Wood Sci Technol (2018) 52:777–791
https://doi.org/10.1007/s00226-018-0998-x

ORIGINAL

Hygroscopic wood moisture: single and dimerized water molecules at hydroxyl-pair sites?

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Received: 2 November 2017 / Published online: 2 March 2018

Abstract A new molecular model is developed for wood moisture sorption in the hygroscopic range of relative humidity (RH < 95%). This model incorporates realistic physical characteristics of wood moisture sorption that cannot be explained by commonly used moisture sorption theories. The model considers a fixed number of active sorption sites over the full hygroscopic RH range. Each site is constituted by a pair of wood hydroxyl groups, which may be occupied by single or dimerized water species. The equilibrium occupation statistics of the sorption sites are controlled by the temperature and RH conditions and appear generally applicable to wood as well as modified wood. The relative amounts of monomer and dimer water can be calculated from the model for any equilibrium moisture content at any temperature and RH, which can be used for future spectroscopic identification and verification. The sigmoid wood moisture adsorption isotherm is calculated to be exclusively composed of monomers at low RH < 50%, while at RH = 100%, moisture is exclusively bound as water dimers, which is supported by a statistical cluster calculation. This state change in adsorbed water species from strongly bound monomers at low RH to relatively loosely bound dimers at high RH fundamentally differs from multilayer or hydration sorption models where a monolayer of strongly bound water remains present at high RH as a substrate layer for loosely bound secondary water.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00226-018-0998-x) contains supplementary material, which is available to authorized users.

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Introduction

A precise description of the complex interaction between wood and moisture is one of the great fundamental challenges in wood science. Advancement in this subject is expected to generate progress in specialised research fields of wood science, for example in long-term mechanical creep, mechanosorption, dimensional stabilisation, wood decay and service-life prediction. This notion has intensified the wood–moisture interaction research in recent years. The review of Engelund et al. (2013) provides a comprehensive discussion on current theories and experimental findings of wood moisture interaction. Recently, hydrogen/deuterium exchange (HDX) has been used to measure the accessible number of hydroxyl (OH) groups as potential moisture sorption sites in natural and modified woods (Rautkari et al. 2013; Popescu et al. 2014; Beck et al. 2018). Quasi-elastic and inelastic small angle neutron scattering (SANS) experiments are being used to study the dynamics of water adsorption onto cellulose (Thibault 2012; Plaza et al. 2016; O’Neill et al. 2017). Numerical molecular dynamics calculations have simulated the behaviour of water molecules in a polysaccharide matrix (Kulasinski et al. 2015; Shi and Avramidis 2017). Finally, spatially resolved spectroscopic techniques have been used to study the wood–moisture interaction simultaneously in adjacent cells or cell wall layers (Fackler and Schwanninger 2012; Passarini et al. 2015; Gezici-Koç et al. 2017).

While these advanced methods provide direct fundamental information on the molecular state of adsorbed water in wood, there is still unexplored potential for important knowledge gain from analysis of experimental wood sorption isotherms. The author has developed novel theoretical tools for this purpose (Willems 2014a, b, 2016). In this research, these tools and a complementary water cluster integral calculation are applied to the moisture adsorption isotherms of natural as well as modified woods (Hill 2006).

Moisture adsorption isotherm analysis

The wood moisture adsorption isotherm is the relation between the equilibrium moisture content (EMC, per cent kg water per kg dry wood) at constant temperature T (K) and *ascending* relative humidity (RH, ratio of partial water vapour pressure p to saturated water vapour pressure p_{sat}, percentage or fraction h). This characteristic has typically a sigmoid shape (IUPAC class II type adsorption), for which many theoretical explanations and empirical models have been published (Skaar 1988; Engelund et al. 2013). Some of these models were specifically developed to analyse the nature of the molecular association with the host matrix. However, since experimental EMC data can be fitted to either of these models, this provides no direct means to discriminate between different models. To obtain scientific confirmation, an independent experimental verification of the state of water in wood is required, which has been unsuccessful, to the best knowledge and judgment of the author.

Hartley et al. (1996) found no correspondence between the relative amounts of high- and low-mobility water from time-domain proton nuclear magnetic resonance

(^{1}H NMR) measurements, compared to the relative amounts of hydration water and monolayer water as calculated from the Hailwood–Horrobin sorption isotherm decomposition (Skaar 1988). The obtained monolayer water contents in natural woods systematically underestimate the accessible OH content (Taniguchi et al. 1978; Berthold et al. 1996; Zaihan et al. 2009; Willems 2015). Olsson and Salmén (2004) observed with FTIR (Fourier transform infrared) spectroscopy that all types of sorption sites on cellulose and hemicellulose in paper respond to an equal relative extent and with equal kinetic rates to humidity changes. Up to 80% RH, these authors did not find a spectroscopic band that could be assigned to the steep increase in wood moisture adsorption above 60% RH.

Another theoretical approach towards wood moisture adsorption is based on the statistical polymer solution thermodynamics according to Flory–Huggins, expanded with excess free volume concepts of glassy polymers (Rosenbaum 1970; Hancock and Zografi 1993; Vrentas and Vrentas 1996). One of the attractive features of this "Vrentas theory" is the incorporation of the plasticising effect of water on the glassy polymer matrix, providing an explanation for the steep increase in moisture adsorption with increasing RH above 60%, as well as a mechanism for moisture sorption hysteresis (Engelund et al. 2013). Hill and Beck (2017) applied this theory to the wood–water system with satisfactory fitting results of adsorption as well as desorption isotherm data. The Vrentas theory essentially states that the adsorption is distinctly different above versus below the glass transition temperature of the wood matrix and its associated critical RH (Engelund et al. 2013). However, the present paper provides evidence that there is no such transition in the wood moisture adsorption isotherm, illustrating the need for improved concepts of the association of water to the wood matrix.

Equilibrium occupancy of water adsorption sites in wood

Normalised wood moisture adsorption isotherms

The use of normalised wood moisture sorption isotherms was introduced by the author in the analysis of the T-dependence of the sorption isotherm shape (Willems 2014a). It was found that the T-dependence of the standard EMC curves of the Wood Handbook (Glass and Zelinka 2010) has a reversible and a non-reversible part. The non-reversible part is contained in the extrapolated $\mathrm{EMC}_{\max}(T)$ at RH = 100% ($h = 1$), whereas the reversible part is in the normalised moisture content $\omega(\mu) \equiv \mathrm{EMC}(h,T)/\mathrm{EMC}_{\max}(T)$, which is entirely described by the water chemical potential μ (Willems 2016):

$$\mu = -RT\ln h, \tag{1}$$

adopting a positive-sign convention, where RT (kJ mol^{-1}) has the usual meaning of the unit molar thermal energy. In this representation, sigmoid EMC versus RH isotherms are transformed into a monotonously decreasing function $\omega(\mu)$. The $\omega(\mu)$ correlation as found by Willems (2016) is drawn in Fig. 1a against klinki pine data of Kelsey (1957), in Fig. 1b, c against beech and spruce data of Weichert (1963),

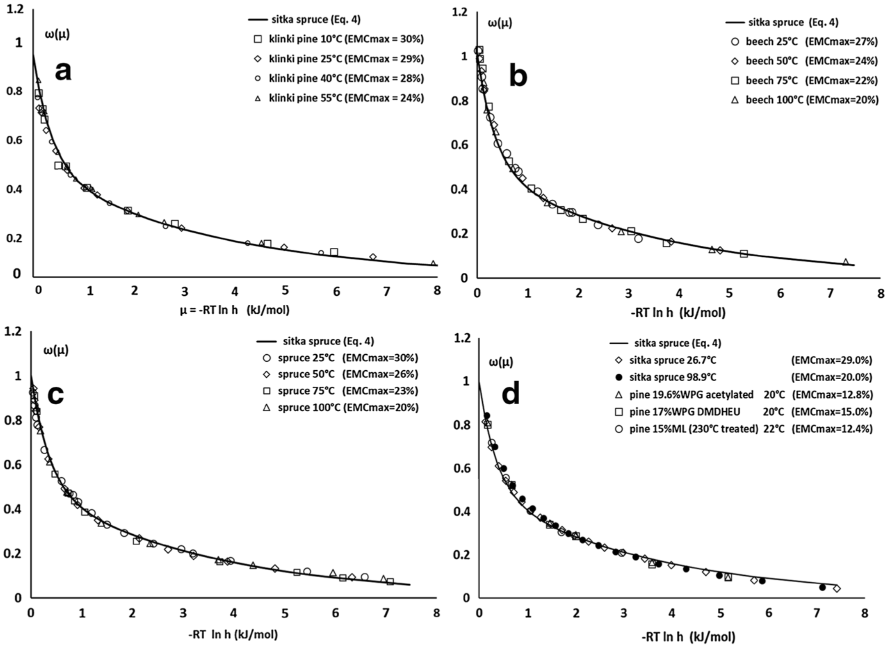


Fig. 1 Universality in $\omega(\mu) = \mathrm{EMC}/\mathrm{EMC}_{\max}$, the normalised equilibrium moisture adsorption versus water chemical potential μ, **a** for klinki pine (Kelsey 1957), **b** beech and **c** spruce (Weichert 1963) and **d** sitka spruce (Wood Handbook: Glass and Zelinka 2010) and three pine chemical modifications, heat treatment (Chaouch et al. 2013), DMDHEU-resin-treatment (Papadopoulos and Mantanis 2012) and acetylation (Papadopoulos and Hill 2003)

showing that the humidity and temperature dependence of $\mathrm{EMC}/\mathrm{EMC}_{\max}$ indeed only depend on μ. This result gives credits to the Wood Handbook EMC data, after Glass et al. (2014) assessed that these data are not scientifically assured.

Figure 1d reproduces the plots of Sitka spruce data of the Wood Handbook for two temperatures 26.7 and 98.9 °C, fitting other $\mathrm{EMC}/\mathrm{EMC}_{\max}$ data for chemically modified pine by 230 °C heat treatment (mass loss (ML) = 15%) (Chaouch et al. 2013), a cured cross-linking resin treatment (weight gain (WPG) = 17%) (Papadopoulos and Mantanis 2012) and reaction with acetic anhydride (WPG = 19.6%) (Papadopoulos and Hill 2003). Note that the three wood modification treatments are very different in their nature how they change the wood chemistry and structure. In heat-treated wood, the dry mass and the total number of OH groups decrease significantly (Seborg et al. 1953; Phuong et al. 2007; Mitsui et al. 2008; Chaouch et al. 2013) and there is some cross-linking in the wood matrix (Salmén et al. 2008; Altgen et al. 2018). DMDHEU is a cross-linking resin, adding mass and new OH groups to the wood structure (Dieste et al. 2010). Acetic anhydride reacts almost exclusively inside the wood matrix, substituting wood-OH groups by bulky acetyl groups, increasing the dry mass and dry volume without cross-linking (Hill 2006).

The $\omega(\mu)$ curve was found similarly applicable (not shown) to other wood species, other heat treatments and wood modifications using different types of anhydrides (Papadopoulos and Hill 2003) and glutaraldehyde (Xie et al. 2011). On the other hand, there are examples of sorption data that do not fit into the correlation of Fig. 1, notably for formaldehyde-treated pine (Himmel and Mai 2016) and natural African wood species wengé and doussié in the data of Popper et al. (2009). These anomalous adsorption isotherms either (1) belong to wood specimens lacking a fast cell wall relaxation capability (Willems 2015) and/or the equilibration time may have been chosen too short (Glass et al. 2017) or (2) are subject to a stress interaction σ from swelling/shrinkage constraints in the wood matrix.

In the first case, the data cannot be used for accurate sorption isotherm analysis, because there is no equilibrium. In the second case, the entire correlation of Fig. 1 is left-shifted by $v_w\sigma$ along the μ-axis for compressive stress on the wood matrix (Willems 2014a), with v_w the molar volume of water. The discussion of these stress interactions will be postponed to a future paper for didactical reasons. It is practically justified for most wood specimens to ignore stress interactions, when one is interested in moisture adsorption in the hygroscopic range (roughly $<95\%$ RH). Taking note of this limitation, one may postulate from Fig. 1 that for RH $<95\%$:

- EMC_{max} represents the number of active sorption sites in (modified) wood, since EMC_{max} corresponds to the calculated moisture content when each active OH group is occupied by one water molecule (Berthold et al. 1996; Willems 2014b).
- Each active sorption site has the same equilibrium occupancy probability determined by μ.

Through different modes of action (degradation, substitution, bulking, cross-linking, lumen-filling) wood modification thus primarily changes the active number of sorption sites, rather than the occupancy of these sites. In other words, the sigmoid sorption isotherm seems associated with *each* individual active sorption site.

Sorption site occupancy (SSO) model

Based on an indirect analysis, allowing the determination of the water occupancy of sorption sites in thermally modified wood as a function of h, Willems (2014b) found a $h^{0.7}$ (Freundlich) type of occupancy, instead of a sigmoid one. This inconsistency can be fixed by considering an apparent increase in the number of sorption sites with increasing RH, responsible for the increase in EMC at high RH: the sorption site occupancy (SSO) model states that the momentary moisture content $u(h)$ [mol water/kg dry wood] can be factored into a part $c(h)$ [mol/kg] that is proportional to the density of sorption sites and a part $\theta(h) = h^n$ that describes the statistical occupancy of a sorption site:

$$u(h) = c(h)h^n \tag{2}$$

It was shown (Willems 2014b, 2015) that the occupancy function $\theta(h) = h^n$ is generally valid for wood moisture adsorption (increasing h) and desorption (decreasing

h). The exponent n is found from the adsorption isotherm $u_{\mathrm{eq}}(h)$ as the slope of the double logarithmic relation $\ln(u_{\mathrm{eq}})$ versus $\ln(h)$ in the range $0<h<0.5$, where $c(h)$ appears nearly constant. Peleg (1993) proposed an empirical sigmoid adsorption isotherm equation that complies with Eq. 2:

$$u_{\mathrm{eq}}(h) = u_1 h^n + u_2 h^{n+m} = \left(u_1 + u_2 h^m\right) h^n \tag{3}$$

Krupińska et al. (2007) found that wood sorption isotherms fit to the Peleg Eq. 3 with the same accuracy as the standard Hailwood–Horrobin isotherm (Skaar 1988; Glass and Zelinka 2010). The room temperature (T_0 = 293 K) moisture adsorption isotherm from Glass and Zelinka (2010) is fitted accurately with $u_1=u_2=u_{\mathrm{max}}/2$, $n_0=0.71$ and $m_0=6.28$ (curve drawn in Fig. 1):

$$\omega(h) = \frac{u_{\mathrm{eq}}}{u_{\mathrm{max}}} = \left(\frac{1+h^{6.28}}{2}\right) h^{0.71} \tag{4}$$

The factor outside parentheses of Eq. 4, $\theta=h^{0.71}$ at T_0, or more generally $\theta(\mu)=\exp(-0.29\mu)$, are the occupancy of the accessible sorption sites and

$$c_{\mathrm{eq}}(h) = \frac{1+h^{6.28}}{2} u_{\mathrm{max}} \tag{5}$$

is the apparent sorption site density at T_0, or more generally $c_{\mathrm{eq}}(\mu)=½(1+\exp(-2.57\mu))$, drawn in Fig. 2.

An interesting observation from Eq. 5 is that at low RH ($\mu\rightarrow\infty$), c_{eq} approaches $c_L=u_{\mathrm{max}}/2$, while the limiting value of c_{eq} is $c_H=u_{\mathrm{max}}$ at $h=1$ ($\mu=0$). In view of the universality in Fig. 1, the apparent number of accessible sorption sites at $h=1$ then always becomes twice the number at low h. The author failed finding any viable explanation of this property in the Vrentas theory. Qualitatively, at low RH, the number of accessible sorption sites is nearly constant, consistent with the

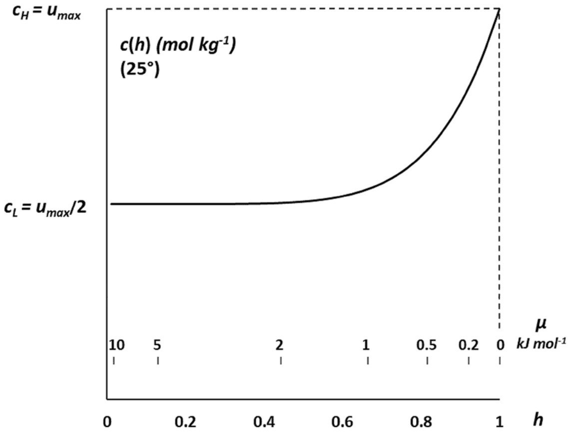


Fig. 2 Density of sorption sites $c(h)$ as calculated according to the SSO theory (Eq. 5). The correspondence between h and μ is for 25 °C

considerations that wood at low humidity is in a glassy state (Hill and Beck 2017). At high RH, mechanical softening might be considered responsible for an increased number of accessible OH groups; however, ω is hardly affected by neither cross-linking (DMDHEU and heat treatment), nor thermal softening of the wood matrix as evidenced from the similarity in Sitka spruce normalised $\omega(\mu)$ data at 98.9 and 26.7 °C (Fig. 1).

Reflections on bound wood moisture in a polysaccharide hydrogen bond network

Bulk water requires a saturated water vapour environment to prevent its evaporation. Equilibrium wood moisture is maintained in unsaturated water vapour by adhesion forces that exceed the cohesion forces in bulk water. It was shown by Willems (2016) that ω_{eq} is an explicit function of μ (Fig. 1), the differential heat of adsorption h_{ads} is necessarily equal to μ. h_{ads} is the extra enthalpy needed for the evaporation of 1 mol of adsorbed water in comparison with that of 1 mol of bulk water ($h_v = 44$/ kJ mol^{-1} at 25 °C). The heat required for evaporation is then given by the sum of h_v and h_{ads} which ranges typically from 44 kJ mol^{-1} (at $h = 1$) to 50 kJ mol^{-1} (at $h = 0.05$).

Water may form up to 4 hydrogen bonds (H-bonds), having two hydrogens for donation and an oxygen atom with two hydrogen-accepting orbitals (Jeffrey and Saenger 1994). However, water has effectively only 2 full-strength H-bonds, each of which can bifurcate into two H-bonds of half-strength (Keutsch and Saykally 2001). Hence, each water molecule in wood is *effectively* bound by two H-bonds of 22–25 kJ mol^{-1} each, consistent with the accepted range of H···OH hydrogen bond energies between 20 and 25 kJ mol^{-1} (Steiner 2002). At low RH, wood moisture is then considered dispersed in isolated water molecules, firmly bound by two relatively strong H-bonds with a pair of nearby OH groups of the amorphous polysaccharide polymers of the wood matrix (Fig. 3a). With increasing moisture concentration, the water-polysaccharide H-bonds may become weakened under strain in the swelling matrix. Meanwhile, the cooperativity

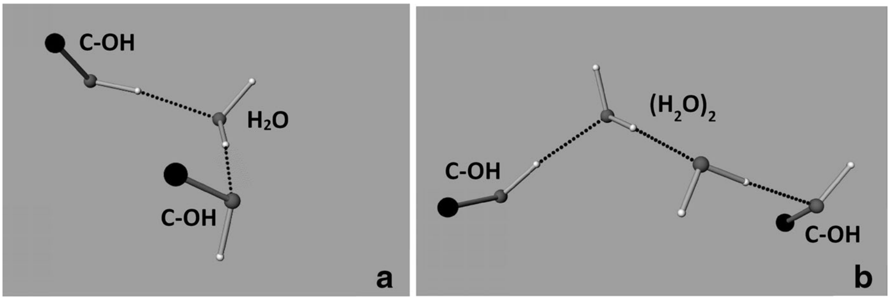


Fig. 3 Proposed configurations of adsorbed water at hydroxyl (OH) pair sites: **a** monomer water bridge. **b** Dimer water bridge. Large black spheres: C(*sp*3) atoms. Medium, dark grey spheres: O atoms. Small white spheres: H atoms. Sticks: covalent bonds. Dotted lines: H-bonds

in the H-bond network increases with increasing moisture content (Jeffrey and Saenger 1994), gradually allowing the coalescence of water vapour molecules with already adsorbed water molecules to form water dimers. These dimers are thought to be bound by relatively weak H-bonds with a OH group pair (Fig. 3b), thermodynamically stabilised by the small μ at RH > 50% (Willems 2016).

The arrangement of atoms in Fig. 3 is neither verified by quantum chemical calculation nor by experiment, merely providing a visualisation of the H-bond interactions between the hydroxyl groups and water molecules. The geometries of the hydroxyl group and the water monomer are taken from textbook values for isolated methanol and water molecules, respectively. The geometry of the water dimer is taken from Keutsch and Saykally (2001) for the isolated dimer. The used H-bond length of 1.8 Å and O–H···O bond angle of 177° are typical values as catalogued by Jeffrey and Saenger (1994).

Monomer–dimer decomposition of wood moisture

The two configurations in Fig. 3 would fit into the humidity dependence of the sorption site density (Fig. 2). At high RH, each active pair of OH groups may be saturated with 1 dimer molecule, i.e. $c_H = u_{\max}$. At low RH, the water "monomer" between two OH groups is consistent with $c_L = u_{\max}/2$.

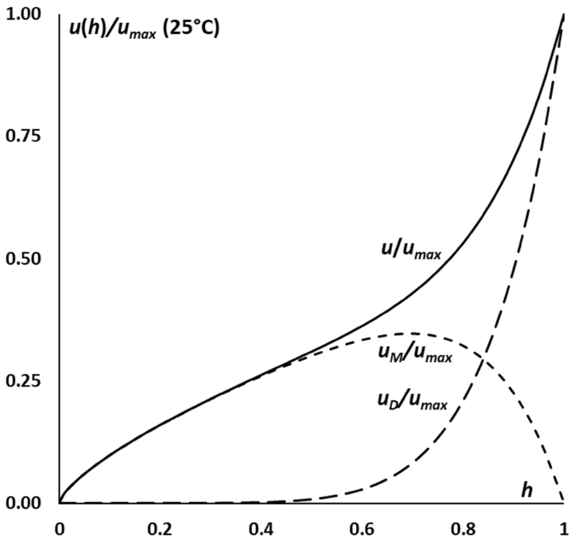
Since the occupancy function $\theta = h^n$ in Eq. 2 applies to the entire h-range, where the relative amounts of monomer and dimer water would vary significantly, it is considered applicable to monomeric (u_M) as well as the dimeric (u_D) contributions in $u = u_M + u_D$. Consequently, u_M and u_D can be calculated from u. The density of sorption sites (2 OH groups per site) is $u_{\max}/2$. The total number of occupied sorption sites is then $(u_{\max}/2)\ \theta = u_M + (u_D/2)$. Solving for u_M and u_D:

$$\begin{aligned} u_M &= u_{\max}\theta - u \\ u_D &= 2u - u_{\max}\theta \end{aligned} \tag{6}$$

Note that Eq. 6 is considered locally valid in a small wood volume element, without necessity for a true moisture content equilibrium. The calculated monomer and dimer contributions of the sigmoid EMC curve $u = u_{\mathrm{eq}}(h)$ are drawn in Fig. 4, showing an exponential increase in water dimers for RH > 50%. Water cluster formation in this RH range has been earlier suggested conceptually (Hartley et al. 1992), experimentally (Olsson and Salmén 2004; Cox et al. 2010; Gezici-Koç et al. 2017) and emerged in molecular dynamics calculations (Kulasinski et al. 2015; Shi and Avramidis 2017).

The replacement of strongly bound monomers by loosely bound dimer species with increasing h (Fig. 4) is fundamentally different from multilayer or hydration sorption models, where a strongly bound monolayer remains present as a substrate for loosely bound secondary water at high RH.

Fig. 4 Standard wood equilibrium moisture sorption isotherm $u(h)$ at 25 °C, decomposed into monomer $u_M(h)$ and dimer $u_D(h)$ contributions



Ruckenstein–Shulgin water cluster analysis

It has been argued by the author that wood moisture sorption might be best explained by considering the pool of active OH groups in wood being in a liquid mixture with the wood moisture molecules (Willems 2014b). To investigate this mixture for the likelihood of water clusters, a statistical evaluation tool is used, as put forward by RS (Ruckenstein and Shulgin 2009). The RS calculation results in a number Δn_{11}, expressing the excess number of water molecules in a small control volume around a chosen central water molecule, compared to the expectation value, based on the average concentration and molecular sizes of the components of the solution. Other excess numbers Δn_{ij} (where i and j are either 1 = water or 2 = wood-OH) can also be calculated. The RS calculation improves an earlier version of the theory by ZL (Zimm and Lundberg 1956), by explicitly accounting for $\Delta n_{ij} = 0$ in case of an ideal mixture and for the interdependency of Δn_{ij}'s for the local excess of one species depleting the other. In both theories (ZL and RS), the relative interaction strengths between the solution components are derived from the slope of sorption isotherm (Zimm 1953).

Defining the molar volumes (v_1, v_2) for liquid water molecules (1) and a unit of wood containing on average one active OH group (2), the limiting moisture content $u_{\max}$ (mol kg^{-1}) is supposed to be reached when all active OH groups are occupied by one water molecule. The molar volume of a OH group is then calculated as $v_2 = (\rho_2 u_{\max})^{-1}$ with the true density of dry wood substance ($\rho_2 \approx 1500$ kg m^{-3}). The molar volume of water is $v_1 = 1.8 \times 10^{-5}$ m^3 mol^{-1}. Defining the molar volume ratio $\gamma = v_1/v_2$, the original RS expression for Δn_{11} (see Appendix in Electronic Supplementary Material) is evaluated to

$$\Delta n_{11} = \frac{\frac{h}{\omega}\frac{\partial \omega}{\partial h} - 1 - \omega}{(1 + \gamma\omega)^2} \tag{7}$$

for direct application to Eq. 4. Δn_{11} is plotted in Fig. 5 as a function of h, at T_0 and $\mathrm{EMC}_{\max}=25\%$. The limiting values of Δn_{11} at $h=0$ and $h=1$ may, respectively, correspond (see Fig. 4) to the local excesses at monomer sites ($\Delta n_{11,M}\approx-0.4$) and dimer sites ($\Delta n_{11,D}\approx 1.2$). The broken line in Fig. 5 shows that these excesses remarkably fit the entire $\Delta n_{11}(h)$ curve as a weighted average, using the calculated u_M and u_D at each $u_{\mathrm{eq}}(h)$ with Eq. 6:

$$\langle\Delta n_{11}\rangle=\frac{u_M\Delta n_{11,M}+u_D\Delta n_{11,D}}{u_M+u_D}=\frac{-0.4u_M+1.2u_D}{u} \tag{8}$$

The graphical comparison between Δn_{11} and $\langle\Delta n_{11}\rangle$ is given in Fig. 5.

Discussion

By plotting $\omega(\mu)$, the normalised EMC as a function of the water chemical μ, one obtains a curve that seems to describe the h- and T-dependency of the occupancy of each *active* sorption site in wood. An active site is always an accessible site, but not vice versa. Acetylation reduces the accessible OH group content of wood by the number of acetyl-substituted OH groups (Beck et al. 2018), while the active OH group content c_H is reduced by the (larger) number of water molecules that fit within the volume of the bulky acetyl substituents (Papadopoulos and Hill 2003). $\mathrm{EMC}_{\max}$ corresponds to the moisture content when all active OH groups are occupied by one water molecule. Bulking limits the number of active sites but does not determine which of the accessible sites is active. Mobile moisture molecules may dynamically move between *all* accessible sites and HDX accordingly deuteriates all accessed OH groups successively even if they cannot be simultaneously active. In this work, the site occupancy θ relates to the active sorption site content.

The universal $\omega(\mu)$ has a fundamental significance. It was shown by Willems (2016) that in such case, the differential enthalpy of adsorption h_{ads} is equal to μ and

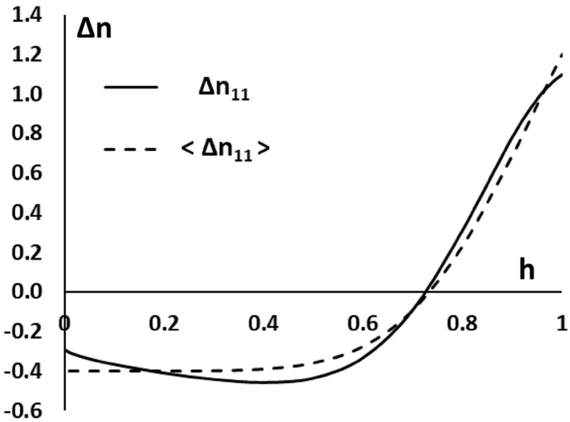


Fig. 5 Local moisture excess Δn_{11} from Ruckenstein–Shulgin water cluster calculation (Eq. 7) of the standard moisture adsorption isotherm (Eq. 4), compared to a fit with a weighted average of monomer and dimer contributions (Eq. 8)

the entropy of wood moisture is necessarily invariant at each h along the sorption isotherm. This property is speculated to originate from: (1) the local mobility of water in the wood matrix at all RH, as evidenced by time-domain ^{1}H-NMR relaxation measurements (e.g. Cox et al. 2010; Gezici-Koç et al. 2017), and (2) the H-bond network in the polysaccharide-rich wood matrix (Jeffrey and Saenger 1994), providing an equal environment for water molecules as in capillary stressed bulk water.

It must be noted here that $\mathrm{EMC_{max}}$ is generally found T-dependent, which is related to structural changes (Skaar 1988; Willems 2014a, 2016). When this non-reversible T-dependence is included into a thermodynamic analysis with the Clausius–Clapeyron relation, the constant entropy result is erratically lost (Willems 2014a). Figure 1 confirms that a non-reversible T-dependent $\mathrm{EMC_{max}}$ is to be regarded as a modified wood case.

The constant entropy of wood moisture with h-variation is inconsistent with the localised sorption theories of Langmuir, Brunnauer–Emmet–Teller (BET) and Guggenheim–Andersson–de Boer (GAB). It is neither consistent with Flory–Huggins and Vrentas type of polymer-penetrant solution theories, where the configurational entropy of polymer segments determines the isothermal water sorption at high RH.

The sigmoid sorption isotherm has a steep slope at high RH (Fig. 4), which the sorption site occupancy (SSO) theory (Willems 2014b) attributes to a strong increase in the number of sorption sites at high RH (Fig. 2). Remarkably, the SSO analysis of the universal normalised EMC curve of Fig. 1 results in a doubling of the number of sorption sites from low h to $h=1$ (Fig. 2) and the shape of $c(h)$ curve is not influenced by different wood modifications, including a cross-linking and a softening treatment. The supposed influence of glass softening on the shape of the wood moisture adsorption isotherm in Vrentas theory (Hill and Beck 2017) does therefore not seem to hold as a generic mechanism.

Since the sigmoid sorption isotherm was found associated with each individual active sorption site, a change in the local bonding state of moisture at different h might be a more likely explanation. From the argument that a stable state in unsaturated water vapour requires each adsorbed water molecule to be H-bonded with either (1) two wood-OH groups or (2) one wood-OH and another water molecule, two bonding configurations were proposed (Fig. 3) that could account for the relative increase in the apparent number of sorption sites through the conversion of water monomers into dimers at high RH. The actual number of sorption sites (number of active pairs of OH groups) is therein considered constant at each RH. Each sorption site has a statistical h^n occupancy for either a monomer or a dimer, consistent with the analysis of Willems (2014b). The h^n-like dependency of all moisture-related integrated FTIR absorption bands, as determined by Olsson and Salmén (2004), suggests that these data show no sensitivity for monomer or dimer occupation of the moisture sorption sites in wood.

The relative quantities of monomer and dimer water can be calculated at any moisture content, temperature and humidity from Eq. 6. Applied to desorption isotherms, hysteresis would be attributed to an excess of dimers and a coupled depletion of monomers in comparison with adsorption. It might be speculated that dimers formed in relatively high numbers at high RH are metastable at lower RH in desorption, in which case a suitable spectroscopic technique might be able to identify the monomer/dimer species by comparison of spectra in adsorption and desorption.

Verification experiments on the postulate of hydroxyl-pair nature of sorption sites are currently being conducted, whereby the EMC changes with respect to quantitative OH content variation are studied. These studies are particularly interesting in conjunction with the poorly understood effect of the partial reversibility of EMC modification in dry heat-treated wood (Obataya and Tomita 2002; Altgen and Militz 2016). In the present model, it requires the destruction of only one OH group to inactivate a OH group pair as a sorption site for water; hence, the short-term effect on EMC is the loss of 1 mol of moisture per 1 mol of removed OH groups (Willems 2014b). However, the OH group singles of the destructed sorption sites may reorganise (mechanical relaxation) to form new OH group pairs. The time required for the reorganisation process increases with the level of cross-linking in the cell wall, and reorganisation is accelerated in varying climates. In effect, the EMC reduction may ultimately attain only ½ mole of moisture per 1 mol of removed OH groups, when all OH group singles have formed new pairs. The available EMC data on dry-heated wood (Obataya and Tomita 2002; Altgen and Militz 2016) indeed show a recovery of around 50% of the thermal EMC reduction after several wet–dry cycles.

The model configurations in Fig. 3 might be extended with larger clusters than dimers, which are deemed important only for $\mathrm{RH} > 95\%$. Unfortunately, there are at present no measurement techniques for the determination of the water cluster size distribution in wood to directly verify this assumption. Instead, the RS calculation of Δn_{11} was used to analyse the likelihood of and the average size of water clusters (Fig. 5). This local excess water number may be directly probed by small angle scattering of X-rays (SAXS) or neutrons (SANS) (Sinibaldi et al. 2008). RS-calculated Δn_{11} are difficult to interpret in pictorial configurations as in Fig. 3, because the correlation volume of the cluster is undetermined, as pointed out by RS. Moreover, in case of a simultaneous presence of monomers and dimers, Δn_{11} obviously cannot refer to just one type of interaction. A linear combination of contributions from monomers $\Delta n_{11,M} = -0.4$ and dimers $\Delta n_{11,D} = 1.2$ was successfully fitted to the overall excess number (Fig. 5). Naively, one might have expected the values 0 (no cluster) for a monomer and 1 for a dimer, respectively. The fitted negative value (depletion) for the monomer may result from an excess of wood-OH drawn towards the monomer by strong H-bonds. The excess water number for dimers reasonably agrees with the expected value, giving some support to the proposed water monomer/dimer model.

Conclusion

Based on the present moisture sorption isotherm shape analysis, some firm conclusions regarding wood moisture sorption can be drawn:

1. Wood moisture sorption is an enthalpic process

2. Wood moisture adsorption results from a universal occupation law of mobile water species at active sorption sites, controlled by the water chemical potential μ
3. Wood modification treatments primarily change the number of active water sorption sites, each giving an equal contribution to the overall water adsorption isotherm of wood
4. The steep increase in EMC in the sigmoid water adsorption isotherm above RH = 60% is not caused by a softening transition in the wood matrix. Conversely, the increase in EMC at high RH can be suppressed by large compressive stresses, acting on the wood matrix.

These conclusions do not rely on results from the application of the Sorption Site Occupancy theory or any of the model assumptions made in the proposed molecular bonding model of wood moisture.

The model considers a constant number of sorption sites, constituted by wood-OH pairs, binding water as isolated molecules (monomers) or dimers. This provides an alternative explanation for the steep EMC increase at high RH, by preferential occupation of sorption sites by monomers at low RH being converted to dimers at high RH. The occupation of sorption sites by water dimers at high RH is supported by a theoretical cluster calculation result.

The model allows a direct calculation (Eq. 6) of the relative amounts of monomers and dimers at any given EMC, $\mathrm{EMC}_{\max}$, RH and T, in adsorption as well as desorption isotherms. This may be used in the spectroscopic identification of water dimer and monomer species in wood and in sorption hysteresis studies. A second feature of the model, postulating the hydroxyl-pair nature of sorption sites, can be tested by investigating quantitative relationships between accessible OH groups and EMC, taking bulking and structural relaxation effects in the wood cell wall into account.

References

Altgen M, Militz H (2016) Influence of process conditions on hygroscopicity and mechanical properties of European beech thermally modified in a high-pressure reactor system. Holzforschung 70:971–979

Altgen M, Uimonen T, Rautkari L (2018) The effect of de- and re-polymerization during heat-treatment on the mechanical behavior of Scots pine sapwood under quasi-static load. Polym Degrad Stab 147:197–205

Beck G, Strohbusch S, Larnøy E, Militz H, Hill C (2018) Accessibility of hydroxyl groups in anhydride modified wood as measured by deuterium exchange and saponification. Holzforschung 72(1):17–23

Berthold J, Rinaudo M, Salmén L (1996) Association of water to polar groups; estimations by an adsorption model for ligno-cellulosic materials. Colloids Surf A Physicochem Eng Asp 112:117–129

Chaouch M, Dumarçay S, Pétrissans A, Pétrissans M, Gérardin P (2013) Effect of heat treatment on some conferred properties of different European softwood and hardwood species. Wood Sci Technol 47:663–673

Cox J, McDonald PJ, Gardiner BA (2010) A study of water exchange in wood by means of 2D NMR relaxation correlation and exchange. Holzforschung 64:259–266

Dieste A, Krause A, Mai C, Militz H (2010) The calculation of EMC for the analysis of wood/water relations in *Fagus sylvatica* L. modified with 1, 3-dimethylol-4, 5-dihydroxyethyleneurea. Wood Sci Technol 44:597–606

Engelund ET, Thygesen LG, Svensson S, Hill CAS (2013) A critical discussion of the physics of wood–water interactions. Wood Sci Technol 47:141–161

Fackler K, Schwanninger M (2012) How spectroscopy and microspectroscopy of degraded wood contribute to understand fungal wood decay. Appl Microbiol Biotechnol 96:587–599

Gezici-Koç Ö, Erich SJ, Huinink HP, van der Ven LG, Adan OC (2017) Bound and free water distribution in wood during water uptake and drying as measured by 1D magnetic resonance imaging. Cellulose 24:535–553

Glass SV, Zelinka SL (2010) Moisture relations and physical properties of wood. In: Ross RJ (ed) Wood handbook, Chapter 04. Forest Products Laboratory, Madison

Glass SV, Zelinka SL, Johnson JA (2014) Investigation of historic equilibrium moisture content data from the forest products laboratory. General technical report FPL–GTR–229. Forest Products Laboratory, Madison

Glass SV, Boardman CR, Zelinka SL (2017) Short hold times in dynamic vapor sorption measurements mischaracterize the equilibrium moisture content of wood. Wood Sci Technol 51:243–260

Hancock BC, Zografi G (1993) The use of solution theories for predicting water vapor absorption by amorphous pharmaceutical solids: a test of the Flory–Huggins and Vrentas models. Pharm Res 10:1262–1267

Hartley ID, Kamke FA, Peemoeller H (1992) Cluster theory for water sorption in wood. Wood Sci Technol 26:83–99

Hartley ID, Avramidis S, MacKay A (1996) H-NMR studies of water interactions in sitka spruce and western hemlock: moisture content determination and second moments. Wood Sci Technol 30:141–148

Hill CAS (2006) Wood modification: chemical, thermal and other processes. Wiley, Chichester

Hill C, Beck G (2017) On the applicability of the Flory–Huggins and Vrentas models for describing the sorption isotherms of wood. Int Wood Prod J 8:50–55

Himmel S, Mai C (2016) Water vapour sorption of wood modified by acetylation and formalisation—analysed by a sorption kinetics model and thermodynamic considerations. Holzforschung 70:203–213

Jeffrey GA, Saenger W (1994) Hydrogen bonding in biological structures, 2nd edn. Springer, Heidelberg

Kelsey KE (1957) The sorption of water vapour by wood. Aust J Appl Sci 8:42–54

Keutsch FN, Saykally RJ (2001) Water clusters: untangling the mysteries of the liquid, one molecule at a time. Proc Natl Acad Sci USA 98:10533–10540

Krupińska B, Strømmen I, Pakowski Z, Eikevik TM (2007) Modeling of sorption isotherms of various kinds of wood at different temperature conditions. Dry Technol 25:1463–1470

Kulasinski K, Guyer R, Derome D, Carmeliet J (2015) Poroelastic model for adsorption-induced deformation of biopolymers obtained from molecular simulations. Phys Rev E 92:02260578

Mitsui K, Inagaki T, Tsuchikawa S (2008) Monitoring of hydroxyl groups in wood during heat treatment using NIR spectroscopy. Biomacromol 9:286–288

O'Neill H, Pingali SV, Petridis L, He J, Mamontov E, Hong L, Urban V, Evans B, Langan P, Smith JC, Davison BH (2017) Dynamics of water bound to crystalline cellulose. Sci Rep 7:11840

Obataya E, Tomita B (2002) Hygroscopicity of heat-treated wood II. Reversible and irreversible reductions in the hygroscopicity of wood due to heating. Mokuzai Gakkaishi 48:288–295

Olsson AM, Salmén L (2004) The association of water to cellulose and hemicellulose in paper examined by FTIR spectroscopy. Carbohydr Res 339:813–818

Papadopoulos AN, Hill CAS (2003) The sorption of water vapour by anhydride modified softwood. Wood Sci Technol 37:221–231

Papadopoulos AN, Mantanis G (2012) Vapour sorption studies of Belmadur wood. Adv For Lett 1:1–6

Passarini L, Malveau C, Hernández RE (2015) Distribution of the equilibrium moisture content in four hardwoods below fiber saturation point with magnetic resonance microimaging. Wood Sci Technol 49:1251–1268

Peleg M (1993) Assessment of a semi-empirical four parameter general model for sigmoid moisture sorption isotherms. Food Process Eng 16:21–37

Phuong L, Takayama M, Shida S, Matsumoto Y, Aoyagi T (2007) Determination of the accessible hydroxyl groups in heat-treated *Styrax tonkinensis* (Pierre) Craib ex Hartwich wood by hydrogen–deuterium exchange and ^{2}H NMR spectroscopy. Holzforschung 61:488–491

Plaza NZ, Pingali SV, Qian S, Heller WT, Jakes JE (2016) Informing the improvement of forest products durability using small angle neutron scattering. Cellulose 23:1593–1607

Popescu CM, Hill CAS, Curling S, Jalaludin Z, Xie Y (2014) The water vapour sorption behaviour of acetylated birch wood: how acetylation affects the sorption isotherm and accessible hydroxyl content. J Mater Sci 49:2362–2371

Popper R, Niemz P, Croptier S (2009) Adsorption and desorption measurements on selected exotic wood species. Analysis with the Hailwood–Horrobin model to describe the sorption hysteresis. Wood Res 54:43–56

Rautkari L, Hill CAS, Curling S, Jalaludin Z, Ormondroyd G (2013) What is the role of the accessibility of wood hydroxyl groups in controlling moisture content? J Mater Sci 48:6352–6356

Rosenbaum S (1970) Solution of water in polymers: the Keratin-Water isotherm. J Polym Sci Polym Symp 31:45–55

Ruckenstein E, Shulgin IL (2009) Thermodynamics of solutions. Springer, New York

Salmén L, Possler H, Stevanic JS, Stanzl-Tschegg SE (2008) Analysis of thermally treated wood samples using dynamic FT-IR-spectroscopy. Holzforschung 62:676–678

Seborg RM, Tarkow H, Stamm AJ (1953) Effect of heat upon the dimensional stabilization of wood. J For Prod Res Soc 3:59–67

Shi J, Avramidis S (2017) Water sorption hysteresis in wood: III physical modeling by molecular simulation. Holzforschung 71:733–741

Sinibaldi R, Ortore MG, Spinozzi F, de Souza Funari S, Teixeira J, Mariani P (2008) SANS/SAXS study of the BSA solvation properties in aqueous urea solutions via a global fit approach. Eur Biophys J 37:673–681

Skaar C (1988) Wood–water relations. Springer, Berlin

Steiner T (2002) The hydrogen bond in the solid state. Angew Chem Int Ed 41:48–76

Taniguchi T, Harada H, Nakato K (1978) Determination of water adsorption sites in wood by a hydrogen–deuterium exchange. Nature 272:230–231

Thibault X (2012) Neutron techniques for wood chemistry. Cellul Chem Technol 46:421–425

Vrentas JS, Vrentas CM (1996) Hysteresis effects for sorption in glassy polymers. Macromolecules 29:4391–4396

Weichert L (1963) Untersuchungen über das Sorption- und Quellungsverhalten von Fichte, Buche und Buchen-Preßvollholz bei Temperaturen zwischen 20 ° und 100 °C (Investigations on sorption and swelling of spruce, beech and compressed-beech wood at temperatures between 20 °C and 100 °C) (In German). Holz Roh Werkst 21:290–300

Willems W (2014a) The hydrostatic pressure and temperature dependence of wood moisture sorption isotherms. Wood Sci Technol 48:483–498

Willems W (2014b) The water vapor sorption mechanism and its hysteresis in wood: the water/void mixture postulate. Wood Sci Technol 48:499–518

Willems W (2015) A critical review of the multilayer sorption models and comparison with the sorption site occupancy (SSO) model for wood moisture sorption isotherm analysis. Holzforschung 69:67–75

Willems W (2016) Equilibrium thermodynamics of wood moisture revisited: presentation of a simplified theory. Holzforschung 70:963–970

Xie Y, Hill CAS, Xiao Z, Mai C, Militz H (2011) Dynamic water vapour sorption properties of wood treated with glutaraldehyde. Wood Sci Technol 45:49–61

Zaihan J, Hill CAS, Curling S, Hashim WS, Hamdan H (2009) Moisture adsorption isotherms of *Acacia mangium* and *Endospermum malaccense* using dynamic vapour sorption. J Trop For Sci 21:277–285

Zimm BH (1953) Simplified relation between thermodynamics and molecular distribution functions for a mixture. J Chem Phys 21:934–935

Zimm BH, Lundberg JL (1956) Sorption of vapors by high polymers. J Phys Chem 60:425–428