Wood Science and Technology (2018) 52:1701–1706
https://doi.org/10.1007/s00226-018-1035-9

ORIGINAL

Myth versus reality: Do parabolic sorption isotherm models reflect actual wood–water thermodynamics?

Samuel L. Zelinka[1] · **Samuel V. Glass**[1] · **Emil Engelund Thybring**[2]

Received: 20 November 2017 / Published online: 30 July 2018

Abstract
It has been known for over 35 years that commonly used sorption isotherm models fail to correctly predict wood–water properties such as heat of sorption. Despite this, their use to determine thermodynamic quantities and monolayer moisture contents persists and in fact is increasing in frequency. In this paper, we recommend the use of the "ABC isotherm," which is mathematically equivalent to sorption isotherm models commonly used for wood but has the added benefits of simplicity, avoidance of a conceptual image of water sorption that is contradicted by measurements, and avoidance of any additional step of identifying quantities that are physically incorrect.

In the last 10 years, there have been many publications on water vapor sorption isotherms for wood and other cellulosic materials. Undoubtedly, the rise in the number of publications on sorption isotherms is correlated to the widespread adoption of automated sorption balances in wood laboratories throughout the world. These instruments have made it possible to obtain isotherms in less than a week that would have previously taken more than a year to measure. In many studies, the water vapor sorption data on wood have been fit to one or more of several existing sorption isotherm models.

Sorption isotherm models are frequently used to fit experimental sorption data for giving smooth curves when plotting the data, interpolating between measured values, or inferring wood properties. The three most commonly used models for wood are: (1) the Guggenheim–Anderson-de Boer (GAB) model (Anderson 1946; Anderson and Hall 1948; De Boer 1953; Guggenheim 1966); (2) the Dent

✉ Samuel L. Zelinka
szelinka@fs.fed.us

[1] Building and Fire Sciences, US Forest Service, Forest Products Laboratory, 1 Gifford Pinchot Dr, Madison, WI, USA

[2] Department of Geosciences and Natural Resource Management, University of Copenhagen, Rolighedsvej 23, DK-1958 Frederiksberg C, Denmark

model (1977); and (3) the Hailwood–Horrobin (HH) model (Hailwood and Horrobin 1946). These three isotherm models are all derived from statistical mechanics: Both the Dent and GAB models are modifications to the Langmuir (1918) and Brunauer–Emmett–Teller (BET) (1938) isotherm models, whereas the HH model is derived from solution thermodynamics. When fit to experimental data, the model parameters are often assumed to correspond to physically meaningful quantities, such as the monolayer coverage, as has been done in numerous publications (Spalt 1958; Chen and Wangaard 1968; Popper and Bariska 1972; Araujo et al. 1994; Yasuda et al. 1994; Hartley 2000; Chauhan et al. 2001; Papadopoulos and Hill 2003; Papadopoulos 2005; Papadopoulos et al. 2005; Popper et al. 2005). However, number and frequency of these publications have become increasingly common over the past decade (Esteban et al. 2006; Popper et al. 2006; Krupińska et al. 2007; Dieste et al. 2008; Esteban et al. 2008a, b, 2009; Hill et al. 2009; Zaihan et al. 2009; Esteban et al. 2010; Hill et al. 2010; Jalaludin et al. 2010a, b; Xie et al. 2010; Papadopoulos 2011; Zaihan et al. 2011; Bratasz et al. 2012; Papadopoulos 2012; Murata et al. 2013; Olek et al. 2013; Simón et al. 2017).

It has been known for over 35 years that the HH model fails to correctly predict wood–water properties such as heat of sorption (Simpson 1980). Simpson (1980) showed that the differential heat of sorption calculated from the HH model is positive (endothermic) meaning that bound water requires less energy to vaporize than bulk liquid water, in contrast to experimental measurements, which show the opposite. Willems (2015) recently expanded this analysis by examining how water is partitioned in the model between the strongly bound primary water (called "hydrate state") and weakly bound secondary water (called "dissolved state") at different temperatures. Thermodynamically, we would expect to see less weakly bound water as the temperature increases. However, the HH model predicts the opposite trend: When fit to data at different temperatures, the HH model attributes a higher percentage of the total moisture to secondary water at higher temperatures.

Because the commonly used Dent and GAB isotherms are mathematically equivalent to the HH isotherm (Boquet et al. 1980), it makes sense to reevaluate whether any of these isotherms can give physically meaningful fitting parameters. Logically, because these isotherms are mathematically equivalent but derived from different starting points, at most only one of these isotherms could potentially have physically meaningful parameters. Although they all derive from different starting points, the Dent, GAB, and HH isotherms all partition bound water into two types: a more strongly bound primary water (m_1) and a less strongly bound secondary water (m_2). Following the analysis of Willems (2015), the ratio of m_1/m_2 at a relative humidity of 100% is plotted for the GAB, Dent, and HH isotherms in Fig. 1 using the model parameters of Hartley (2000) who fit the experimental absorption isotherm data of Kelsey (1957) at four temperatures (with HH parameters calculated from the Dent model parameters). Thermodynamically, this ratio should increase as a function of temperature; however, it decreases for all three models. It is therefore not possible to derive physically meaningful wood properties from the Dent, GAB, or HH isotherms because their predictions are directly contradicted by reality.

To prevent the proliferation of incorrect wood physical properties being derived from sorption isotherm models, we recommend the "ABC isotherm" (Eq. 1).

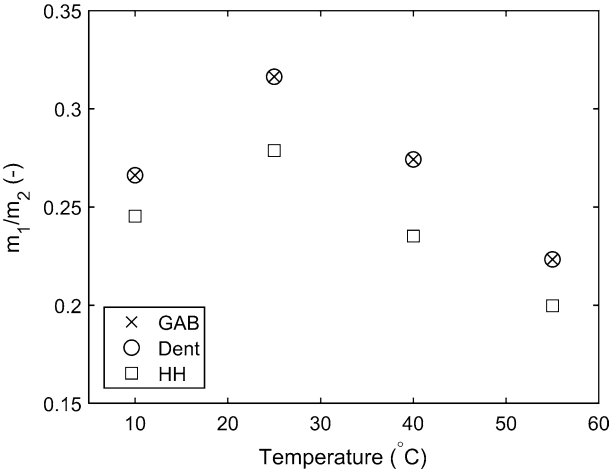

Fig. 1 Ratio of the primary water to secondary water as calculated from the model fit parameters of different isotherms as a function of temperature

$$\frac{h}{m} = Ah^2 + Bh + C \tag{1}$$

where h is the fractional relative humidity (or water activity); m is the fractional moisture content (g/g); and A, B, and C are arbitrary fitting parameters with no implied physical meaning. Attentive readers may realize that the ABC isotherm is mathematically equivalent to the HH isotherm, the Dent isotherm, and the GAB isotherm. In fact, an equation of this form was given both by Hailwood and Horrobin (1946) and Dent (1977) as being equivalent to their models, and various authors have also shown that these models can be reduced to a parabolic equation (e.g., Spalt 1958; Skaar 1988; Siau 1995). Figure 2 shows the fit of the ABC isotherm to water vapor sorption data collected on untreated southern pine in absorption (Zelinka and Glass 2010); the fits of the GAB, Dent, and HH isotherms are also included in Fig. 2 for reference.

From Fig. 2, it can be seen that the ABC isotherm fits the data equally well as these commonly used models. Furthermore, the ABC isotherm is equally good at interpolating between measured values. However, the ABC isotherm has the added benefits of simplicity, avoidance of a conceptual picture that is contradicted by measurements, and avoidance of any additional step of identifying quantities that are physically incorrect.

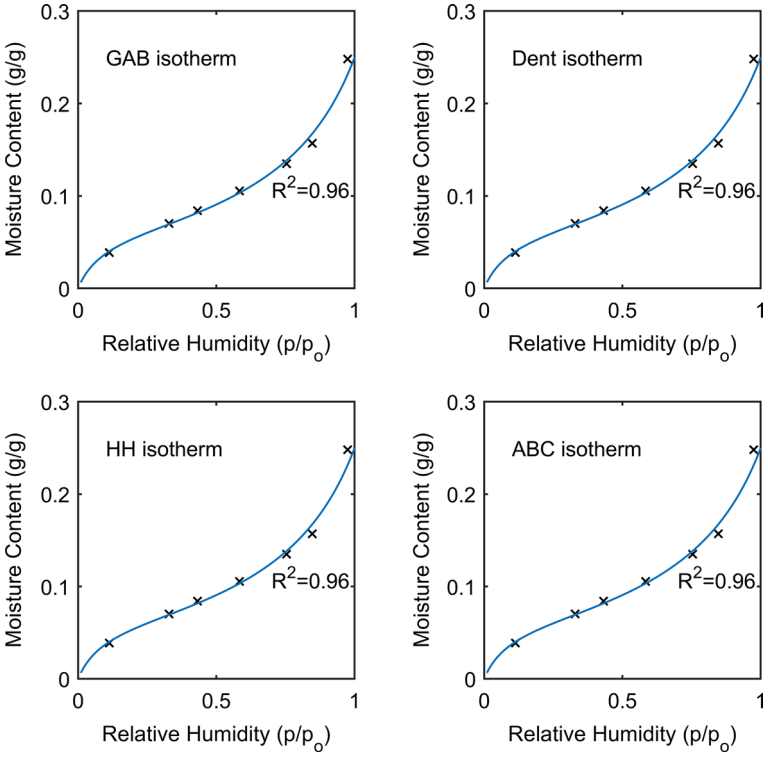

Fig. 2 Absorption data for southern pine fit with the commonly used GAB, Dent, and HH isotherms compared against the proposed ABC isotherm

Conclusion

Commonly used sorption models include parameters that are not physically meaningful when applied to wood and should not be used to infer wood properties. Despite this fact which has been known for many years researchers continue to ascribe wood physical characteristics to the isotherm fit parameters. While it is acceptable to use any of the GAB, HH, Dent, or ABC isotherms to provide smooth curves, it is entirely inappropriate to relate the curve fits to meaningful quantities for wood–moisture interactions. In summary, we recommend the ABC isotherm: it is as easy as 1, 2, 3.

Acknowledgements The authors thank JF Scott's paper (2007) playfully criticizing data published on supposedly ferroelectric materials for an inspiration to this paper. SLZ and EET are thankful for the traveling grant for SLZ from "IGN International Academy," while EET acknowledges funding from the VILLUM FONDEN postdoc program.

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