an approach velocity of 1 µm s\(^{-1}\) and 64 measurement points. Spring constants for each cantilever were measured using the Bechhoefer and Hutter thermal method.\(^{46}\)

**Quartz Crystal Microbalance:** QCM with dissipation (QCM-D) measurements were performed using a QSense-E4 from Biolin Scientific Ltd. Silicon dioxide coated quartz crystals (QSensor QSX 303) were used after treating with UV–ozone for 10 min. The sensors were placed in QCM liquid cell modules, and ultrapure water was pumped to make a flat and stable baseline. After that, 0.5 mg mL\(^{-1}\) CNC dispersions in the presence and absence of either 0.1 mm DTAB or 10 mm TEAC were pumped in the modules with a flow rate of 150 µL min\(^{-1}\). Measurements continued until CNCs fully adsorbed on the sensor surface and saturation was attained. The change in the sensor’s frequency and dissipation was monitored for different overtones simultaneously. After equilibration, the sensor’s surface was flushed with the ultrapure water to assess whether CNCs could be stripped from the sensor surface. Experiments were repeated for negative controls containing only DTAB or TEAC, with the TEAC experiment also being undertaken on gold coated quartz crystals (QSensor QSX 301).

**Statistical Analysis:** Preprocessing of data: AFM data were processed with a polynomial baseline correction following removal of defect lines (up to 3 per 256 line image). Surface pressure was calculated as the change in surface tension in mN m\(^{-1}\) from an uncompressed system, normalized to \(\frac{A}{A_0}\). QCM data were processed following standard protocols for QSense software with runs, replicates and overtones as stated below.

Data presentation and sample size (n): Dynamic light scattering (3 runs of 5 cycles), zeta potential (5 runs of 20 cycles), and contact angle (n = 3) data were presented as mean ± standard deviation. AFM data were presented as absolute height profiles as measured at the instrument piezo (n > 3). Cross sectional thickness was presented as the mean across the area ± standard deviation (n = 1, consistent with AFM height profiles). Breakthrough force measurements were presented as frequency histograms with bins of 2 nm for distance and 0.1 nN for force (n = 64). Surface pressure was presented in mN m\(^{-1}\) as a function of compression (\(\frac{A}{A_0}\)) (presented with n = 1, but qualitatively consistent across repeated pendant drop tensiometry experiments and two different Langmuir troughs). XRR data were reduced to 1D intensity versus q plots and presented as the mean ± standard deviation, with corresponding scattering length density profiles (n = 1 for each system at each compression level). QCM were presented as the change in dissipation and frequency over time for three relevant overtones (n = 1 for presented data for all systems, however the experiment was repeated for the CNC and TEAC system and negative controls with consistent results).

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**
The authors would like to acknowledge the Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, for use of their X-ray reflectivity instrumentation (P3875 and P9494). This work was supported in part by the grant of an ARC Future Fellowship (FT160100191) to R.F.T. and an Australian Government Research Training...
Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
adsorption, cellulose nanocrystals, coating, hydrotropes, reflectometry

Received: April 10, 2022
Revised: August 17, 2022
Published online: September 14, 2022

[1] F. Bresme, M. Oettel, J. Phys.: Condens. Matter 2007, 19, 413101.
[2] A. Donev, F. H. Stillinger, P. Chaikin, S. Torquato, Phys. Rev. Lett. 2004, 92, 255506.
[3] F. Cherhal, F. Cousin, I. Capron, Biomacromolecules 2016, 17, 496.
[4] M. Vis, J. Opdam, I. Van’t Oor, G. Soligno, R. Van Rijoi, R. H. Tromp, B. H. Erné, ACS Macro Lett. 2015, 4, 965.
[5] W. Ramsden, Proc. R. Soc. Lond. 1904, 72, 156.
[6] S. U. Pickering, J. Chem. Soc., Trans. 1907, 91, 19.
[7] B. P. Brinks, T. S. Horozov, Colloidal Particles at Liquid Interfaces, Cambridge University Press, Cambridge 2006.
[8] S. Reynaert, P. Moldenaers, J. Vermant, Langmuir 2006, 22, 4936.
[9] W. Kunz, K. Holmberg, T. Zemb, Curr. Opin. Colloid Interface Sci. 2016, 22, 99.
[10] G. A. Turpin, S. A. Holt, J. M. Scofield, B. M. Teo, R. F. Tabor, Adv. Mater. Interfaces 2020, 7, 1901810.
[11] I. Capron, O. J. Rojas, R. Bordes, Curr. Opin. Colloid Interface Sci. 2017, 8, 83.
[12] W. Orts, L. Godbout, R. Marchessault, J.-F. Revol, Macromolecules 1998, 31, 5717.
[13] J. Araki, S. Kuga, Langmuir 2001, 17, 4493.
[14] Y. Habibi, I. Hoeger, S. S. Kelley, O. J. Rojas, Langmuir 2010, 26, 990.
[15] N. T. Cervin, E. Johansson, J.-W. Benjamins, L. Wågberg, Biomacromolecules 2015, 16, 822.
[16] P. Bertsch, P. Fischer, Langmuir 2019, 35, 7937.
[17] X. M. Dong, D. G. Gray, Langmuir 1997, 13, 2404.
[18] D. Coetze, M. Venkataraman, J. Milityk, M. Petru, Polymers 2020, 12, 742.
[19] L. Zhao, H. Wang, K. Huo, L. Cui, W. Zhang, H. Ni, Y. Zhang, Z. Wu, P. K. Chu, Biomaterials 2011, 32, 5706.
[20] R. Prathapan, J. D. Berry, A. Fery, C. Garnier, R. F. Tabor, ACS Appl. Mater. Interfaces 2017, 9, 15202.
[21] J. Goswami, E. Haque, D. Fox, J. Gilman, G. Holmes, R. Moon, K. Kalaitzidou, Materials (Basel) 2019, 12, 1951.
[22] M. Al-Hussein, E. M. Herzig, M. Schindler, F. Löhrer, C. M. Palumbiny, W. Wang, S. V. Roth, P. Müller-Buschbaum, Polym. Eng. Sci. 2016, 56, 889.
[23] Z. Hu, S. Ballinger, R. Pelton, E. D. Cranston, J. Colloid Interface Sci. 2015, 439, 139.
[24] Y. Wang, Y. Zhang, X. Li, M. Sun, Z. Wei, Y. Wang, A. Gao, D. Chen, X. Zhao, X. Feng, Sci. Rep. 2015, 5, 10107.
[25] A. Brinkmann, M. Chen, M. Couillard, Z. J. Jakubek, T. Leng, L. J. Johnston, Langmuir 2016, 32, 6105.
[26] A. Alam, M. Howlader, M. Deen, J. Micromech. Microeng. 2014, 24, 035010.
[27] Y. Habibi, L. Foulon, V. Aguié-Béghin, M. Molinari, R. Douillard, J. Colloid Interface Sci. 2007, 316, 388.
[28] J. Berry, M. Neeson, R. Dagastine, D. Chan, R. Tabor, J. Colloid Interface Sci. 2015, 454, 226.
[29] E. Huang, A. Skoufs, T. Denning, J. Qi, R. R. Dagastine, R. F. Tabor, J. D. Berry, J. Open Source Software 2021, 6, 2604.
[30] M. Basavaraj, G. Fuller, J. Fransaer, J. Vermant, Langmuir 2006, 22, 6605.
[31] A. Nelson, J. Appl. Crystallogr. 2006, 39, 273.
[32] A. D. Prescott, J. Appl. Crystallogr. 2019, 52, 193.
[33] G. Sauerbrey, Z. Phys. 1959, 155, 206.
[34] S. Garcia-Manyes, G. Oncins, F. Sanz, Biophys. J. 2005, 89, 4261.
[35] E. Kontturi, L.-S. Johansson, K. S. Kontturi, P. Ahonen, P. C. Thune, J. Laine, Langmuir 2007, 23, 9674.
[36] R. Prathapan, R. Thapa, G. Garnier, R. F. Tabor, Colloids Surf. A 2016, 509, 11.
[37] P. Bertsch, M. Diener, J. Adamcik, N. Scheuble, T. Geue, R. Mezzenga, P. Fischer, Langmuir 2018, 34, 15195.
[38] R. F. Tabor, D. Y. Chan, F. Grieser, R. R. Dagastine, Angew. Chem. 2011, 123, 3516.
[39] C. Brinatti, J. Huang, R. M. Berry, K. C. Tam, W. Loh, Langmuir 2016, 32, 689.
[40] I. Chae, D. Ngo, M. Makarem, Z. Ounaies, S. H. Kim, J. Phys. Chem. C 2019, 123, 25628.
[41] A. Tanaka, S. Ikeda, Colloids Surf. 1991, 56, 217.
[42] J. Pang, Y. Wang, G. Xu, T. Han, X. Lv, J. Zhang, J. Phys. Chem. B 2011, 115, 2518.
[43] T. Kolarov, R. Yankov, N. Esipova, D. Exerowa, Z. Zorin, Colloid Polym. Sci. 1993, 271, 519.
[44] S. Ahualli, G. Iglesias, W. Wachter, M. Dulle, D. Minami, O. Glatter, Langmuir 2011, 27, 9182.
[45] E. Homede, A. Zigelman, L. Abezgauz, O. Manor, J. Phys. Chem. Lett. 2018, 9, 5226.
[46] E. Homede, M. Abi Jabel, O. Manor, Adv. Funct. Mater. 2020, 30, 2005486.
[47] S. J. Miklavcic, J. Chem. Phys. 1995, 103, 4794.
[48] J. L. Hutter, J. Bechhoefer, Rev. Sci. Instrum. 1993, 64, 1868.