

# Assessment of the Water Sorption Properties of Several Microcrystalline Celluloses

John Roja<sup>1\*</sup>, Sebastian Moren<sup>1</sup>, Alvin Lopez

*Department of Pharmacy, School of Pharmaceutical Chemistry, The University of Antioquia, Medellin, Columbia*

## Abstract

This paper compares the water sorption behavior of commercial microcrystalline celluloses with those of cellulose II materials using several nonlinear models. Aqueous dispersions of cellulose II were spray-dried employing an inlet drying air temperature of 195 °C; atomizing air pressure of 1.0 kg-f/cm<sup>2</sup>; drying air flow-rate of 0.44 m<sup>3</sup>/min; feed flow-rate of 2.0 mL/min and nozzle diameter of 0.7 mm. Cellulose II samples were also spheronized in a Fuji Paudal spheronizer for 10 min at 1000 rpm. Products were analyzed for water sorption on a VTI<sup>®</sup> symmetrical gravimetric analyzer in triplicates. The Guggenheim-Anderson-de Boer (GAB), Hailwood-Horrobin (HH), Generalized D'Arcy and Watt (GDW) and Young and Nelson (YN) models were employed for the data analysis. Most of the sorption isotherms exhibited a type II sigmoid shape. Celphere<sup>®</sup>203, presented a type III isotherm and showed the highest monolayer capacity ( $m_0$  of 0.15 g water/g cellulose) and the lowest monolayer energy constant ( $C=1.0$ ) given by the GAB model. The GDW model indicated that the monolayer capacity ( $m_0$ ) and the fraction of sorption sites available for multilayer sorption ( $w$ ) were the highest for Celphere<sup>®</sup>203 (1.0 g/g cellulose and 1.0, respectively). The HH model indicated that Celphere<sup>®</sup>203 had the highest sorption capacity ( $W$  of 3.0 g/g sorption site). The YN model showed that this material had the largest water uptake by absorption into the core of the particles. Celphere<sup>®</sup>203 and SPCII were the most hydrophilic materials. Neither polymorphic form, nor silicification, was responsible for the difference in the hydrophilic properties of cellulose.

**Keywords:** Microcrystalline cellulose, sorption models, water sorption behavior

## 1. INTRODUCTION

Microcrystalline cellulose (MCC) is produced from cellulose, the most abundant natural linear polymer – made up of  $\beta(1\rightarrow4)$ -linked D-glucose repeat units – by heating in dilute strong mineral acids at boiling temperature until the level-off degree of polymerization is reached [1]. The acid-catalyzed hydrolysis of cellulose cleaves the  $\beta(1\rightarrow4)$ -glycosidic bonds of the chains that are present in the amorphous regions. Currently, spray-dried MCCs such as Avicel PH101 and Avicel PH102 are the most commonly and widely used direct compression excipients, since they render compacts of high strength. However, these materials suffer from long disintegration times. Prosolv<sup>®</sup>50 and Prosolv<sup>®</sup>90 are silicified co-processed products of MCC: SiO<sub>2</sub> at a 98:2 ratio. They show better flowability and compressibility and are less sensitive to magnesium stearate, but also have poor disintegrating properties [2]. Celphere<sup>®</sup>203 is a special densified MCC composed of spherical beads, used in the manufacturing of granules for sustained-release applications. These beads are produced by the extrusion and spheronization of the wet mass of MCC.

The above-mentioned materials all consist of the cellulose I (CI) allomorph, which is the most prevalent natural form of cellulose. However, a new microcrystalline cellulose II (CII), produced by mercerization of cellulose, has been introduced as a new direct compression excipient [3]. In cellulose I, the glucan chain orientation is exclusively parallel [4], whereas in CII the orientation is anti-parallel. CI can be converted to the more stable CII allomorph. CII is compatible with other excipients and active ingredients,

offering high dilution potential; it is a good disintegrant and relatively inexpensive [5].

The mechanical and disintegrating properties of these materials are related to their moisture content and water uptake capacity, respectively. In turn, the water uptake may depend on the polymorphic form of the polymer and also on the morphology of the material. Knowledge of the water sorption behavior of these processed materials is essential to understand and predict their stability, especially during storage, alone or combined with other materials in a dosage form under variable ambient conditions. Studies of the sorption ability of these cellulosic materials allow for selecting the appropriate storage conditions to maintain their quality requirements.

An isotherm is a graph of the equilibrium sorption of water plotted against water activity. Brunauer and collaborators classified isotherms in five types, according to their shape [6,7]. Type I is the typical Langmuir isotherm, which is applicable to microporous solids. Type II and type III isotherms describe the adsorption of gases on macroporous or non-porous solids, while type IV and V isotherms are applicable to both mesoporous and microporous solids. Type II isotherms are common in hydrophilic polymers such as microcrystalline cellulose [8]. The goal of this study is to compare and evaluate for the first time the water sorption properties of various MCCs by using several nonlinear models, such as the Guggenheim-Anderson-de Boer (GAB), Hailwood and Horrobin (HH), generalized D'Arcy and Watt (GDW) and Young and Nelson (YN) models. The StatGraphics 5 software (Statpoint Technologies, Warrenton, VA) was used for the nonlinear model fitting and calculation of the resulting parameters. The results of this study can be used as a point of

reference during drug development to choose the right excipient, according to its hygroscopicity.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Cotton linters (grade # R270) were obtained from Southern Cellulose Products, Inc., Chattanooga, TN, sodium hydroxide (97.5%; lot # 051758) from Fisher Scientific, Fair Lawn, NJ, concentrated hydrochloric acid (37%; lot # 2612KLHV) from Mallinckrodt Specialty Chemicals Co. (St. Louis, MO), Avicel®PH102 (lot 2339) and Avicel®PH101 (lot 1430) from FMC Biopolymers (Newark, DE), Prosolv®50 (lot XCSD9D661X) and Prosolv®90 (lot XCSD5B61X) from Penwest Company (Former Mendel, Patterson, NY) and Celphere®203 (lot 26J1) from Asahi Kasei Chemical Corp (Tokyo, Japan).

### 2.2. Preparation of Cellulose II Powders by Spray-drying (SDCII)

Cotton linter strips (~0.5x5 cm) were soaked in 7.5 N NaOH for 72 h (ratio of cellulose:NaOH solution of 1:6, w/v) at room temperature. The cellulose II (CII) strips were then washed with distilled water until washings reached a neutral pH. Approximately 280g of this material was hydrolyzed with 2L of 1 N HCl for about 2h at 105°C. The cooled material was then filtered and washed with distilled water until neutralization. An aqueous dispersion (5%, w/v) of CII was prepared in a homogenizer (Biospec products, Inc, Bartlesville, OK) for 10 min at 10,000 rpm. The dispersions were spray-dried in a Yamato Pulvis spray-drier (Model GB-22, Yamato Scientific, Co. Tokyo, Japan). The operating conditions used were: inlet air temperature 195°C; atomizing air pressure 1.0 kg-f/cm<sup>2</sup>; drying air flow-rate 0.44 m<sup>3</sup>/min; feed flow-rate 2.0 ml/min and nozzle diameter 0.7 mm.

### 2.3. Preparation of Cellulose II Powder by Spheronization (SPCII)

The homogeneous wet cake of CII was dried to a moisture content (MC) of 40-50 % and sequentially extruded from an Erweka oscillating granulator (Model AR400, Chemical and Pharmaceutical Company, Inc., New York, NY) through 710, 250 and 150 µm mesh screens, when the MCs of the slurries reached ~ 45, 35 and 25%, respectively. The wet granules thus obtained were put in the spheronizer bowl (QJ-230T Marumerizer, Fuji Paudal Co. Ltd., Charlotte, NC), which was operated at 1000 rpm for 10 min to produce spherical beads. Beads were then air-dried until the MC was less than 5%.

### 2.4. Water Sorption Isotherms

Water sorption isotherms were generated with a Symmetrical Gravimetric Analyzer (SGA-100,

VTI Corporation, Hialeah, FL), equipped with a chilled mirror dewpoint analyzer (Dewprime IF, Edgetech, Milford, MA), at 25 °C. The water activity range employed was between 0 and 0.9. Water uptake was said to reach equilibrium when consecutive sample weights differed by no more than 0.01%. Samples were analyzed in triplicate.

### 2.5. Water Sorption Models

#### 2.5.1. The Guggenheim-Anderson-de Boer (GAB) Model

This model was derived independently by Guggenheim, Anderson and de Boer. It has been adopted widely among scientists, as it fits data of non-ideal water sorption at water activities from 0 to 0.95 [9,10]. The GAB model is based on the theory of water adsorption on the surface of solids developed by BET [6]. This model assumes that the partition functions for the second and higher layers of adsorbed water are energetically the same, but different from that of liquid water and also from that of the first adsorbed water layer [11]. The model also assumes that the heat of adsorption in the multilayer system is less than the heat of liquefaction. The GAB model is depicted in equations 1-3 [12]:

$$m = \frac{k a_w m_0 C_{GAB}}{(1 - k a_w)(1 - k a_w + C_{GAB} k a_w)} \quad (1)$$

$$C = D e^{(H_m - H_c)/RT} \quad (2)$$

$$k = B e^{(H_c - H_n)/RT} \quad (3)$$

where m is the fractional moisture content, a<sub>w</sub> the water activity and m<sub>0</sub> the monolayer moisture content. The value of the monolayer moisture content (m<sub>0</sub>) can be used to estimate the optimum moisture content for the stability and preservation of food and pharmaceutical additives. H<sub>m</sub>, H<sub>n</sub> and H<sub>c</sub> are the molar sorption enthalpies of the monolayer and multilayer and the heat of condensation of water, respectively. R is the gas constant (8.31 J/K mol), T is the absolute temperature, and D and B are entropic accommodation factors. K is the energy constant related to the multilayer properties. It is the ratio of the partition function of the secondary adsorbed molecules to that of an external condensed liquid at equilibrium. This constant is usually less than 1 [13]. The constant C is related to the energetic properties of the monolayer. It is the ratio of the partition function of the first layer molecules to that of the multilayers [14].

### 2.5.2. Generalized D'Arcy and Watt (GDW) Model

This model assumes the existence of a monolayer and multilayer adsorption sites on the solid surface and the possibility that one water molecule attached to a primary center can give rise to more than one secondary adsorption site [15]. This means that not all water molecules adsorbed on the primary sites can create secondary centers. Thus, the number of secondary sites created from primary molecules will vary, making the multilayer coverage non-homogeneous. This model can be written as:

$$m = \left( \frac{a_w m_0 K}{1 + a_w K} \right) \left( \frac{1 - C(1 - w)a_w}{1 - a_w C} \right) \quad (4)$$

where  $m$  is the total fractional moisture content,  $m_0$  the monolayer capacity,  $a_w$  the water activity,  $w$  a parameter determining what fraction of water molecules adsorbed on the primary sites nucleate secondary adsorption sites and  $K$  and  $C$  have the same meaning as described in the GAB model [9,16].

### 2.5.3. Hailwood & Horrobin Model (HH)

This solid-solution model was created to describe the water sorption properties of cotton and thus can be used to determine the sorption properties of cellulosic materials. This model assumes that water can be adsorbed as a multilayer and a monolayer. Thus, it considers that the unhydrated polymer, hydrated polymer and multilayer water as in equilibrium [17]. The HH model is expressed by equations 5 and 6:

$$m = m_h + m_s \quad (5)$$

$$m = \frac{W}{18} * \left( \frac{a_w K_1 K_2}{1 + a_w K_1 K_2} \right) + \frac{W}{18} * \left( \frac{a_w K_2}{1 - a_w K_2} \right) \quad (6)$$

where  $m$  is the total fractional moisture content,  $m_h$  and  $m_s$  are the fractional moisture contents of the monolayer and multilayer, respectively.  $W$  is the number of moles of polymer involves in the sorption site,  $a_w$  the water activity, 18 the molar mass of water in grams/mol,  $K_1$  and  $K_2$  are the equilibrium constants for the formation of monolayer and multilayer, respectively [18].

### 2.5.4. Young-Nelson Model (YN)

This model distinguishes between the tightly bound monolayer ( $m_m$ ), normally condensed externally adsorbed water ( $m_c$ ) and internally absorbed ( $m_i$ ) water [15]. In this model, water uptake is given by equations 7 and 8:

$$m = m_m + m_c \quad (7)$$

Or

$$m = A(\theta + \beta) + B\Psi \quad (8)$$

$$\theta = \frac{a_w}{a_w + (1 - a_w)E} \quad (9)$$

$$\Psi = a_w \theta \quad (10)$$

$$E = e^{-(H_1 - H_L)/RT} \quad (11)$$

$$\beta = -\frac{E a_w}{E - (E - 1)a_w} + \left( \frac{E^2}{E - 1} \right) \ln \frac{E - (E - 1)a_w}{E} - (E + 1) \ln (1 - a_w) \quad (12)$$

where  $m$  is the total fractional moisture content,  $\theta$  the fraction of surface covered by a monomolecular layer,  $\Psi$  the fraction of surface covered by a layer of water two or more molecules thick,  $\beta$  the total amount of adsorbed water in the multilayer.  $H_1$  is the heat of adsorption of water bound to the surface,  $H_L$  the heat of condensation,  $k$  the gas constant (8.31 J/Kmol), and  $T$  the temperature.  $A$  and  $B$  are dimensionless constants related to the fraction of adsorbed and absorbed water on the polymer, respectively.  $E$  is the equilibrium constant between the monolayer and liquid water. The product  $A\theta$  is related to the amount of water in the monolayer and  $A(\theta + \beta)$  is the externally adsorbed moisture during the sorption phase.  $B\Psi$  is the amount of moisture absorbed during the sorption phase [19].

## 3. RESULTS

### 3.1. The Guggenheim-Anderson-de Boer (GAB) model

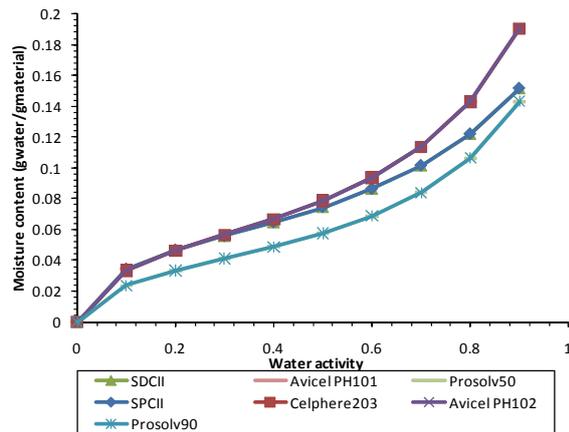
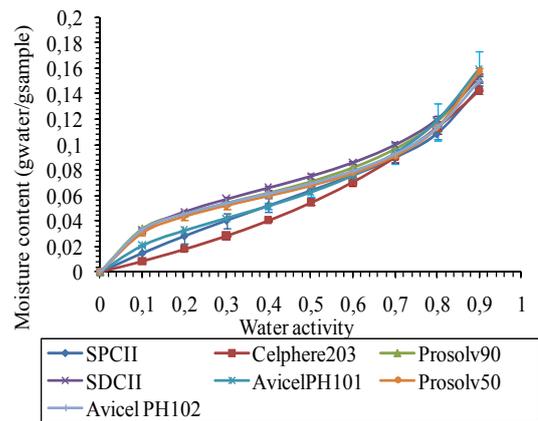
Figure 1 shows the GAB model curves fitted to the water uptake data and Table 1 shows the parameters derived from this model. Except for Celphere<sup>®</sup>203, all materials had a typical sigmoidal type II isotherm. Conversely, Celphere<sup>®</sup>203 followed a type III isotherm. All the data fitted well to the GAB model, since correlation coefficients were higher than 0.9959. Celphere<sup>®</sup>203 exhibited the highest monolayer sorption capacity of 0.15g water/g material. This value is about three times larger than those obtained for SDCII and the commercial products. This means that the primary sites of Celphere<sup>®</sup>203 are able to form more hydrogen bonds with water molecules than all other materials.

The energy constant for multilayer sorption ( $K$ ) did not vary among the Prosolv and Avicel

**Table 1:** GAB Parameters obtained from sorption isotherms of the cellulosic materials

Sample	k	m <sub>0</sub>	C	H <sub>c</sub> -H <sub>n</sub>	H <sub>m</sub> -H <sub>n</sub>	R <sup>2</sup>
	Mean (SD)	Mean (SD)	Mean (SD)	kJ/mol	kJ/mol	
Prosolv <sup>®</sup> 90	0.8 (0.0)	0.04 (0.00)	29.9 (3.4)	0.6	8.4	0.9990
Prosolv <sup>®</sup> 50	0.8 (0.0)	0.04 (0.00)	15.8 (2.6)	0.6	6.8	0.9994
Avicel <sup>®</sup> PH102	0.8 (0.0)	0.04 (0.00)	35.3 (3.4)	0.6	8.8	0.9980
Avicel <sup>®</sup> PH101	0.8 (0.0)	0.05 (0.01)	17.4 (12.2)	0.6	7.1	0.9989
SDCII	0.8 (0.0)	0.05 (0.00)	21.3 (1.7)	0.6	7.6	0.9988
SPCII	0.7 (0.1)	0.06 (0.00)	4.3 (1.7)	0.8	3.6	0.9959
Celphere <sup>®</sup> 203	0.6 (0.1)	0.15 (0.01)	1.0 (0.1)	1.4	0.0	0.9897

SD, standard deviation from three replicates; SDCII, Spray-dried cellulose II; SPCII, Spheronized cellulose II; k, energy constant of multilayer sorption; C, energy constant of monolayer sorption; H<sub>c</sub>-H<sub>n</sub>, enthalpy of multilayer sorption; H<sub>m</sub>-H<sub>n</sub>, enthalpy of monolayer sorption; m<sub>0</sub>, monolayer capacity (gwater/g sample); R<sup>2</sup>, correlation coefficient.

**Figure 1:** Moisture uptake behavior for the cellulosic materials fitted by the GAB model.**Figure 2:** Moisture sorption behavior for the cellulosic materials fitted by the GDW model.**Table 2:** GDW Parameters obtained from sorption isotherms of cellulosic materials

Sample	C	m <sub>0</sub>	K	w (g/mol)	H <sub>m</sub> -H <sub>n</sub>	H <sub>c</sub> -H <sub>n</sub>	R <sup>2</sup>
	Mean (SD)	Mean (SD)	Mean (SD)	Mean (SD)	kJ/mol	kJ/mol	
Prosolv <sup>®</sup> 50	7.4 (1.8)	0.05 (0.00)	0.9 (0.0)	0.6 (0.1)	4.9	0.3	0.9998
Prosolv <sup>®</sup> 90	14.1 (1.4)	0.05 (0.00)	0.8 (0.0)	0.7 (0.0)	6.6	0.6	0.9997
Avicel <sup>®</sup> PH101	6.6 (0.8)	0.05 (0.00)	0.8 (0.0)	1.0 (0.3)	4.7	0.6	0.9992
Avicel <sup>®</sup> PH102	11.2 (1.3)	0.06 (0.00)	0.9 (0.0)	0.5 (0.0)	6.0	0.3	0.9997
SDCII	8.1(1.4)	0.07 (0.00)	0.8 (0.0)	0.5 (0.1)	5.2	0.6	0.9997
SPCII	0.7 (1.3)	0.23 (0.02)	1.0 (0.1)	0.1 (0.2)	-1.0	0.1	0.9975
Celphere <sup>®</sup> 203	0.1 (0.1)	1.00 (0.01)	0.6 (0.1)	1.0 (0.2)	-6.6	1.4	0.9886

SD, standard deviation from three replicates; SDCII, Spray-dried cellulose II; SPCII, Spheronized cellulose II; K, energy constant of multilayer sorption; C, energy constant of monolayer sorption; H<sub>c</sub>-H<sub>n</sub>, enthalpy for multilayer sorption; H<sub>m</sub>-H<sub>n</sub>, enthalpy for monolayer sorption; m<sub>0</sub>, monolayer capacity (gwater/gsample); w, fraction of primary sites which become centers for secondary sorption; R<sup>2</sup>, correlation coefficient

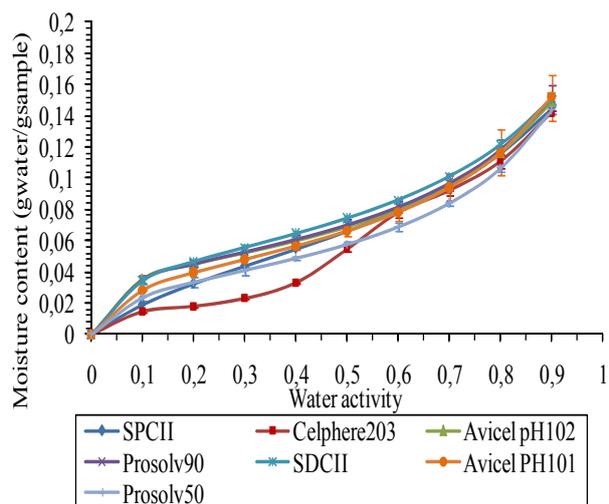
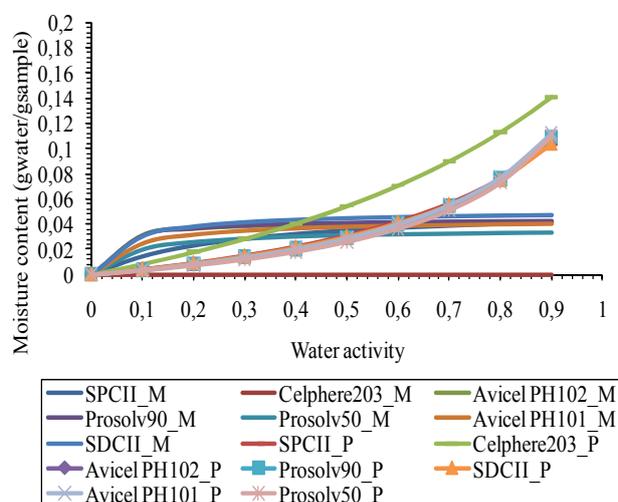
materials and SDCII (0.8 kJ/mol). However, it was lower for SPCII (0.7 kJ/mol) and Celphere<sup>®</sup>203 (0.6 kJ/mol). Likewise, these two materials had the highest enthalpy (H<sub>c</sub>-H<sub>n</sub>) of multilayer formation (0.8 kJ/mol and 1.4 kJ/mol, respectively). The energy constant for monolayer sorption (C) was the lowest for SPCII and Celphere<sup>®</sup>203 (4.3 and 1.0, respectively). Similarly, these two materials

had the lowest H<sub>m</sub>-H<sub>n</sub> difference (3.6 and 0.0 kJ/mol, respectively). In all other materials it ranged from 6.8 to 8.8 kJ/mol. The values of m<sub>0</sub>, k and C reported here for Avicel PH101 (0.05 g water/g cellulose, 0.8 and 17.4) are comparable to those obtained in an earlier study for the same product (0.04 g water/g cellulose, 0.8 and 14.2, respectively) [20].

**Table 3:** HH Parameters obtained from sorption isotherms of the cellulosic materials

Sample	k	W	C	k/C	R <sup>2</sup>
	Mean (SD)	Mean (SD)	Mean (SD)		
Prosolv <sup>®</sup> 50	14.8 (2.6)	0.7 (0.0)	0.8 (0.0)	17.5	0.9994
Avicel <sup>®</sup> PH101	16.4 (2.2)	0.8 (0.1)	0.8 (0.0)	20.5	0.9988
Avicel <sup>®</sup> PH102	34.3 (3.4)	0.8 (0.0)	0.8 (0.0)	42.9	0.9980
Prosolv <sup>®</sup> 90	28.9 (3.4)	0.8 (0.0)	0.8 (0.0)	36.1	0.9994
SDCII	20.3 (1.7)	0.9 (0.0)	0.8 (0.0)	25.4	0.9988
SPCII	5.2 (1.8)	1.0 (0.1)	0.7 (0.0)	7.4	0.9961
Celphere <sup>®</sup> 203	2.0 (0.1)	3.0 (0.0)	0.5 (0.1)	4.0	0.9897

SD, standard deviation from three replicates; SDCII, Spray-dried cellulose II; SPCII, Spheronized cellulose II; k, monolayer equilibrium constant; C, multilayer equilibrium constant; W, grams of polymer/ mol sorption site; R<sup>2</sup>, correlation coefficient

**Figure 3:** Moisture sorption behavior for the cellulosic materials fitted by the HH model.**Figure 4:** Deconvoluted sorption behavior for the monolayer and multilayer according to moisture sorption behavior for the cellulosic materials fitted by the HH model.

### 3.2. Generalized D'Arcy and Watt (GDW) Model

The GDW model assumes the existence of primary (Langmuir-type) adsorption sites on the surface. Each site adsorbs one water molecule, which can serve as a secondary adsorption site for

consecutive molecules. Figure 2 shows the curves resulting from the GDW model. All materials exhibited a typical sigmoid curve, except for Celphere<sup>®</sup>203, which had a type III isotherm. Table 2 shows the parameters obtained from the GDW model. This model showed an excellent fit to the sorption data for all materials ( $R^2 > 0.9975$ ). SPCII and Celphere<sup>®</sup>203 showed the highest monolayer capacity,  $m_0$  (0.23 and 1.00 g water/g polymer). Avicel and Prosolov samples had an  $m_0$  of only 0.05 g water/g polymer. Except for SPCII and Celphere<sup>®</sup>203, the enthalpy change for the monolayer was higher than that for the multilayer ( $H_m - H_n > H_c - H_n$ ), indicating that the formation of a monolayer is more prevalent than that of the multilayer. Conversely, the enthalpy change for the monolayer ( $H_m - H_n$ ) was the lowest for SPCII and Celphere<sup>®</sup>203 (-1.0 and -6.6 kJ/mol, respectively), favoring the formation of multilayers on these materials. All other samples had  $H_m - H_n$  values between 4.7 and 6.6 kJ/mol. Celphere<sup>®</sup>203 showed the highest possible value of  $w$  (1.0), indicating that all the primary sorption sites became nuclei for the formation of secondary binding sites.

### Hailwood and Horrobin Model (HH)

The HH model assumes the formation of three species in equilibrium (unhydrated polymer, polymer with the monolayer and polymer with a multilayer). HH is a solution-based theory and is not based on the layering method described in the GAB and GDW models. Figure 3 shows the fitted HH model and Figure 4 shows the deconvoluted curves in which the monolayer and multilayer are shown as saturation and exponential curves, respectively. The sorption curve of Celphere<sup>®</sup>203 resembles a type III isotherm. The formation of a monolayer was prevalent from 0.0 to 0.1 water activities and then the rate of water uptake decreased (Figure 4). The shape of these monolayer curves resembles the Brunauer type I isotherm. There are also exponential curves, which look like type III isotherms. These curves are related to the multilayer formation. Celphere<sup>®</sup>203 showed a preference for multilayer

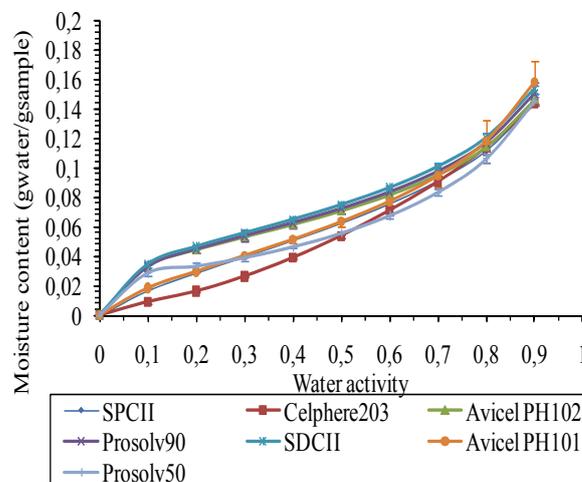
formation, rather than the formation of only a monolayer. On the other hand, for the samples of Avicel, Prosolv, SDCII and SPCII, the amount of water molecules forming a monolayer and multilayers became equal at a water activity between 0.5 and 0.6. In this range, a single water molecule has the same probability of binding to a monomolecular occupied or an empty sorption site. Further, at water activities larger than 0.6, incoming water molecules are more likely to be attracted to already occupied sites than to the few remaining empty centers.

Table 3 shows the parameters obtained the HH model. In all cases, correlation coefficients were higher than 0.9961, indicating a good fit of the model to the experimental data. The monolayer equilibrium constant  $k$  was higher than the multilayer equilibrium constant  $C$ , for all materials. In fact, the ratio of these two equilibrium constants ( $k/C$ ) was lowest for SPCII and Celphere<sup>®</sup>203, indicating that in these materials the formation of a multilayer is more prevalent than that of a monolayer. This means that the formation of a complete monomolecular water layer is not required before a multilayer is formed. Celphere<sup>®</sup>203 was the most hydrophilic material, having 3.0 mol polymer/sorption site. Other materials had a  $w$  value between 0.7 to 1.0 g polymer/mol sorption site.

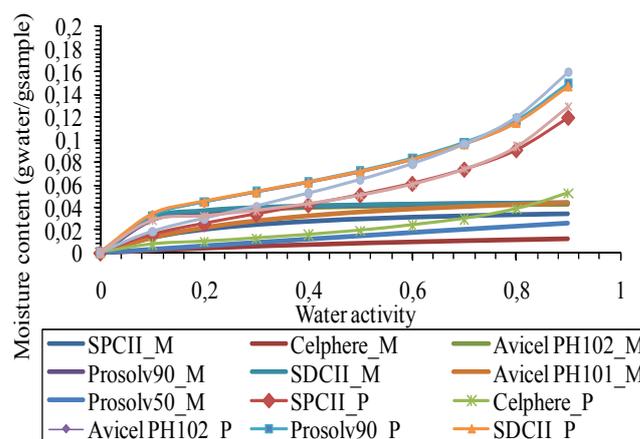
### 3.3. Young-Nelson Model (YN)

Figure 5 shows the isotherms resulting from the YN model. Most samples exhibited a type II isotherm, whereas Celphere<sup>®</sup>203 showed a typical type III isotherm. Figure 6 shows the deconvoluted curves for the monolayer and multilayer formation, respectively. Celphere<sup>®</sup>203, SPCII and Prosolv<sup>®</sup>50 showed the lowest fraction of water molecules that formed a monolayer and multilayer, respectively. Initially, most of the water molecules, instead of layering one on top of the other, are absorbed into the core of the particles. Thus, Celphere<sup>®</sup>203, SPCII and Prosolv<sup>®</sup>50 had the highest water absorption uptake (Figure 7). In other words, water molecules first penetrate the

core of the cellulose particles and then further incoming water molecules start forming an adsorbed monolayer and multilayer, simultaneously. Conversely, the amount of water absorbed by Avicel was negligible, indicating the dominance of surface layering.



**Figure 5:** Sorption isotherms for the cellulosic materials fitted by the YN model.



**Figure 6:** Deconvoluted sorption behavior for the monolayer and multilayer according to the YN Model. M indicates monolayer and P indicates multilayer.

**Table 4:** YN Parameters obtained from sorption isotherms of the cellulosic materials.

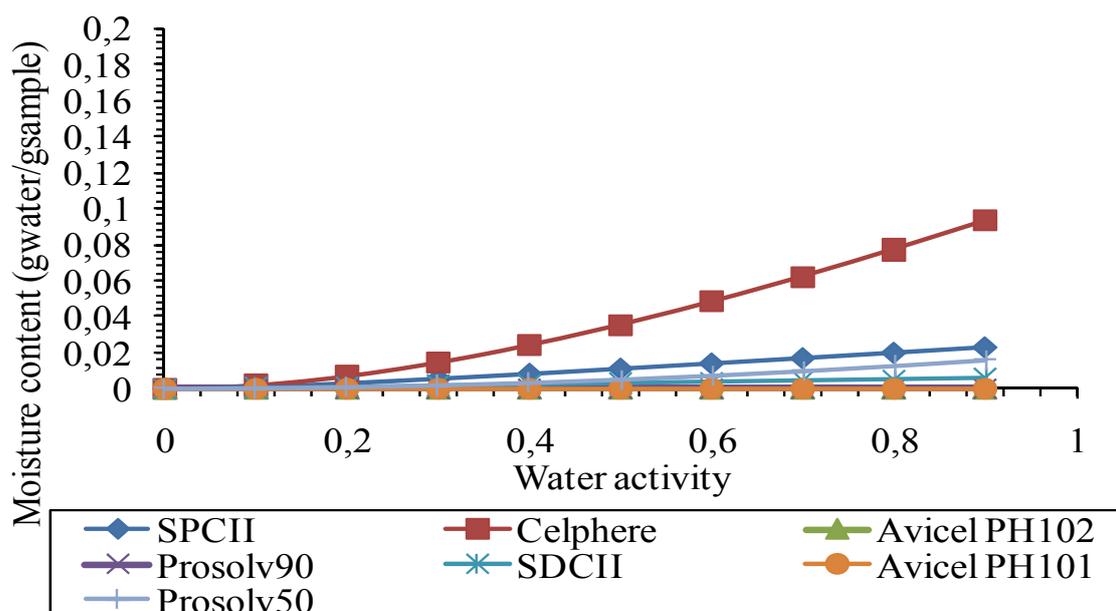
Sample	A	B	E	$H_1-H_L$	$R^2$
	Mean (SD)	Mean (SD)	Mean (SD)	kJ/mol	
Celphere <sup>®</sup> 203	0.01 (0.00)	0.11 (0.00)	0.54 (0.02)	1.5	0.9919
SPCII	0.03 (0.00)	0.03 (0.00)	0.18 (0.09)	4.3	0.9941
Prosol <sup>®</sup> 50	0.03 (0.00)	0.02 (0.00)	0.92 (0.03)	1.2	0.9980
Avicel <sup>®</sup> PH102	0.04 (0.00)	0.00 (0.00)	0.05 (0.01)	7.4	0.9960
Prosol <sup>®</sup> 90	0.04 (0.00)	0.00 (0.00)	0.06 (0.01)	7.0	0.9990
SDCII	0.04 (0.00)	0.01 (0.00)	0.05 (0.01)	7.4	0.9990
Avicel <sup>®</sup> PH101	0.04 (0.01)	0.00 (0.00)	0.26 (0.05)	3.3	0.9980

SD, standard deviation from three replicates; SDCII, Spray-dried cellulose II; SPCII, Spheronized cellulose II; A, fraction of adsorbed water; B, fraction of absorbed water; E, equilibrium constant between the monolayer and liquid water;  $H_1-H_L$ , heat difference between adsorption and condensation of water;  $R^2$ , correlation coefficient

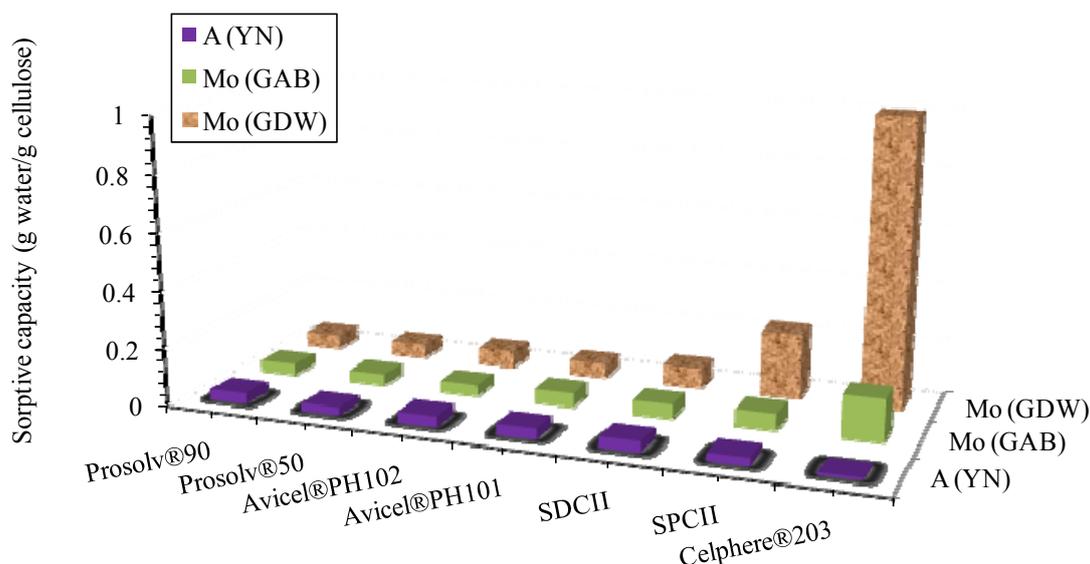
#### 4. DISCUSSION

All the models employed showed Celphere<sup>®</sup>203 as the most hydrophilic material. In fact the GAB and GDW models determined a monolayer capacity for this material of 0.15 g water/g polymer and 1.0 g water/g polymer, respectively. This value is about four and 20 times larger than the adsorptive capacity of Avicel, Prosolv and SDCII, according to the GAB and GDW models, respectively. Differences in these values might be due to the assumptions made in each model. For example, the GAB model assumes that the multilayer is formed once the monolayer is complete. However, the GDW model assumes the existence of primary adsorption sites on the surface, and not all of them can serve as secondary adsorption sites for consecutive molecules. In this case, Celphere<sup>®</sup>203 had all its primary sorption sites participating as secondary centers. This contributed to its high sorption capacity. Further, this material had the highest value of  $w$  (3.0 moles/sorption site) as obtained from the HH model confirming its high sorption capacity. The HH and YN models both assume that the monolayer and multilayers of water molecules are formed simultaneously at very low water activities, but the YN model considers the absorption of water into the core of particles to be the first step, followed by the layering process on the surface. For Celphere<sup>®</sup>203, the HH model predicts the formation of a multilayer alone, without the formation of a monolayer (Figure 4). In contrast, the YN model suggests that most of

the water uptake in Celphere<sup>®</sup>203 is by absorption rather than the layering process (Figure 7). The GAB and GDW models determined the energy constant for monolayer formation to be higher than that for multilayer formation, except Celphere<sup>®</sup>203. This means that, in this sample, it is expected that water molecules tend to pile up, because of the low enthalpy requirements. Likewise, Celphere<sup>®</sup>203 had the lowest  $k/c$  ratio (Table 3), indicating that the equilibrium constant for the formation of a multilayer is more favorable than that for monolayer formation. The YN model also demonstrated that the fraction of water absorbed in Celphere<sup>®</sup>203 was larger than the fraction adsorbed as a monolayer and multilayer (0.11 and 0.01, respectively). Also, the  $H_1-H_L$  value for Celphere<sup>®</sup>203 was very low, indicating the prevalence for multilayer formation, reinforcing the high hydrophilicity of this material. Figure 8 compares the sorption capacity of all materials, showing Celphere<sup>®</sup>203 and SPCII as the most hygroscopic materials, followed by SDCII, Avicel PH101, Avicel PH102, Prosolv50 and Prosolv90. This trend proved that neither the polymorphic form of cellulose, nor the silicification of MCC, contributed to their sorption capacity. In fact, the sorption patterns of Avicel<sup>®</sup> and Prosolv<sup>®</sup> (silicified MCC) samples were comparable. Further, the sorption capacity of Avicel (spray-dried MCC) samples was comparable to that of SDCII (spray-dried cellulose II).



**Figure 7:** Deconvoluted sorption behavior for the intrinsic absorbed water according to the YN model.



**Figure 8:** Comparison of the Sorption Capacity Parameters Obtained from the GAB, GDW and YN Models.

## 5. CONCLUSIONS

Most of the sorption isotherms exhibited a type II sigmoid shape. Celphere®203 showed the highest monolayer capacity ( $m_0$  of 0.15 g water/g cellulose) and the lowest monolayer energy constant ( $C=1.0$ ) as resulted from the GAB model. The GDW model indicated that the monolayer capacity ( $m_0$ ) and the fraction of sorption sites available for multilayer sorption ( $w$ ) were the highest for Celphere®203 (1.0 g/g cellulose and 1.0, respectively). The HH model indicated that Celphere®203 had the highest sorption capacity ( $W$  of 3.0 g/g sorption site). The YN model showed that this material had the largest water uptake by absorption into the core of the particles. The above results indicated that Celphere®203 and SPCII were the most hydrophilic materials and that neither polymorphic form, nor silicification was responsible for the difference in the hydrophilic properties of cellulose.

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