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Characterization of cellulose surface free energy

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Abstract—The thin-layer wicking technique was used to determine the surface free energy components and the surface character of three celluloses (Sigmacell 101, Sigmacell 20, and Avicel 101), using an appropriate form of the Washburn equation. For this purpose, the penetration rates of probe liquids into thin porous layers of the celluloses deposited onto horizontal glass plates were measured. It was found that the wicking was a reproducible process and that the thin-layer wicking technique could be used for the determination of the celluloses' surface free energy components. The size of the cellulose particles was characterized with the Galai CIS-100 system and their crystallinity was measured by X-ray diffraction. The three celluloses have high apolar ($\gamma_s^{LW} = 50-56$ mJ/m^2) and electron donor ($\gamma_s^- = 42-45$ mJ/m^2) components, while the electron acceptor component (γ_s^+) is practically zero. The free energy interactions of cellulose/water/cellulose calculated from the components are positive, regardless of the cellulose crystallinity. This would mean that the cellulose surfaces have a hydrophilic character. However, the work of spreading of water has a small negative value (3–9 mJ/m^2), indicating that the surfaces are slightly hydrophobic. It is believed that the work of spreading characterizes better the hydrophobicity of the surface than the free energy of particle/water/particle interaction, because in the latter case, no electrostatic repulsion is taken into account in the calculations.

Keywords: Cellulose; particle size; crystallinity; surface free energy components; hydrophobicity.

1. INTRODUCTION

Native cellulose is a high-molecular-weight linear polymer composed of D-glucanopyranose units joined by β-1,4-linkages in a long-chain molecule. Adjacent molecules are stabilized laterally by hydrogen bonding between hydroxyl groups, resulting in three-dimensional structures called fibrils [1, 2]. The purified cellulose materials consist of amorphous cellulose areas, in addition to well-ordered crystalline

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regions [2]. In nature, cellulose is usually mixed with lignin and hemicellulose, and probably amorphous and crystalline areas exist as well.

The surface free energy plays an important and determining role in the behaviour of cellulose materials in liquid media, for instance in what concerns solubility, particle aggregation, enzyme adsorption. However, the problem of surface and interfacial free energy determination has not been fully solved, even today [3, 4]. One of the methods used for the determination of solid surface free energy is the thin-layer wicking technique [4–8].

The approach of van Oss *et al.* [9], which considers the surface free energy as the sum of the apolar Lifshitz–van der Waals, γ_s^{LW}, and polar, γ_s^{AB}, interactions, is very likely the most popular one at present [3]. However, its validity is still a matter of controversy. Keeping that in mind, we still decided to use this approach in this work. Even if it does not provide absolute values for the polar components of the surface free energy, it does provide relative values, and a large set of data has already been published and is available for comparison. In any case, the work of water spreading was also used in the characterization of the cellulose interfacial properties.

The apolar interactions consist mainly of London dispersion forces. In general, the polar interactions can have an electron donor, γ^- (base), and/or an electron acceptor, γ^+ (acid), character [9]. In many cases, these interactions are only due to hydrogen bonding. Thus, the surface free energy of a given material (i) is expressed as follows [9, 10]:

$$\gamma_i^{TOT} = \gamma_i^{LW} + \gamma_i^{AB} = \gamma_i^{LW} + 2\left(\gamma_i^+\gamma_i^-\right)^{1/2}, \tag{1}$$

and the total interfacial free energy between two distinct condensed phases i and j (such as cellulose and water) can be expressed as

$$\gamma_{ij}^{TOT} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} = \left[\gamma_i^{LW} + \gamma_j^{LW} - 2\left(\gamma_i^{LW}\gamma_j^{LW}\right)^{1/2}\right] + 2\left[\left(\gamma_i^+\gamma_i^-\right)^{1/2} + \left(\gamma_j^+\gamma_j^-\right)^{1/2} - \left(\gamma_i^+\gamma_j^-\right)^{1/2} - \left(\gamma_i^-\gamma_j^+\right)^{1/2}\right]. \tag{2}$$

Then the interfacial free energy (ΔG^{IF}) between two particles of the same material (l) (for example, cellulose), in the water phase (w), is given by the equation [9, 10]:

$$\Delta G_{lwl}^{IF} = -2\gamma_{lw}. \tag{3}$$

When ΔG_{lwl}^{IF} is negative, there is attraction between the two surfaces of material l immersed in water (w), and hence this material is said to be hydrophobic. When ΔG_{lwl}^{IF} is positive, there is repulsion between the two surfaces, which indicates that the dispersion is stable (excluding electrostatic interactions). In this case, this material may be considered to be hydrophilic [11]. On the other hand, the hydrophobicity of a solid surface can also be described by the work of spreading of water, W_s, over the surface, which is the difference between the work of

adhesion, W_a, and the work of cohesion of water, W_c:

$$W_s = W_a - W_c = 2\left[\left(\gamma_s^{LW}\gamma_l^{LW}\right)^{1/2} + \left(\gamma_s^{+}\gamma_l^{-}\right)^{1/2} + \left(\gamma_s^{-}\gamma_l^{+}\right)^{1/2}\right] - 2\gamma_w. \quad (4)$$

The purpose of this work was to determine the surface free energy components of three celluloses (Sigmacell 101, Sigmacell 20, and Avicel pH 101), using the thin-layer wicking technique [4–7] and to evaluate the hydrophilic/hydrophobic character of their surfaces.

2. MATERIALS AND METHODS

Three celluloses, Sigmacell 101, Sigmacell 20 (both from Sigma), and Avicel pH 101 (Fluka) were used for the study. They were characterized as to their size distribution and crystallinity.

The particle size distribution of each cellulose was measured using a Galai CIS-100 granulometer (Galai Production Lda, Israel). For each cellulose, the experimental procedure was as follows: a suspension (10 mg/ml) in distilled water was prepared. Then, 100 μl of this suspension was added to 3 ml of distilled water in a magnetically stirred cuvette, and the size range was scanned from 0.5 to 150 μm [12]. The sample size distribution was also determined after 5 min of ultrasound treatment. The crystallinity of the celluloses was analysed by X-ray diffraction. The crystallinity index [I_{cr} (%)] was calculated from the X-ray diffraction spectra, as described by Segal *et al.* [13].

The thin-layer wicking experiments were carried out by starting with the preparation of a 5% (w/v) cellulose suspension in ultrapure water. Portions (4 ml) of the suspension were evenly distributed over the surfaces of horizontal glass plates (25 × 100 mm) and left at room temperature for the water to evaporate. Then the plates were dried at 110°C for 2 h and kept in a desiccator for 5 days. Afterwards, some plates were allowed to equilibrate for 12 h in a closed vessel with the saturated vapour of the probe liquids: *n*-hexane, *n*-decane, water, and formamide [4, 6–8]. The remaining plates were kept inside the desiccator.

The thin-layer wicking experiments were carried out in a closed sandwich chamber, where the plates were placed in a horizontal position upside down. A flannel wick about 2 cm long transported the probe liquids. The surface of the liquid used was at the same level as that of the tested plates in the sandwich chamber, to avoid any hydrostatic effect [8]. The wicking times corresponding to each centimetre section of the cellulose thin-layer were recorded, using a ruler placed next to the plates. The surface tensions of the probe liquids used for the wicking experiments are listed in Table 1. Wicking experiments were also performed with previously sonicated samples. In this case, cellulose samples were subjected to ultrasound for 30 min. As reported by Ragnar *et al.* [1], after sonicating a sample of Avicel pH 101 for 30 min the fragmentation was maximized.

Table 1.
Surface tension (at 20°C) and its components of the probe liquids used in the wicking experiments (van Oss and Good [14]), in mJ/m^2

Liquid	γ_l^{LW}	γ_l^+	γ_l^-	γ_l
n-Decane	23.8	—	—	23.8
n-Hexane	18.4	—	—	18.4
Water	21.8	25.5	25.5	72.8
Formamide	39	2.28	39.6	58

3. RESULTS AND DISCUSSION

The particle size distribution, as mentioned above, was characterized with the Galai CIS-100. The results (Table 2) are presented according to their mean sizes [d_{50} (μm)] of a volume distribution. As in all polydisperse systems, the median size of untreated samples represents individual particles and their agglomerates. Ultrasound treatment breaks down part of the agglomerates. The same effect has already been reported for Avicel pH 101 by Ragnar *et al.* [1] and Gama *et al.* [12]. Each value presented in Table 2 is the average of five independent assays. Each assay is the average of three measurements.

From the results presented in Table 2 it is also seen that Sigmacell 101 is mostly an amorphous cellulose ($I_{cr} < 60\%$), while Sigmacell 20 and Avicel are much more crystalline. Using these cellulose samples, it should be possible to find out whether the particle size, crystallinity, and ultrasound treatment affect the surface free energy components.

In order to determine the surface free energy components of the celluloses, a set of 24 plates of each cellulose was prepared [4, 6–8]. Twelve of them were used for pre-contacting with the test liquids. The wicking experiments with each probe liquid (both for bare and pre-contacted plates) were performed in triplicate. Each set of experiments was performed four times for the untreated samples, and twice for the sonicated ones. Figure 1 shows an example of the relationship between the time of thin-layer wicking and the squared distance obtained for Sigmacell 101 wicked by decane. The results obtained with the other liquids (hexane, water, and formamide) showed similar linear trends. For practical reasons, time t as a function of the penetrated distances x^2 was plotted, instead of the opposite relationship resulting from the Washburn equation (5) [4, 6–8]:

$$x^2 = \frac{Rt}{2\eta}\Delta G, \tag{5}$$

where R is the effective diameter of the inter-particle capillaries, η is the liquid viscosity, and ΔG is the specific free energy change accompanying the wicking process.

Table 2.
Median sizes [d_{50} (μm], and standard deviations [σ (μm)], on a volume basis, of the celluloses obtained with the Galai CIS-100 granulometer, and crystallinity

Cellulose	NT	US	I_{cr} (%)
Sigmacell 101	15.02 ± 0.91	12.42 ± 0.07	54.70
Sigmacell 20	37.20 ± 0.77	20.30 ± 0.41	91.54
Avicel	49.27 ± 1.10	34.77 ± 0.21	92.97

NT = Untreated samples; US = sonicated samples; I_{cr} = degree of crystallinity.

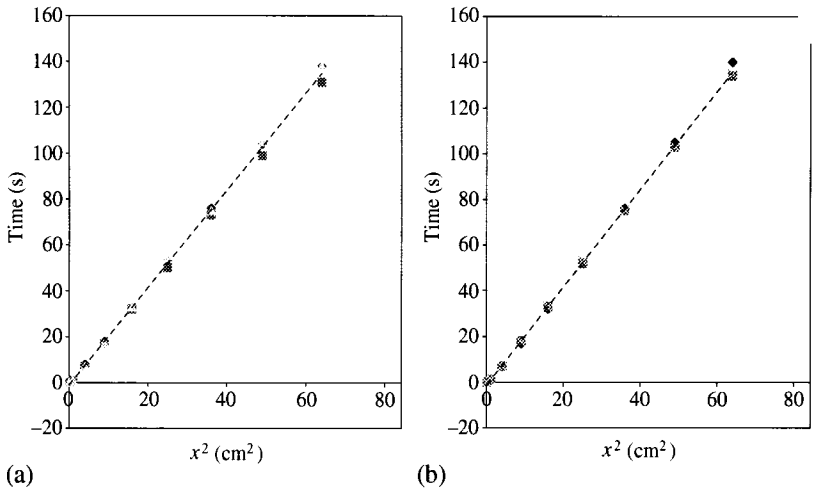

Figure 1. Time of decane wicking against the squared distance for Sigmacell 101-covered glass plates: (a) bare plates; (b) pre-contacted ones.

The extrapolated time corresponding to a 10 cm wicking distance was then calculated. An average time value was finally calculated from all of the experiments. The results obtained are presented in Tables 3 and 4.

The Washburn equation suits well the wicking process for all celluloses. Indeed, a good fit, like the one observed in Fig. 1, was obtained in each wicking experiment (minimum $r = 0.994$). The wicking experiments showed good reproducibility, as can be seen by the standard deviation of the average wicking times (Tables 3 and 4).

In order to calculate the parameter R, the wicking times for the celluloses pre-contacted with n-decane and n-hexane were used in the Washburn equation [equation (5)]. In this case, the ΔG value was equal to the surface tension of the probe liquid. The R values obtained are presented in Tables 5 and 6. From these tables, it can be stated that the reproducibility was good.

The apolar component of the surface free energy of the celluloses (Tables 7 and 8) was calculated using equation (5) and the wicking times for bare plates of decane

Table 3.
Average times (in s) for a 10 cm wicking distance for each cellulose. Untreated samples

	Bare plates				Pre-contacted plates			
	Decane	Hexane	Water	Formamide	Decane	Hexane	Water	Formamide
Sigmacell 101								
Average	431	206	762	2905	464	213	614	3160
σ	10	6	24	237	13	7	37	458
Sigmacell 20								
Average	438	205	387	1614	456	206	292	1525
σ	28	13	33	257	51	8	8	333
Avicel								
Average	190	90	189	882	169	98	142	666
σ	21	15	5	32	7	14	2	120

Table 4.
Average times (in s) for a 10 cm wicking distance for each cellulose. Sonicated samples

	Bare plates				Pre-contacted plates			
	Decane	Hexane	Water	Formamide	Decane	Hexane	Water	Formamide
Sigmacell 20								
Average	448	222	383	1603	475	216	340	1403
σ	18	15	24	149	20	24	51	21
Avicel								
Average	226	92	180	775	222	107	178	725
σ	21	15	36	109	23	2	25	13

Table 5.
R (μm) values obtained for the celluloses from pre-contacted plates with n-decane and n-hexane. Untreated samples

Cellulose	R_{decane} (μm)	R_{hexane} (μm)	Average R (μm)
Sigmacell 101	1.63	1.78	1.70 ± 0.11
Sigmacell 20	1.65	1.85	1.75 ± 0.14
Avicel	4.47	3.89	4.18 ± 0.41

alone. The hexane wicking times were not used for these calculations because hexane is a highly volatile liquid. In this case, when conducting these experiments, hexane vapour probably adsorbs ahead of the visible penetrating front. Thus, in fact, a duplex film forms ahead of the visible border of wicking hexane.

Table 6.
R (μm) values obtained for the celluloses from pre-contacted plates with n-decane and n-hexane. Sonicated samples

Cellulose	R_{decane} (μm)	R_{hexane} (μm)	Average R (μm)
Sigmacell 20	1.59	1.76	1.67 ± 0.13
Avicel	3.40	3.57	3.78 ± 0.12

Table 7.
Surface energy components of cellulose, interfacial free energy of the cellulose/water interaction, and the work of water spreading, W_s, in mJ/m^2. Untreated samples

Cellulose	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s^{TOT}	ΔG_{sls}^{IF}	W_s
Sigmacell 101	54.49	0.11	47.83	4.49	58.98	20.56	−3.54
Sigmacell 20	52.94	0.11	41.70	4.24	57.18	12.99	−9.11
Avicel	51.82	0.00	50.14	0.00	51.82	28.23	−8.15

Table 8.
Surface free energy of the celluloses, interfacial free energy of the cellulose/water interaction, and the work of water spreading, W_s, in mJ/m^2. Sonicated samples

Cellulose	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s^{TOT}	ΔG_{sls}^{IF}	W_s
Sigmacell 20	53.72	0.00	54.83	0.00	53.72	33.41	−3.75
Avicel	52.10	0.01	58.43	1.09	53.19	38.66	−0.27

Now, for the calculation of γ_s^{LW} from decane penetration, in equation (5), ΔG equals the work of wetting of the cellulose surface by the alkane (W_s) [4, 6–8]:

$$W_s = W_a - W_c = 2\left(\gamma_s^{LW}\gamma_l^{LW}\right)^{1/2} - 2\gamma_l. \tag{6}$$

The polar components for each cellulose were calculated as follows: the wicking times of water and formamide (Tables 3 and 4) were used to calculate the specific free energy changes [equation (5)], with either bare (ΔG_b) or pre-contacted (ΔG_p) plates. The W_s values [equation (7)] of water and formamide were used to solve the system of equations (8) and (9) [4, 6–8]:

$$\Delta G_b - \Delta G_p = W_a - W_c = W_s, \tag{7}$$

$$\text{(water)} \qquad W_s = 2\left[\left(\gamma_s^{LW}\gamma_w^{LW}\right)^{1/2} + \left(\gamma_s^+\gamma_w^-\right)^{1/2} + \left(\gamma_s^-\gamma_w^+\right)^{1/2}\right] - 2\gamma_w, \tag{8}$$

$$\text{(formamide)} \qquad W_s = 2\left[\left(\gamma_s^{LW}\gamma_f^{LW}\right)^{1/2} + \left(\gamma_s^+\gamma_f^-\right)^{1/2} + \left(\gamma_s^-\gamma_f^+\right)^{1/2}\right] - 2\gamma_f. \tag{9}$$

Table 9.
Apolar γ_s^{LW} and electron donor γ_s^- components of the solid surface free energy, in mJ/m^2

Solid	γ_s^{LW}	γ_s^-
Dextran 150	42	55
Cellulose acetate	38	33

The final results are presented in Tables 7 and 8. The interfacial free energy of the cellulose/water/cellulose interaction was then calculated from direct application of equation (3). The work of water spreading on the cellulose surfaces [equation (4)] was also determined. These results are listed in Tables 7 and 8.

Although Sigmacell 101 and Sigmacell 20 have different particle sizes (Table 2), the apparent porosity of the thin layers is quite similar, as seen by their similar R values (Table 5). These results also indicate that wicking occurs through inter- and intra-agglomerate pores.

From the polar components obtained, for each cellulose (Table 7), one can see that they have a high electron donor component. This could be expected by comparison with the surface free energy components of similar solid polymers [9, 14], such as dextran 150 and cellulose acetate (Table 9). However, the apolar components of the surface free energy for the celluloses studied are higher than those of the polymers in Table 9. Owing to the presence of hydroxyl groups at the cellulose surface, it is very much likely that the polar interactions are mainly due to hydrogen bonding.

The calculated values of the interfacial free energy of interaction, as obtained from equation (3) (Table 5), are positive for the three samples (Table 7), indicating a hydrophilic character. For Sigmacell 101, this could be expected, because the median particle size (Table 2) of both untreated and sonicated samples does not differ much, which means that this cellulose is stable in aqueous media. As to Sigmacell 20 and Avicel, the calculated hydrophilic character is in contradiction with the observed ability to aggregate (Table 2). As reported by Gama *et al.* [12], individual particles of Avicel pH 101 tend to form agglomerates. Therefore, not only should Avicel present a smaller value for the interfacial free energy, but it should also be a negative one, indicating its hydrophobic character. The same surface character should be expected for Sigmacell 20 because it is a crystalline cellulose, like Avicel, and also aggregates.

In contrast to the positive values of the celluloses' interfacial free energy, the work of spreading (Table 7) has a small negative value, implying that the surfaces are weakly hydrophobic. Moreover, the smallest value was calculated for the sample with the lowest crystallinity (Sigmacell 101), while for the samples having higher crystallinities the work of spreading for water was also higher. This is in accordance with the aggregation character shown by the celluloses. As to Sigmacell 101, it is possible that this cellulose exhibits a weak hydrophobic character (Table 7)

in aqueous media. However, owing to a higher density of hydroxyl groups at the particle surface, the hydration effects outweigh the hydrophobic effects, thus conferring particle stability. Thus, it seems that the work of spreading describes the interfacial properties better than the interfacial free energy of interaction.

As to the wicking experiments performed with previously sonicated samples, Sigmacell 101 was not used, as discussed before, because this cellulose is quite stable in aqueous media. The wicking times of the sonicated samples (Sigmacell 20 and Avicel, Table 4) and the R values (Table 6) are similar to those of the untreated ones. Hence, it can be concluded that the porosity of the solid thin-layer is almost the same, whether cellulose samples are presented in the form of agglomerates or individual particles resulting from sonication. However, for untreated and sonicated samples there are significant differences in the calculated values of the electron donor components while the apolar component is practically the same (Tables 7 and 8). The electron donor components, γ_s^-, of the sonicated samples are higher.

The interfacial free energy of interaction, ΔG_{sls}^{IF}, and the work of spreading, W_s, both have increased. Because the apolar component does not change and the electron donor component is higher (Tables 7 and 8), one can conclude that during sonication some of the hydrogen bonds between the cellulose particles are broken, which is demonstrated by an increased electron donor component.

From the results presented in this work, it was not possible to relate the surface properties of the cellulose materials to their crystallinity. In fact, the crystallinity, as measured by X-ray diffraction, represents an average value of the degree of organization of particles. Structural differences might be located in the 'inner' regions of the particles. However, as verified from kinetic studies of cellulose enzymatic hydrolysis [15], one would expect to find differences in the degree of organization in the first layers of the cellulose particles, since endoglucanase, which acts preferentially on the more amorphous areas of cellulose, seems to attack amorphous materials more easily than crystalline ones, at the very beginning of the reaction. Even if the number of accessible hydroxyl groups is similar in the two types of material, in a more crystalline cellulose they are probably organized in a more regular array, implying an extra reduction in entropy for adsorbed water molecules, compared with an amorphous cellulose. However, if such differences exist, they are not detected by the methodology used for surface characterization.

4. CONCLUSIONS

It is concluded that the wicking of porous layers of different celluloses is a reproducible process. The wetting rates agree with the Washburn equation. Therefore, the thin-layer wicking technique is suitable for the determination of the surface free energy components for celluloses, although it seems to be very sensitive to small experimental errors. This technique is especially useful in the analysis of particulate samples, where the contact angle technique cannot be used due to the porosity and difficulties in obtaining flat and homogeneous surfaces.

The cellulose samples studied show relatively strong apolar and electron donor components. In total, they exhibit a low hydrophobic character, as determined by the work of water spreading. This variable seems to describe the cellulose surface properties better than the interfacial free energy of interaction, as calculated from the van Oss approach, which suggests that the celluloses are hydrophilic. From the calculated values of the work of water spreading, W_s, the cellulose water suspensions would be expected to be unstable, as is observed, in some cases [12]. However, it was not possible to relate the surface properties of the celluloses to their crystallinities, because the technique is not sensitive enough for these differences and/or differences in crystallinity do not exist in the surface layer.

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