Interfacial activity and emulsion stabilization of dissolved cellulose

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A B S T R A C T

Some aspects of the interfacial behavior of cellulose dissolved in an aqueous solvent were investigated. Cellulose was found to significantly decrease the interfacial tension (IFT) between paraffin oil and 85 wt% phosphoric acid aqueous solutions. This decrease was similar in magnitude to that displayed by non-ionic cellulose derivatives. Cellulose’s interfacial activity indicated a significant amphiphilic character and that the interfacial activity of cellulose derivatives is not only related to the derivatization but inherent in the cellulose backbone. This finding suggests that cellulose would have the ability of stabilizing dispersions, like oil-in-water emulsions in a similar way as a large number of cellulose derivatives. In its molecularly dissolved state, cellulose proved to be able to stabilize emulsions of paraffin in the polar solvent on a short-term. However, long-term stability against drop-coalescence was possible to achieve by a slight change in the amphiphilicity of cellulose, effected by a slight increase in pH. These emulsions exhibited excellent stability against coalescence/oiling-off over a period of one year. Ageing of the cellulose solution before emulsification (resulting in molecular weight reduction) was found to favour the creation of smaller droplets.

1. Introduction

Emulsions find applications within a wide spectrum of technical areas ranging from pharmaceuticals, foods and cosmetics, to coatings, oil recovery and metalworking [1]. The efficient creation of an emulsion often requires an emulsifier, which facilitates dispersion by lowering the interfacial tension, and a stabilizer that prevents coalescence and flocculation of droplets by creating a net repulsion between them. Typically, surfactants, polymers and particles are used as emulsifier or stabilizer agents, but some amphiphilic polymers, like block copolymers, can accomplish both functions [2].

Several non-ionic cellulose derivatives are well-known and widely used commercially as emulsion stabilizers [3–9]. In more recent years, nano-celluloses have also been shown to have the ability to stabilize interfaces and thus work as alternative and more environmentally friendly emulsion stabilizers [10–16]. The progress in this area is fast and several promising applications have already emerged [17].

Recent reports argue that the amphiphilic nature of non-ionic cellulose derivatives cannot be taken as a solo effect of the different chemical modifications but also as a direct consequence of the native cellulose backbone [18,19]. Based on these considerations it would be reasonable to expect that, in its molecularly dissolved state, cellulose would have the ability to locate itself at the interface between oil and polar liquids and possibly act as a good emulsion stabilizer. The advantage of using native dissolved cellulose for emulsion stabilization would be that no previous chemical modification would be required. Of particular interest is the possibility to achieve cellulose dissolution in water-based solvents, such as aqueous sodium hydroxide solutions. In such a case, neutralization of the solvent after emulsification would result in water and salt, which could either remain in the final formulation or be easily removed.

The behavior of molecularly dissolved cellulose at interfaces is expected to be close to that of typical cellulose derivatives or any semiflexible amphiphilic polymer that shows interfacial activity, i.e., the tendency to adsorb at oil-water interfaces and reduce the free energy between the two phases [20]. In fact, recent molecular dynamics simulations indicate that molecularly dispersed cellulose gradually assembles at the oil-water interface eventually surrounding the oil droplet [21]. However, the properties of molecularly dissolved cellulose are clearly much less explored due to its well-known dissolution limitations [22,23].

Rein et al. were the first to report on the use of dissolved cellulose as the starting point for the production of emulsions [24]. They used two different approaches for creating emulsions, starting from a cellulose solution in the ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIMAc), namely: 1) coagulation of cellulose with water prior to dispersion of the oil and 2) dispersion of the oil into the cellulose solution, followed by coagulation of cellulose at the interface with water (in-situ regeneration of cellulose) (see in Fig. 1. for a schematic of the steps involved in the two methods). Shortly afterwards, Jia et al. reported on emulsions prepared via the former approach using a 85 wt% phosphoric acid...
acid solution in water as a solvent for cellulose [25,26]. The emulsions produced by either of the two methods were reported to display very good stability against drop coalescence.

In the first approach, particle stabilized (so called, Pickering) emulsions are produced by first regenerating cellulose from solution and then dispersing the oil in the resulting suspension of cellulose particles. Jia et al. suggested that the mechanism behind droplet stabilization in emulsions prepared this way was similar to the one for emulsions stabilized by nano-celluloses as described elsewhere, i.e., a combination of particle adsorption (Pickering stabilization) and network formation in the continuous phase [11,17,25,27–29]. On the other hand, in the second approach, the mechanism of drop stabilization appears to be different. In this case, drops appear to be stabilized by a continuous “film-coating” which forms as regeneration of cellulose takes place on the surface of the oil droplets [24,30].

Apart from differences in the features of the resulting cellulose-coated drops, there is another fundamental difference between the two emulsifying mechanisms described. This difference has to do with the existence of dissolved cellulose during the initial stage of emulsification in the second approach. This aspect, to our knowledge not addressed in detail in any previous studies, is the focus of the present investigation.

The objective of this work is to gain a better understanding of the emulsification process via in-situ regeneration of cellulose from water-based solvents. In this particular case, a 85 wt% phosphoric acid solution was used for the purpose. Specifically, the work aims at assessing the interfacial activity of cellulose prior to in-situ regeneration and studying its possible influence on the properties of oil/w water emulsions produced before and after cellulose regeneration. As ageing of cellulose in acidic solutions has been reported to induce a reduction of its molecular weight due to acid hydrolysis [31], its effect on the interfacial and emulsion stabilizing properties of cellulose was also investigated. The molecular weight of cellulose in solution after different ageing times was assessed by means of size exclusion chromatography, while the interfacial tension between oil and aqueous solutions of phosphoric acid was assessed by means of gel permeation chromatography (GPC), cellulose was regenerated from the acidic solution (85 wt%) at room temperature and placed in an ultrasound water bath until complete dissolution was attained. This process took typically ca. 1–2 h. Cellulose solutions were allowed to age from 24 h to 360 h under stirring and at room temperature.

2.3. Molecular weight analysis

To measure the molecular weight of cellulose by gel permeation chromatography (GPC), cellulose was regenerated from the acidic solution by coagulation with water. The solvent was removed by a sequence of centrifugation steps (16,000 rpm for 10 min), until the pH of the supernatant was 7. Most of the water was then carefully removed and the wet sediment of cellulose was freeze-dried for 48 h. Before the GPC analysis the different samples were treated as follows: 25 mg of pulp were solvent exchanged three times with 5 ml of Milli-Q water for 30 min, 5 ml of methanol for 30 min, followed by three times for 30 min with DMac. The excess of DMac was removed and 5 ml of 8% (w/v) LiCl/DMac was added, and left overnight at room temperature with gentle magnetic stirring. The samples were thereafter diluted with 20 ml of DMac. GPC measurements were performed on a PL-GPC 210 (Polymer Laboratories Ltd., UK) at 70 °C with 0.5% (w/v) LiCl/DMac as the mobile phase at a flow rate of 1 ml/min. A guard column, Mixed-A 20 μm 7.5 × 50 mm, and two Mixed-A 20 μm 300 × 7.5 mm were connected in series, and a refractive index detector was used (Polymer Laboratories Ltd., UK). Eight pullulan standards were used for the molecular mass calibration (708, 344, 200, 107, 47, 21, 9,6, and 6.1 kDa, Polymer Laboratories Ltd., UK). The sample injection volume was 100 μL and the results were processed by the Cirrus GPC software (Polymer Laboratories Ltd., UK).

2.4. Shear viscosity measurements

Flow curves of the solvent and cellulose solutions were determined using a controlled stress MCR 300 rheometer (Anton Paar) equipped with a Peltier measuring cell that kept the temperature constant at 20 °C. A bob and cup measuring geometry was used and the shear rate interval was 1 to 1000 s for all samples. Before each measurement, samples were allowed to equilibrate for 120 s and an inverse log time scale was used to ensure that the experimental points at low shear rates were measured for longer times, so that steady state viscosity was achieved for each of the points.

Fig. 1. Two established approaches of preparing emulsions stabilized by cellulose [24–26,30,32].

The cellulose used was a commercial sulfite dissolving pulp provided by Domjö Fabriker, Sweden, with a weight average molecular weight (M_w) of 3.2 × 10^5 g/mol and a polydispersity index of 10, as determined by size exclusion chromatography in a LiCl/DMac solvent system calibrated by pullulan standards. This cellulose is free of any additives and the content of extractable components (in acetone) is below 0.05%, which is the quantification limit of the analysis (SCAN-CM 49:03). Based on this, the calculated maximum amount of wood resins (e.g. oleic acid and abietic acid) in 0.1% cellulose solutions is lower than 2 μL. The phosphoric acid solution (85 wt%) was obtained from VWR Chemicals, France. The oil phase used was liquid paraffin (dynamic viscosity of 110–230 mPa·s) from Merck KGaA, Germany.

2.2. Cellulose dissolution

Cellulose sheets were ground in a blender prior to dissolution. Then, the desired amount of ground cellulose was mixed with the phosphoric acid solution (85 wt%) at room temperature and placed in an ultrasound water bath until complete dissolution was attained. This process took typically ca. 1–2 h. Cellulose solutions were allowed to age from 24 h to 360 h under stirring and at room temperature.

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2.5. Interfacial tension

The interfacial tension (γ) between paraffin oil and the different cellulose solutions was measured as a function of time by means of an automated drop tensiometer OCA40 coupled to a piezo-electric oscillation generator (DataPhysics, Germany). The measurements were based on axisymmetric drop shape analysis of an oil droplet (4 μl) immersed in a cuvette containing ca. 3.5 ml of the cellulose solutions. A crooked needle was used in order to be able to handle drops with lower density than that of the surrounding medium. The interfacial tension values were typically followed during 6–7 min and measurements were repeated 3 to 4 times for each solution.

2.6. Emulsification procedure

Emulsions of paraffin in cellulose-phosphoric acid solutions were produced by means of ultrasonic homogenization using a VCX 750 ultrasonic processor equipped with a microtip at a frequency of 20 kHz and maximum amplitude of 40%. 10 ml of a 0.1 wt% cellulose solution and 1.5 ml of oil were poured in a beaker subsequently. The sonicator’s tip was then placed close to the oil-water interface to ensure good mixing of both phases and sonication was turned on and conducted for a total time of 10 min in a pulse mode (10 s ON, 5 s OFF). After the first 2 min of homogenization, 8.5 ml of water were added slowly while sonication continued for the remaining time. The pH of the emulsions by the end of the process was approximately 0.5.

2.7. Drop size distribution

The drop size distribution (DSD) of freshly prepared emulsions was determined by means of laser light diffraction (Mastersizer 3000; Malvern Instruments, UK). For these measurements, a small volume of the emulsion was added drop-wise into a water-filled flow cell until an obscuration (i.e. indirect indication of the amount of drops) between 10% and 12% was attained. A value of 1.473 was used as the refractive index of the paraffin oil. The drop size analysis is presented as the distribution frequency in volume. The DSD was determined in emulsions both before and after neutralization with 10 M NaOH solution (pH~8). Samples were analysed in duplicates.

3. Results and discussion

3.1. Cellulose molecular weight and solution viscosity: effect of cellulose hydrolysis

Fig. 2 shows the molecular weight distributions of the ground cellulose pulp (black line) and the regenerated cellulose pulps (RCP) after ageing in phosphoric acid solutions for 24, 96, 168 and 360 h (i.e. 1, 4, 7 and 15 days, respectively). The molecular weight averages and polydispersity index (PDI) for each sample are presented in Table 1. The process of grinding the cellulose sheets prior to dissolution had already an effect on the molecular weight of cellulose, and the polydispersity of the sample was reduced from 10 to 9.0. Dissolution in phosphoric acid brings about a significant reduction of the molecular weight of cellulose, the largest drop occurring within the first 24 h after dissolution (Fig. 2). After the first 24 h of ageing the Mw continues to drop at a slower pace and the Mw distribution becomes narrower. After 15 days of ageing, the sample displays a significantly lower polydispersity (PDI in Table 1) and exhibits a viscosity very close to that of the solvent (Fig. 3), being then stable for at least one month.

The drop of the viscosity along with the decrease in molecular weight can be very useful because it facilitates the mixing of the two phases in the emulsification procedure, and also, smaller fragments of cellulose are expected to diffuse and adsorb faster compared to high molecular masses. Furthermore, the cellulose concentration can be increased in these systems without a major rise in viscosity.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Mn (g/mol)</th>
<th>DPW</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground pulp</td>
<td>310,000</td>
<td>240,000</td>
<td>34,000</td>
<td>1700</td>
<td>9.0</td>
</tr>
<tr>
<td>RCP-24 h</td>
<td>25,000</td>
<td>23,000</td>
<td>11,000</td>
<td>140</td>
<td>2.4</td>
</tr>
<tr>
<td>RCP-96 h</td>
<td>17,000</td>
<td>15,000</td>
<td>7800</td>
<td>92</td>
<td>2.1</td>
</tr>
<tr>
<td>RCP-168 h</td>
<td>13,000</td>
<td>11,000</td>
<td>6700</td>
<td>72</td>
<td>2.0</td>
</tr>
<tr>
<td>RCP-360 h</td>
<td>7700</td>
<td>5400</td>
<td>4600</td>
<td>43</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Fig. 2. Molecular weight distributions of the ground cellulose pulp (black line) and the regenerated celluloses after ageing in phosphoric acid solutions (lines in colour), labelled as RCP (regenerated cellulose pulp) followed by the corresponding ageing time in solution.

3.2. Interfacial activity of cellulose

The extent of initial liquid break-up into droplets, resulting from the mechanical shearing during the homogenization process, is largely controlled by the interfacial tension between the two immiscible phases: the lower the interfacial tension, the easier it is to break-up large droplets into smaller ones [2]. To gain insight into the interfacial activity of
cellulose, the interfacial tension (IFT) between paraffin oil and phosphoric acid solutions was measured in the presence and absence of dissolved cellulose; in the former case, the effect of the ageing time was investigated (Fig. 4a). Mineral acids are classified as direct solvents for cellulose, i.e., solvents that only interact with the polymer by physical means and do not form any covalent bonds [33,34]. Thus, any functionalization of the polymer in 85 wt% phosphoric acid solution is discarded.

The IFT between paraffin oil and the acidic solvent was found to decrease with time starting at 45 mN/m and reaching ca. 31 mN/m after 400 s. As it can be inferred from Fig. 4a, the presence of cellulose (0.1 wt%) induces a significant reduction of the IFT with respect to that of the paraffin/acidic solvent system. For cellulose solutions aged from 24 h to 168 h (7 days), the IFT measured at 400 s was 14 mN/m units lower than the one found for the acidic solvent alone, and it was further decreased by 3 mN/m for the cellulose solution aged for 360 h (15 days). Thus, cellulose displays interfacial activity when dissolved in aqueous phosphoric acid solutions, the effect being slightly different for different molecular weights. The fact that the IFT is slightly lower for the lowest molecular weight of cellulose can have both thermodynamic and kinetic origins. Shorter molecules diffuse faster to the interface and allow the packing of a larger amount of emulsifier creating a more compact assembled layer, which in turn affects IFT. Larger molecules usually have slow and limited molecular rearrangements at an interface [2,35]. For an understanding of the behavior of molecularly dissolved cellulose it is of particular interest to compare the findings with those of cellulose derivatives, for which the solution and interfacial behavior has been thoroughly investigated. As an example there is a very similar pattern observed for methyl cellulose (MC) and hydroxypropylmethyl cellulose (HPMC). Lower molecular weights of these polymers were found to be more efficient in reducing the IFT between immiscible phases, which is explained by the diffusion of polymer molecules to the interface [36,37]. Moreover, solutions of 0.1 wt% MC and HPMC have been reported to lower the IFT between paraffin oil and water (45 mN/m) by similar amounts as observed for dissolved cellulose in this study. For these two cellulose derivatives, the IFT was found to decrease down to 17–30 mN/m, depending on the degree of substitution (DS-methoxyl) and molar substitution (MS-hydroxypropyl) [8]. A high content of hydroxypropyl groups was found to lead to an increase in IFT, while a high content in methoxyl groups counteracts this effect. We can thus conclude, firstly, that cellulose is interfacially active and, secondly, that the IFT values fall in the same range as for methylated celluloses. The interfacial activity of cellulose indicates a significant amphiphilicity. Recently, it has been argued from dissolution and other studies that cellulose has both hydrophobic and hydrophilic properties [18,19]. This was also inferred from considerations of the chemical structure of cellulose. The analogous behavior of cellulose and cellulose derivatives suggests that the interfacial activity of the latter results mainly from the cellulose backbone and is less related to the type of substituent.

3.3. Cellulose as emulsion stabilizer

3.3.1. Cellulose before regeneration

The ability of cellulose to stabilize drops of paraffin in aqueous solutions of phosphoric acid was qualitatively assessed through microscopy and visual observations of systems produced using the protocol described schematically in Fig. 5a. The micrograph in Fig. 5a shows the appearance of dispersions of paraffin oil in aqueous phosphoric acid in the presence of dissolved cellulose. While in the absence of dissolved cellulose the oil exists mainly in the form of large irregular domains (top image in Fig. 4b), in the presence of 0.1 wt% cellulose, the paraffin oil is observed to form small well-defined droplets consistent with those of emulsified systems (bottom image in Fig. 4b and micrograph in Fig. 5a). These emulsions are however short-lived, as drop coalescence, leading to complete phase separation, was found to occur within 24 h after preparation (see schematic in Fig. 5a). This may be a consequence of the intrinsic amphiphilicity of cellulose, which is evidenced by the significant reduction of the IFT in the presence of dissolved cellulose.
of poor steric stabilization due to either cellulose configuration in the solvent and at the interface and/or to the presence of short chain lengths, since a stronger thickening effect of the aqueous phase is usually achieved by long (derivatized) cellulose chains [8].

3.3.2. Cellulose after regeneration

By inducing in-situ regeneration of cellulose through addition of water to dispersions of paraffin in phosphoric acid (see schematic in Fig. 5b) emulsions with radically different properties are obtained. As depicted by the micrograph in Fig. 5b, the emulsions produced in this way are characterized by droplets of significantly smaller sizes and a much more homogeneous distribution of sizes than those seen in the system prior to regeneration. Creaming, with no evidence of oil separation, was observed over the first 24 h after preparation in these emulsions. In fact, these systems displayed an outstanding stability against drop coalescence, with no evidence of oiling off over one year (data not shown).

The smaller drop sizes and outstanding stability against drop coalescence in these systems, can be explained as a combined effect of the decreased solvency of cellulose (i.e. greater affinity for the interface) and the properties of the “cellulose film” that forms at the interface between the paraffin drops and the surrounding media. In the acidic solvent, cellulose is positively charged due to a significant degree of protonation which gives it a polar character. As water is added to the acidic cellulose solutions the degree of protonation decreases and cellulose molecules become less polar, thus increasing their affinity for the interface. This increased interfacial activity is expected to result in further reduction of the interfacial tension which in turn facilitates the drop break-up process. The simultaneous “precipitation” of the cellulose at the oil-polar solvent interface leads to
the formation of what appears to be a robust interfacial film which effectively prevents the coalescence of drops once they reach the low shear zones in the emulsification vessel.

A very slight increase in pH was needed to trigger the permanent adsorption of the cellulose molecules at the interface; the amount of water added to the metastable emulsion changed the pH from 0.1 to 0.5. No larger structural changes were observed in the emulsions when subsequently neutralizing them completely.

The stability of emulsions obtained after in-situ regeneration of cellulose, made them amenable for investigations of the effect of ageing time of the cellulose solutions on emulsion properties such as their particle size distribution. The droplet size distribution (DSD) and the median droplet size (D(0.5)) of the emulsions produced from the aged cellulose solutions are displayed in Fig. 6 and Table 2, respectively. The ageing time of the cellulose solutions was found to have an effect on the D(0.5) and the polydispersity of the size distributions for the different emulsions. In this respect, longer ageing times result in smaller median sizes and less polydisperse emulsions. The smallest drop sizes and narrower droplet size distribution is obtained for emulsions prepared with cellulose solutions aged for 360 h. This can be explained in terms of a combined effect of the low molecular weight and the low IFT of these systems. A low molecular weight favours faster diffusion to the newly created oil-water interface during homogenization. This, combined with a low IFT, is expected to favour drop break-up. Once again, these findings are in agreement with what is reported for HPMC. Droplet size increased with increasing molecular weight of HPMC at a fixed concentration [37]. Although no detailed analysis of the stability of these emulsions was carried out, all of them displayed no evidence of drop coalescence over a period of one year. It is worth mentioning that the pH of the emulsions after regeneration was typically 0.5. Further neutralization to pH 8 was found to have a minor effect on the average drop size of the emulsions and did not result in any apparent structural changes (Table 2).

4. Conclusions

The possibility of using molecularly dissolved cellulose to stabilize oil-in-water emulsions is investigated. The interfacial tension between oil and water is found to be lowered by cellulose dissolved in the aqueous medium, which is a concentrated solution of phosphoric acid. This interfacial activity demonstrates that cellulose molecules have a significant amphiphilicity. The lowering of the interfacial tension is similar in magnitude to that shown by some cellulose derivatives and it is argued that the amphiphilicity of those is to a large extent due to the cellulose backbone. Dispersion of oil in water is very much facilitated by dissolved cellulose, but the emulsions are not stable instead showing coalescence. This is ascribed to a too polar character of the cellulose molecules, due to protonation. If the balance between polar and nonpolar properties is slightly changed by addition of small amounts of water highly stable emulsions are formed. The droplet size and the stability of the emulsions were investigated for different molecular weights of cellulose. For the formation of stable emulsions with small droplets lower molecular weights are favourable, which can be understood from kinetics of macromolecular adsorption and rearrangements. This approach of doing emulsions, with dissolved cellulose, reveals very promising and might open a new perspective on making emulsions with non-modified cellulose.

Declaration of Competing Interest

None.

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