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Dynamics of Cellulose Nanocrystals in the Presence of Hexadecyltrimethylammonium Bromide

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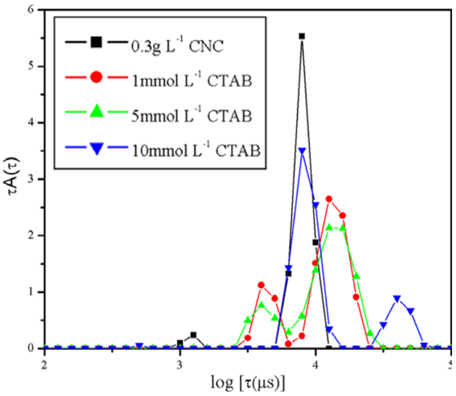
Abstract: A dynamic light scattering (DLS) study was performed to investigate the interactions of maize straw cellulose nanocrystals (CNC) with the cationic surfactant hexadecyltrimethylammonium bromide (CTAB). Phase analysis light scattering (which gives access to zeta potential (ζ) and electrical conductance) technique was used with the aim to obtain additional information. Zeta potential behavior demonstrated the colloidal systems are stable. By electrical conductance data, it was verified that the process of formation of micelles is thermodynamically spontaneous. Dynamic light scattering was shown to be very useful to find the optimum hydrolysis time so as to obtain well dispersed and more isolated nanocrystals. In the presence of the cationic surfactant CTAB, the formation of micelles and aggregates CNC/CTAB were well identified by DLS showing that the dynamics of cellulose nanocrystals in aqueous suspensions is strongly affected by the surfactant.



Keywords: cellulose nanocrystals, hydrolysis time, maize straw, light scattering, cationic surfactant, hexadecyltrimethylammonium bromide, micelles.

1. Introduction

Cellulose nanocrystals (CNC) are elongated needle-like nanoparticles commonly isolated by acid hydrolysis with sulfuric acid rendering negative charges on their surface.[1] Their good performance in the reinforcement of polymers was well documented in various studies.[1-3] In recent years new application fields have been opened for CNC as for example nanomedicine and catalysis.[1,4]

Recently it was shown some features of nanocrystals originated from maize straw cellulose.[5] Structures in the form of needles and some aggregates were detected through transmission electron microscopy (TEM) technique. By using an environmental friendly multistep procedure, the nanocrystals were isolated from maize straw cellulose being negatively charged due to the presence of sulfate groups on the surface. The CNC dimensions were obtained: the length value was L=(388±43) nm and the thickness was d=(19±2) nm resulting a value of 20 for the aspect ratio.[5] The aggregates of these strongly interacting nanostructures are formed through hydrogen bonding due to the high density of hydroxyl groups on the surface of cellulose chain molecules.[6,7]

The main studied application of cellulose nanocrystals has been as reinforcing fillers of polymer matrices, being the final material a polymer nanocomposite. It was reported by many researchers that a good dispersion of the nanocrystals in the polymer matrix is important to obtain a good reinforcing effect. If CNC are aggregated, they will not be well dispersed in the matrix and, by acting as stress concentrators, the reinforcing effect will be poor.[8,9] The natural tendency for aggregation of cellulose nanocrystals can be prevented - in water suspensions or even in polymer matrices - by modifying the CNC surface through the use of surfactants. The action of the surfactant is to make the hydrophilic head group of the surfactant molecule adsorb to the cellulose surface.[2,10] Modification of a cellulosic surface involves several types of interactions such as electrostatic and hydrophobic ones. In the studies of polymer/surfactant systems, two critical concentrations have been used to describe these interactions: the critical aggregation concentration (CAC) and the saturation concentration (C_2). CAC is the concentration of surfactant critical for the formation of polymer-surfactant complexes while C_2 corresponds to the saturation of the polymer by surfactant molecules.[11]

As observed in the literature, there are several physical techniques being used on CNC/surfactant aqueous suspensions studies, especially electrical conductivity and electrophoretic mobility measurements.[11-14] In spite of giving valuable information, dynamic light scattering technique (DLS) was scarcely used in CNC/surfactant studies. In this way more efforts should be made to improve the understanding of the interactions CNC/surfactant by using DLS.

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Characterization of CNC has basically aimed at the determination of sizes. The use of DLS for determining CNC size is not straightforward; it requires theoretical models as for example that of Broersma.[15] Being rods, cellulose nanocrystals have the length (L) and the thickness (w) as characteristic dimensions. In DLS the decay rate of intensity autocorrelation is linked to translational diffusion coefficient and, by the Stokes-Einstein equation, the hydrodynamic radius (R_H) of the sphere can be calculated.[16] If the particle under study is not spherical, as the case of CNC, this R_H represents the radius of a sphere hydrodynamically equivalent to the particle under study. Considering CNC, the hydrodynamic radius is not equal to the length or the thickness. Recently Boluk *et al*. reported that the hydrodynamic radius of CNC was much smaller than the length.[17] Consequently, when CNC size characterization is undertaken, the use of R_H is meaningful only for purposes of comparing CNC rods of similar thickness.

Dynamic light scattering (DLS) has become a standard technique for investigating colloidal suspensions and polymer solutions.[17-20] The autocorrelation function of the electric field may be related to a distribution of relaxation times $A(\tau)$ often via a Laplace transform. In complex systems, $A(\tau)$ may contain various components but their identification nowadays is still under investigation.[19-21] Due to the aforementioned restriction of using R_H for CNC, in the present work we have calculated the distribution of relaxation times and not the distribution of hydrodynamic radii.

In this sense, the aim of this research is to investigate by DLS the interactions of CNC, isolated from maize straw cellulose, with the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) in aqueous suspensions. The investigation of the behavior of CNC/surfactant aqueous suspensions is performed with different concentrations of CTAB by using DLS and phase analysis light scattering (PALS). The latter allows the determination of the zeta potential. To our knowledge, this is the first paper that analyses relaxation time distributions of CNC in the presence of CTAB. It is demonstrated the importance of DLS as a very useful tool to better achieve information on the colloidal interactions. The role of these interactions has already shown to be effective in the reinforcement of hydroxypropylcellulose films by CNC.[3] The results of the present work may be thus extended to other application fields of CNC, for instance water treatment, emulsion stabilization, drug delivery and human tissue replacement.

2. Experimental

2.1. Materials

Maize straw was supplied by the agronomic experimental station of Federal University of Rio Grande do Sul (UFRGS). Cellulose was extracted from maize straw according to a procedure described elsewhere.[5] Cellulose nanocrystals (CNC) were isolated by hydrolysis with sulfuric acid as already reported.[5] Hexadecyltrimethyl ammonium bromide CTAB (with ≥98% of purity) was purchased from Sigma Aldrich and used without further purification.

2.2. Preparation of CNC-CTAB aqueous systems

At first it was prepared an aqueous suspension with concentration of 0.3 g L^{-1} of cellulose nanocrystals. Aqueous solution of surfactant CTAB was prepared in this CNC suspension in a way to keep the final surfactant concentration in the range of 0.1 mmol L^{-1} to 10 mmol L^{-1}. The CNC/surfactant aqueous suspensions were then shaked for 12 h on an agitating bath. Each sample was kept at 24 h for agitation so that a clear CNC-surfactant suspension was achieved. In the case of light scattering and zeta potential measurements, each sample was analyzed after 1 h of centrifugation at 1,050 g.

2.3. Characterization techniques

2.3.1. Dynamic light scattering (DLS)

Light scattering measurements have been undertaken on a Brookhaven Instruments spectrometer, with a BI-9000 AT correlator and a He-Ne laser at 632.8 nm with power of 35 mW (Coherent). A Glan-Thomson prism (extinction ratio better than 10^{-7}) was placed at the entrance of the photomultiplier. The correct position of the prism was checked by using the depolarization ratio of toluene (ρ_V=0.359).[22] The measurements were taken at VV-geometry (both incident and scattered light vertically polarized). Before the measurements, each sample was agitated for 24 h in order to ensure equilibrium of CTAB and CNC. The samples were then centrifuged at 1,050 g for 1 h to remove dust. The correlator furnished intensity time autocorrelation functions $G_2(t)$ of the scattered light according to Eq. (1):

$$G_2(t) = \langle I(t) I(t+\tau) \rangle \tag{1}$$

where $I(t)$ denotes the scattered light intensity at time t and $I(t+\tau)$ the intensity at a delay time τ later. $G_2(t)$ was normalized by dividing it by the average intensity squared $<I^2>$ (baseline). The relaxation time distributions were obtained by using the Repes software[18,23] which performed an inverse Laplace transform according to Eq. (2):

$$g_2(t) - 1 = \left[\int A(\tau) \exp(-t/\tau) d\tau\right]^2 \tag{2}$$

with,
$g_2(t)$: normalized intensity autocorrelation function
$A(\tau)$: distribution of relaxation times

2.3.2. Zeta potential

A ZetaPALS equipment Model S/N: 31450 (Brookhaven Instruments, USA) was used to determine the zeta potential of the CNC suspension as well as that of systems CNC/CTAB. This equipment also gives access to the electrical conductance of the systems. Zeta potential (or electrokinetic potential) can be denoted as the potential at the surface of shear between the charged surface and the liquid when the electric double layer is considered.[24] The ZetaPALS instrument determines the zeta potential by using Phase Analysis Light Scattering: the phase shift of scattered light, directly proportional to applied electric field, is measured and related to the electrophoretic mobility.[25] According to the Smoluchowsky equation, zeta potential can be calculated from the electrophoretic mobility as follows:

$$U = \frac{\varepsilon_1 \varepsilon_0 \zeta}{\eta} \tag{3}$$

where
U: electrophoretic mobility
ε_0: permittivity in vacumm
ε_1: permittivity of the liquid
η: viscosity of the liquid
ζ: zeta potential

3. Results and Discussion

When a surfactant is added to a polymer solution, the formation of complexes between the polymer chains and the surfactant molecules is known to cause changes in physical properties, as for example the surface tension, viscosity, electrical conductance *etc*.[16] In this case, depending on the concentration of added surfactant, the stability of the colloidal system may increase.

The determination of zeta potential is a valuable tool for controlling the stability of a colloidal system, a feature which is crucial for extended lifetime of some colloidal market products as paints, food, cosmetic and pharmaceutical dispersions.[16] When the absolute values of the zeta potential increase, it means that the electrical potential at the surface of the charged particle also increases; the electrostatic repulsion forces between the charged particles become higher than the Van der Waals attractive forces, so the particles repel each other and the colloidal system is stable. When the zeta potential absolute values decrease and tend to zero, the electrostatic repulsion is small in comparison to Van der Waals attractive forces; the particles do not repel each other anymore and aggregation becomes possible. The colloidal stability of the system diminishes and eventually sedimentation or phase separation arises.[16]

In order to evaluate the colloidal stability of the nanocrystal suspension as a function of the surfactant concentration, electrophoretic mobilities were measured and zeta potentials were calculated according to Eq. (3). The results are shown in Figure 1. In absence of surfactant, the maize straw cellulose nanocrystals show a zeta potential value of ca. -45 mV. This value is similar to those reported for sisal and cotton nanocrystals.[26,27]

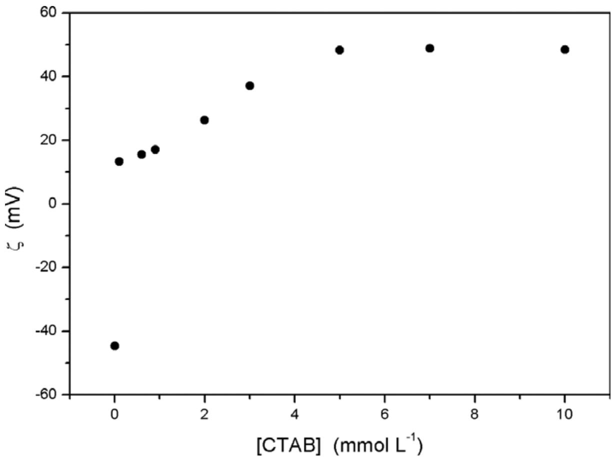

Figure 1. Zeta potential for the systems CNC/CTAB as a function of CTAB concentration.

When CTAB is present, zeta potential values increase, indicating the stability increases. This increase depends on the concentration. A similar dependence was also reported in the literature.[27] The positive values indicate that the cationic surfactant CTAB adsorbs to the surface of the nanocrystals with the cationic head directed outwards.[13] For concentrations higher than 5 mmol L^{-1} CTAB, zeta potential values seem to reach a plateau suggesting a saturation point. According to Dhar et al. such a plateau may be due to the presence of free micelles of the cationic surfactant.[12] However, at small concentrations of cationic surfactant, Dhar et al. and Hu et al. have reported that the surfactant/CNC system presents a negative zeta potential and that a charge reversal takes place at higher concentrations.[12,13] It happens that these authors have examined very low surfactant concentrations down to one tenth the value of the critical micelle concentration (CMC). In the present work this charge reversal was not observed because the lowest surfactant concentration is already near CMC where the zeta potential approaches zero. Furthermore the CNC aqueous suspension used in this work is more dilute than those reported elsewhere being our CNC concentration almost one tenth of that employed by Hu *et al*.[12,13] It seems that CTAB completely covers the CNC surface rendering positive values for the zeta potential irrespective the CTAB concentration.

From the electrophoretic mobility, another important parameter can be obtained, namely the electrical conductance. Figure 2 shows the results of the electrical conductance for nanocrystal suspensions as a function of CTAB concentration at a fixed nanocrystal concentration. The conductance increases with the addition of surfactant and two linear regions can be detected. The interception of the two straight lines allows to determine the critical aggregation concentration (CAC) of the system nanocrystal/CTAB which is [CTAB]=1.2 mmol L^{-1}. This CAC value is close to the CMC one in water at 25 °C reported in the literature[20,21] as [CTAB]=0.95 mmol L^{-1}.

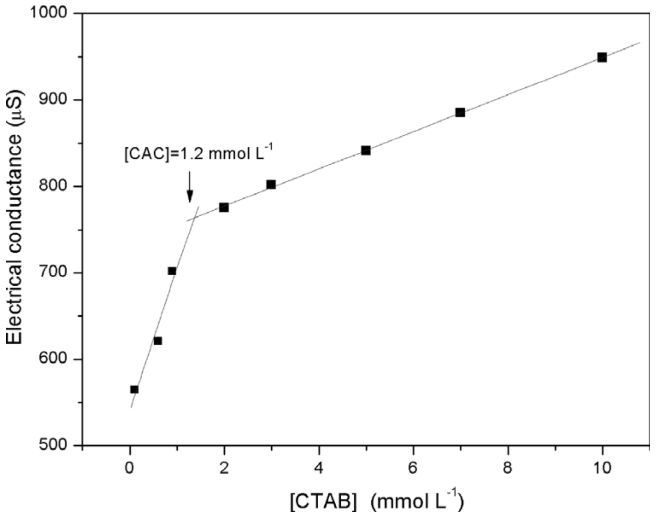

Figure 2. Electrical conductance for the systems CNC/CTAB as a function of CTAB concentration. The critical aggregation concentration (CAC) is indicated by the interception of the straight lines.

The electrical conductance increases linearly with the surfactant concentration both in the premicellar and postmicellar regions due to the concentration increase of ions of the polar group of the surfactant. The slope of the straight line in the premicellar region is higher than that in the postmicellar region. The increase in the electrical conductance in premicellar region is due to the availability of free surfactant ions but at higher surfactant concentration (in postmicellar region), the movement of surfactant free ions is reduced due to interactions with maize straw cellulose nanocrystals. As the surfactant is adsorbed on the surface of cellulose nanocrystals, there is a reduction in the contribution of ionic conductance of surfactant unimers and the formation of surfactant micelles becomes easier, since the free ions contribute more to the conductance of solution in comparison to the ions in micelles.

According to the mass action model for micelle formation of ionic surfactant, the standard Gibbs free energy of micellization (ΔG^o_{mic}) at the critical concentration as well as the degree of counterion binding (β) can be calculated by Eqs. (4) and (5) where S_2 represents the slope of the straight line in the postmicellar region in the electrical conductance plot (Figure 3) and S_1 the slope in the premicellar one.[28-30]

$$\Delta G^o_{mic}=(1+\beta)\,RT\ln X_{cmc} \tag{4}$$

$$\beta=1-(S_2/S_1) \tag{5}$$

The symbol X_{cmc} stands for the mole fraction of surfactant molecules at the critical concentration, R is the universal gas constant (R=8.314 J mol^{-1} K^{-1}) and T is the absolute temperature. The system CNC/CTAB shows a β value of 0.86 meaning that it has 86% binding of Br$^-$ ions to the micelles. The standard Gibbs free energy of micellization is negative (ΔG^o_{mic}=-49.6 kJ mol^{-1}) so the process is thermodynamically spontaneous.

Figure 3 shows distributions of relaxation times obtained at the scattering angle of 45° for suspensions of maize straw nanocrystals prepared with different hydrolysis times. As it can be observed in this figure, the dynamics of the nanocrystal suspension prepared with the shortest hydrolysis time, *i.e.* 15 min, was able to detect two peaks: one with narrow distribution located at longer relaxation times and another with a very low intensity at shorter relaxation times.

On the other hand, when the hydrolysis time increases, the distribution peaks become wider and with lower intensity. In addition the dynamic process shows that the nanocrystal suspensions, prepared with hydrolysis times lower than 120 min, have two peaks: one at shorter times and another at longer times which can be due to individual crystals and to aggregated crystals, respectively. The peaks at longer times (between 10^5 and 10^7 microseconds) should be assigned to the aggregates. The nanocrystals prepared with 150 min hydrolysis time show only one narrow peak (between $10^{3.5}$ and $10^{4.5}$ microseconds). So it can be concluded that 150 min of hydrolysis reaction for maize straw cellulose is the optimum time to obtain well dispersed and more isolated nanocrystals. This is the reason why this sample was chosen for the present study.

Figure 4 shows the effect of the cationic surfactant CTAB on the dynamic behavior of the nanocrystal suspensions prepared with 150 min of hydrolysis time. The scattering angle is 45°. The addition of CTAB brought about significant changes and it generated two peaks as it can be seen in the distributions. Table 1 collects the values of the peak maxima.

The peaks at shorter relaxation times (peaks 1) are due to the isolated nanocrystals. Those peaks at longer relaxation times (peaks 2) can be assigned to aggregates of nanocrystals and micelles. When the CTAB concentration increases, it can be noticed a shift to longer relaxation times, *i.e.* more micelles are formed which bind to each other forming more aggregates. By electrical conductance (Figure 3) it was determined the value of the critical aggregation concentration (CAC) for the system CTAB/nanocrystals which is 1.2 mmol L^{-1}. Dynamic light scattering measurements were also conducted at the scattering angle of 90° but in this case the addition of CTAB shifts the peaks only slightly to longer relaxation times (not shown). This depen-

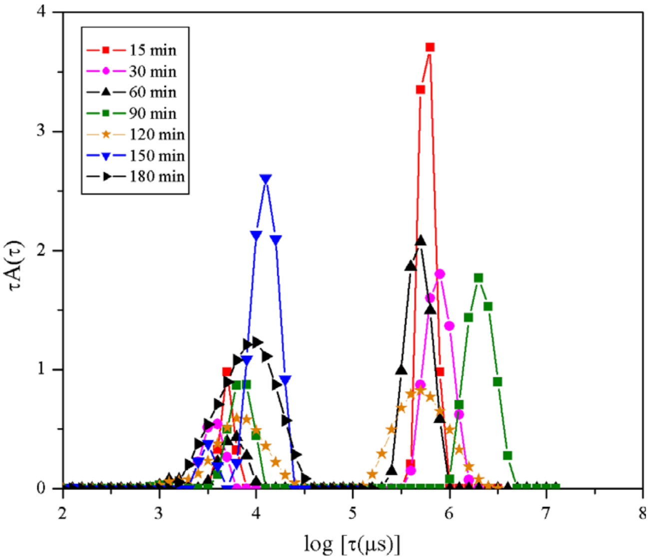

Figure 3. Distribution of relaxation times for the CNC suspensions prepared at various hydrolysis times (CNC=0.3 g L^{-1}, T=298 K and scattering angle 45°).

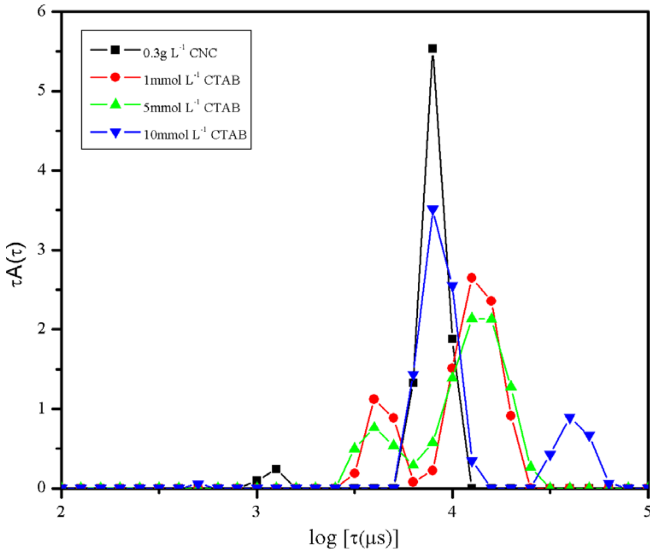

Figure 4. Distribution of relaxation times for the systems CNC/CTAB being the CNC sample that prepared at 150 min hydrolysis time (CNC =0.3 g L^{-1}, T=298 K and scattering angle 45°).

Table 1. Peak maxima (μs) of relaxation time distributions of CNC/CTAB suspensions as a function of CTAB concentration

CTAB concentration (mmol L^{-1})	Peak 1 (μs)	Peak 2 (μs)
0^a	$10^{3.89}$	-
1	$10^{3.58}$	$10^{4.10}$
5	$10^{3.60}$	$10^{4.14}$
10	$10^{3.90}$	$10^{4.59}$

[a] For all samples CNC concentration is 0.3 g L^{-1}.

dence on the scattering angle demonstrates the need to perform DLS measurements not only at 90° angle in the case of the large particles, since it is well known that at lower angles there is less destructive interference of the scattered light.[31]

4. Conclusions

The interaction of maize straw cellulose nanocrystals with the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) was studied by dynamic light scattering (DLS) technique as well as zeta potential (ζ) and electrical conductance data. Zeta potential behavior demonstrated that the colloidal systems are stable and evidences were found that CTAB adsorbs to the surface of the nanocrystals with the cationic head directed outwards and that CTAB completely covers the CNC surface. For concentrations higher than 5 mmol L^{-1} CTAB, zeta potential values seem to reach a plateau that may be due to the presence of free micelles of the cationic surfactant. By electrical conductance data, it was verified that the process of formation of micelles is thermodynamically spontaneous. To our knowledge, this is the first time that relaxation time distributions of CNC were analyzed and they were shown to be very useful in the choice of the optimum hydrolysis time to obtain well dispersed and more isolated nanocrystals. Also, DLS technique was very helpful to better elucidate the role of the colloidal interactions. In the presence of the cationic surfactant CTAB, the formation of micelles and aggregates CNC/CTAB were well identified by DLS showing that the dynamics of CNC in aqueous suspensions is strongly affected by the surfactant. Many applications fields of CNC may benefit from the results of this work.

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