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Sorption of water and ethanol pure vapours and vapour mixtures by four hardwoods

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Abstract

Water is a universal solvent and swelling agent that is widely used in wood industry in association with organic solvents and salts, whether for the fractionation of biomass and the production of bio-based synthons for the chemical industry, the application of sizing agents and painting for the paper industry or the incorporation of preservatives to enhance wood durability for the timber industry. The relevance of solvents and technical treatments used for wood-based products requires a proper identification of the specific role of each solvent on wood biopolymers to better understand and predict their influence on wood properties. In particular, wood impregnated with aqueous solutions of organic solvents has shown to give rise to greater swelling than that observed in pure water, described as “hyperswelling”. To understand this phenomenon, the first step is to examine the existing interactions between wood microstructure and the different solvents present in these mixtures. This study is an attempt to bring to light the sorption behaviour of four different hardwoods in water–ethanol vapour mixtures containing increasing molar fractions of ethanol from 0 to 100%. Contrasted sorption behaviour in pure solvents was observed according to wood species having different biochemical compositions. This behaviour highlights the different affinities of ethanol and water for the macromolecules present in the wood microstructure. With mixed solvents, peculiar effects were confirmed in sorption behaviour of woods with lower mixed solvent uptake at high partial pressures compared to pure solvents. It is also shown that part of the sorbed ethanol molecules remains chemisorbed in the wood structures at the end of the desorption process.

Introduction

Wood is a renewable biomaterial that is used since thousands of years for many purposes such as energy, building material, paper, tools, furniture or packaging. Considering the importance of wood in the current environmental context and the development of bio-economy in many industrial sectors, better characterizing the properties of wood according to species and environmental conditions while considering its specific hierarchical microstructure is of great concern. In particular, the fractionation of biomass by organosolv pulping (Thoresen et al. 2020) and the production of bio-based synthons for the chemical industry in biorefineries (Abu-Omar et al. 2021) involve the use of water in association with salts and/or organic solvents. The interaction of wood with water-dilutable solvents or the action of pure organic solvents on incompletely dried wood is also relevant for surface treatments and incorporation of additives in the timber industry (Chronopoulos et al. 2020). In this regard, the relevance of solvents and technical treatments used for wood-based products requires a proper identification of the specific role of each solvent on the macromolecules present in the wood cell wall and their influence on wood properties. Therefore, the sorption mechanisms of water, organic solvents and their mixtures, their distribution and physico-chemical interactions within wood microstructure need to be better described and understood.

The extent of wood swelling is very dependent on the nature of sorbed liquids (Gordy 1939). Correlations between the physico-chemical properties of the sorbed liquids and their effect on wood swelling have been mainly discussed in terms of size and polarity of solvent molecules. Various researchers have documented a negative relationship between the molar mass of solvent molecules and the rate of wood swelling. This correlation can be attributed to the increased challenge faced by larger molecules in diffusing into the intricate structure of wood cell walls (Stamm and Loughborough 1942; Stamm and Harold 1950). On the other hand, Nayer and Hossfeld observed a greater and faster uptake of polar liquids into wood cell walls (Nayer and Hossfeld 1949), due to their higher bonding capacity towards wood biopolymers. Mantanis et al. (1994a, b, 1995) studied the effect of a wide variety of pure solvents on the swelling of various wood species and confirmed these observations. They found that both higher hydrogen bonding capacity and smaller size of the solvent molecules contribute to the extent of wood swelling. Thus, considering only pure water and organic solvents, the swelling of wood at saturation is well documented (Obataya and Shibusani 2005; Engelund et al. 2013; Bossu et al. 2018).

Nevertheless, in numerous industrial applications, the combination of organic solvents with water is common practice, and water is already inherently present within the microstructure of wood. The phenomena related to the influence of aqueous solutions containing organic solvents on wood are intricate and have resulted in remarkable observations. Indeed, it was observed that an aqueous mixed solvent could induce more swelling than either of the pure solvents (Robertson 1964). Several authors pointed out this synergistic effect of aqueous mixed solvents on wood swelling (Meier et al. 2005; Chang et al. 2009, 2012; Bossu

et al. 2018). Meier et al. (2005) reported that aqueous solutions of ethanol generate “hyperswelling”, resulting from specific interactions with the biopolymers constituting wood microstructure. More precisely, greater swelling was observed for a 50% volume fraction of ethanol in water. Nishida et al. (2003) obtained similar results on gels of acetylated lignin, showing no swelling in ethanol but eight times the initial volume when swelled in a 50%mol water/ethanol mixture. But despite the numerous works that report this phenomenon, few works hypothesize a mechanism that would explain its origin.

Bossu et al. (2018) made microscopic observations of cell walls after swelling of poplar wood in water/ethanol mixtures and showed that ethanol generates intercellular decohesion and disbonding of the different wood cell wall layers. This phenomenon is assumed to be at the origin of the hyperswelling of wood in water/ethanol mixtures, as the release of constraints between the wood cell wall layers is likely to promote greater swelling of the cell walls by water. The synergic effect of the solvents on wood cell wall swelling in this case would consist in a structural mechanism rather than a change in the volume of solvent uptake. This hypothesis suggests that the modification of the microstructure enables to reach higher swelling rate for similar quantities of sorbed water.

To check this hypothesis, a step forward would be to study the effect of mixed vapours on the sorption behaviour of a greater diversity of wood species considering their specific microstructure. With this objective, this work focuses on the sorption properties of four hardwoods, with contrasted biochemical composition, exposed to various water/ethanol mixtures.

Materials and methods

Materials

Four types of hardwood were used in this study, namely poplar (*Populus x Generosa*), oak (*Quercus Robur*), chestnut (*Castanea Sativa*) and walnut (*Juglans x Intermedia*). Specimens were collected from branches of four different wood species collected in March 2019 in two distinct French agroforestry systems: (i) trees from hedgerows (Saint-Etienne-en-Coglès, Brittany)—pedunculate oak (48° 21' 5.62" N; 1° 12' 16.654" W) and common chestnut (48° 21' 5.62" N; 1° 12' 16.654" W) and (ii) trees from an intraparcellar cropping system (Terres de Roumassouze, Vénézobres, Occitania)—hybrid walnut *Juglans x Intermedia* (44° 7' 37.934" N; 4° 5' 0.067" E) and poplar cultivar *Beaupré* (44° 7' 37.934" N; 4° 5' 0.067" E). No reaction wood was detected in the collected branches. The specimens were conditioned as follows by BioWooEB—CIRAD (Montpellier, France): 300×14×2.6 mm long heartwood sticks were cut from branch sections, in the longitudinal direction, considering the width of the sticks in the T direction and thickness in the R direction and then stored for a year in climatic chambers at 20 °C ± 2 °C and 65% ± 5% relative humidity. Later, specimens were cut into thin slivers of 3×1×0.2 mm to decrease the diffusion distance into the wood and stored at room temperature and 45% ± 5% relative humidity before sorption measurements. Biochemical compositions of the

different hardwoods were determined at LERMAB (Nancy, France) and are given in Table 1 (note that α -cellulose contents are lower in wood branches at the expense of hemicelluloses). Oak and walnut wood are both characterized by high content of extractives. Oak wood extractives have been widely characterized for wine and spirits ageing in wooden barrels. Ellagitannins (polyphenols, hydrolysable tannins) represent 10% of the dry weight in oak heartwood. They are responsible for the high durability of wood. Walnut heartwood extractives are also mainly composed of ellagitannins (Fukuda et al. 2003; Yalcin et al. 2018). Deionized water and pure ethanol (Sigma-Aldrich) used for sorption experiments were outgassed before use. The binary mixtures of ethanol and water were prepared with 1:2 and 2:1 ratios, *i.e.* mass fractions of 33.3% and 66.6% ethanol in the aqueous mixture, respectively. These mass fractions are displayed as 33% and 66% in the legends of the figures for the sake of clarity.

Methods

Isothermal sorption analyses were performed using a dynamic vapour sorption (DVS) resolution apparatus (Surface Measurements Systems, London, UK). This apparatus allows determining accurate sorption isotherms at different temperatures and using a pre-set range of partial pressures. The device contains two measurement pans, *i.e.* reference and sample holders, suspended from the arms of a Cahn ultra-sensitive magnetic compensation microbalance, which is capable of measuring sample mass change as low as 0.1 μg . The two measurement pans were connected to the microbalance by hanging wires sitting in a linked double chamber, which is located in a thermostatically controlled cabinet. A constant flow of dry nitrogen gas (100 mL/min), into which is mixed another nitrogen stream containing the vapour, passes through the chambers, thus maintaining a constant partial pressure of vapour. The typical mass used for these sorption experiments was ~ 150 mg. Each run was started in isothermal conditions from 0% partial pressure and then increases to 80% with successive steps of 20%, before decreasing

Table 1 Biochemical composition of the four hardwoods used in this study

Species	Extractives* (%)	Klason Lignin (%)	Holocellulose (%)	α -Cellulose (%)	Hemicelluloses (%)
Poplar	4.09	22.82	68.73	20.9	47.83
Chestnut	7.75	17.36	64.48	16.87	47.61
Oak	10.29	16.29	63.85	18.46	45.39
Walnut	11.49	20.67	63.67	21.5	42.17

*Sum of extractives after successive extraction using dichloromethane, acetone, toluene/ethanol (1 V/2 V) mixture and water. These extractives have not been identified in this study; however, according to the literature, the obtained extractives are mostly tannins, terpenes in the case of oak, whereas they are made of flavonoids, lignans and sterols in the case of walnut (Peng et al. 1991; Balaban and Uçar 2001; Heim et al. 2021). In the case of poplar and chestnut, which have lower extractive contents, sterols and terpenoids are the most present (Szadkowska et al. 2021)

back to 0% in the reverse order. Successive steps of partial pressures of vapour in nitrogen were set for determining the whole sorption isotherm. The typical duration of sorption cycle was 6 days. The equilibrium criterion was decided based on the slope of the curve mass versus time. This parameter, namely dm/dt (where m is in mg and t in min), was set as $\pm 0.004\% \text{ min}^{-1}$ where the percentage is the relative variation of mass in a time window of 10 min. This resulted in ~ 23 h of time required for each partial pressure in the case of ethanol and aqueous mixtures, whereas only ~ 5 h was required in the case of pure water. Examples of mass uptakes versus time are shown in supplementary material (Fig S1, Supplementary Material), as well as the slope of the mass uptake versus time. Interestingly, the desorption processes were faster in the case of ethanol and aqueous mixtures for each partial pressure, *i.e.* only 10 h was required, whereas there was no significant change in the case of pure water compared to sorption times. All the experiments were conducted at 25 °C. The saturation pressures of the mixed solvents have been calculated considering that ethanol/water mixtures are an ideal system on all the molar fractions investigated. In this case, the total pressure of the mixture can be calculated according to the Dalton law:

$$x_{\text{ethanol}} = \frac{P_{\text{ethanol}}}{P_{\text{ethanol}} + P_{\text{water}}} \quad (1)$$

According to the Raoult law, $P_{\text{ethanol}} = x_{\text{ethanol}}P_{\text{ethanol}}^*$, in which P_{ethanol}^* refers to the vapour pressure of pure ethanol, whereas P_{ethanol} refers to the vapour pressure of ethanol in the water/ethanol mixture. In a symmetric fashion, the same equation can be written for water.

Assuming that ethanol and water vapours are perfect gases, the vapour pressure of mixtures can therefore be estimated as:

$$P_{\text{mix}} = P_{\text{ethanol}} + P_{\text{water}} \quad (2)$$

At saturation, the saturation pressure of the mixture can therefore be written:

$$P_{\text{mix}}^{\text{sat}} = P_{\text{ethanol}}^{\text{sat}} + P_{\text{water}}^{\text{sat}} \quad (3)$$

where $P_{\text{ethanol}}^{\text{sat}}$ is the saturation pressure of ethanol in the water/ethanol mixture and $P_{\text{water}}^{\text{sat}}$ is the saturation pressure of water in the same mixture. It can be concluded that:

$$P_{\text{mix}}^{\text{sat}} = P_{\text{ethanol}}^{*,\text{sat}} + x_{\text{water}}(P_{\text{water}}^{*,\text{sat}} - P_{\text{ethanol}}^{*,\text{sat}}) \quad (4)$$

The relative pressure of the mixture can therefore be written as:

$$\frac{P_{\text{mix}}}{P_{\text{mix}}^{\text{sat}}} = \frac{x_{\text{ethanol}}P_{\text{ethanol}}^* + x_{\text{water}}P_{\text{water}}^*}{P_{\text{ethanol}}^{*,\text{sat}} + x_{\text{water}}(P_{\text{water}}^{*,\text{sat}} - P_{\text{ethanol}}^{*,\text{sat}})} \quad (5)$$

The saturation pressures of the pure sorbates were measured at 25 °C in a volumetric sorption apparatus described elsewhere (Trens et al. 2017). They were found to be 3200 Pa and 7866 Pa for water and ethanol, respectively.

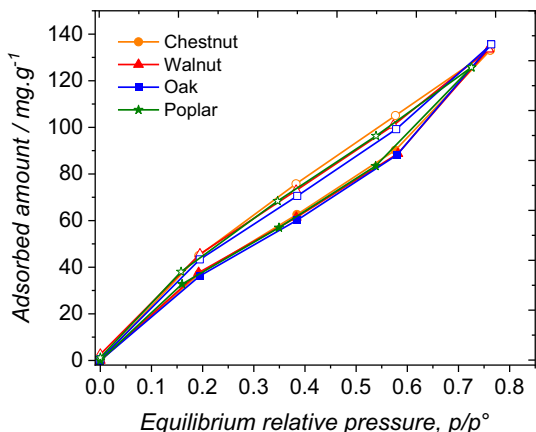
Results and discussion

Pure vapours

The sorption of water and ethanol on the four wood species can be discussed, first considering pure solvent vapour sorption. In the case of pure water, the sorption isotherms obtained have identical general shape as shown in Fig. 1.

The sorption isotherms are nearly superposed for all four wood samples, indicative of a similar wood/water affinity, in the Henry's law sense. A change of slope was observed beyond $p/p^\circ = 0.20$, indicating a possible transition between sorption regimes. Indeed, sorption of primary water requires interaction sites and usually these sites interact first with sorbates. Once these sites are completed, other sorption processes can take place, such as multilayer sorption or sorption with less interactive sites. As above-mentioned, common features can be observed with the four woods used in this study. It can be deduced that the differences in terms of composition of lignin and extractives do not modify the water sorption isotherms. The desorption branches are rather linear down to $p/p^\circ = 0.20$. A thin parallel hysteresis is observed and the desorption is complete at $p/p^\circ = 0$. Therefore, it can be concluded that water sorption process can be considered as almost reversible for all studied hardwoods. This general behaviour is consistent with the studies reviewed in the past by Shi and Avramidis (2017). In other words, the preferential interaction of water with the hydrophilic fraction of the cell wall layer is little disturbed by the presence of extractives compounds (Choong and Achmadi 1991; Nzokou 2004; Bossu et al. 2016). The structure of the ellagitannins extractives present in oak and walnut wood presents several hydroxyl functions (Puech et al. 1999; Jourdes et al. 2003; García-Estévez et al. 2017). The extraneous substances present in the cell wall in these two wood species may thus participate in water sorption. The shape of the observed hysteresis loops is typical of an activated sorption process, which requires more energy for the adsorption process, compared to the desorption process. This is compatible with a swelling mechanism in which the sorbate would be absorbed inside the bulk

Fig. 1 Sorption isotherms of pure water vapour by the four hardwoods at 25 °C (desorption branches as empty symbols)



are higher. The sorption branches are not linear, which indicates that the interaction sites are heterogeneous. Similar conclusions to oak and walnut can be drawn with respect to the hysteresis and irreversibility at $p/p^\circ=0$. Additionally, it is interesting to note that the irreversibility after desorption is higher for walnut and oak, compared to chestnut and poplar, while their affinity for ethanol is lower. The quantitative evaluation of the retention at $p/p^\circ=0$ could depend not only on the structure of the samples but also on mass stability criteria not severe enough to cope with sluggish desorption.

For explaining these observations, the composition of these specimens has to be considered (Table 1). The main difference between these two pairs of specimens is their extractive contents. Indeed, it can be noted that poplar and chestnut have lower extractive contents (4.1% and 7.7%, respectively) compared to oak and walnut (10.3% and 11.5%, respectively). Water seems to be adsorbed, regardless of this parameter, whereas it seems to strongly affect ethanol sorption. It appears that, in the two samples with the highest content of extractives, the ethanol interactions with the hydrophilic macromolecules of the cell wall (amorphous cellulose and hemicellulose) are prevented at low relative pressure, whereas this does not affect water sorption. Additionally, a confirmation of this particular interaction for ethanol can be seen on the sorption isotherms shown in Fig. 2. The absence of inflexion of the adsorption branches (at $p/p^\circ=0.2$) for oak and walnut could be due to a limitation of ethanol access by the extractive components, which are less present in chestnut and poplar specimens, which present a more usual change of isotherm slope.

A high affinity is usually the indication of a strong interaction leading to some irreversibility after the completion of the sorption isotherm. However, this is true only if one sorption process is present. In fact, if different sorption phenomena occur upon increasing pressure, the correlation is not always true. In other words, ethanol can be first adsorbed with a rather low affinity and as the pressure increases, ethanol can react with the wood components. It is interesting to observe that, in the adsorption experiments of Bellat and coworkers on cork components, irreversible retention of ethanol was observed on cork and cellulose but not on lignin and suberin extracted from cork (Lequin et al. 2013). This strongly suggests that ethanol can be chemisorbed on the more hydrophilic components of wood, while less hydrophilic components act as a screen, slowing down sorption and desorption. As more extractives are present in walnut and oak, it is likely that, in their low-pressure isotherms, ethanol sorption as well as desorption are made slower, compared to chestnut and poplar. A remarkable effect of sorption screening was observed by Bossu et al. (2018). Indeed, in the case of poplar veneers, these authors noted that there was almost no adsorption of ethanol at low relative pressures (around 0.1 wt% up to $p/p^\circ=0.3$), while at $p/p^\circ=0.8$ the ethanol uptake was very close to the data obtained in this study. Also in this case, a sluggish ethanol sorption corresponded to a significant retention in desorption at $p/p^\circ=0$ (Bossu et al. 2018).

These differences in affinity can be also quantified by the Henry's constants which have been derived for each system (Table 2). These Henry's constants values are the confirmation that water has a very similar interaction for the four specimens as the values are very close to one another. On the other hand, chestnut and poplar have a higher affinity towards ethanol compared to walnut and oak, as previously

Table 2 Sorbate—specimen Henry's constants derived at low relative pressure at 25 °C

Specimen	Henry's constant/mg g ⁻¹	
	Water	Ethanol
Chestnut	192	255
Walnut	196	124
Oak	186	129
Poplar	205	229

inferred from the adsorption branches at low relative pressure. Interestingly, when comparing water and ethanol affinities, chestnut and poplar have higher affinities for ethanol compared to those for water. This is the opposite for walnut and oak.

An alternative description of these sorption isotherms can be gained by using the GAB approach, which is classically used for biomass-based materials (Anderson 1946). This model was first developed for extending the sorption isotherm modelling of the BET approach (Brunauer et al. 1938) by considering the adsorption interaction level not only of surface monolayers but also between interacting multilayers. It has been recently rationalized in the case of water sorption by wood specimens (Bertolin et al. 2020). The GAB theory is formally similar to other modifications of the BET model (Dent 1977) but also to models based on different approaches (Hailwood and Horrobin 1946; Okoh and Skaar 1980). As an example, in Hailwood and Horrobin (1946), researchers proposed a model to explain the water absorption behaviour of polymer gels. In their study, the authors specifically defined the strongest sorption interaction as the absorption of hydration water molecules that directly interact with the polymer. Concomitantly, a weaker sorption interaction was attributed to “solved” water, which contributes to the gel swelling. One can observe that the formal similarity between the BET and GAB models suggests that, solely relying on uptake isotherms, it becomes challenging to differentiate between surface adsorption and bulk absorption phenomena (Prothon and Ahrné 2004). According to the GAB model:

$$\frac{W}{W_m} = \frac{K_{GAB} \times C_{GAB}}{(1 - K_{GAB} \times p/p^o)(1 - K_{GAB} \times p/p^o + K_{GAB} \times C_{GAB} \times p/p^o)} \times \frac{p}{p^o} \quad (6)$$

where W is the weight uptake at p/p^o and W_m is the monolayer capacity, here expressed as mg g⁻¹. This weight uptake corresponds to “bound” sorbate species. C_{GAB} is an energetic constant related to the ratio between the Gibbs free energies of bound and free sorbate, whereas K_{GAB} is defined as the ratio between the Gibbs free energy of the liquid in the bulk and that of the free sorbate. It can be noted that C_{GAB} and k_{GAB} are reminiscent of the C_{BET} parameter in which multilayer interaction has been ignored. Indeed, C_{GAB} can be defined as:

$$C_{GAB} = C_o \exp\left(\frac{H_o - H_n}{RT}\right) \quad (7)$$

where H_o and H_n correspond to the molar sorption enthalpy of the mono- and multilayers and K_{GAB} is defined according to the following equation:

$$k_{GAB} = k_o \exp\left(\frac{H_n - H_L}{RT}\right) \quad (8)$$

where k_o represents the entropic factor and H_L the molar enthalpy of adsorption of the bulk liquid.

Interestingly, the GAB approach was also proven to be successful for modelling the sorption of vapours penetrating inside low specific surface area materials, particularly in food science. Indeed, a distinction between “bound” and “free” sorbate instead of monolayer and multilayer adsorption was further introduced by Quirijns et al. (2005). Even if this distinction is still an issue, it is strongly supported by the observation that on wood samples, typical GAB monolayer sorption values are more than one hundred times larger than monolayer adsorption values measured using non-penetrating nitrogen derived using the BET model (Clair et al. 2008; Bratasz et al. 2012; Bossu et al. 2018). On the basis of these observations, we will not consider the parameters of the GAB model as representative of a monolayer-multilayer adsorption on a free surface but as correlated to the sorption of sorbate at different energy levels (“bound” and “free” sorbate or primary and secondary water), albeit the monolayer–multilayer terminology will be still used for comparison with previous literature. In any case, the derivation from the BET model introduces a strong simplifying hypothesis in the interpretation of the isotherm, as all “bound” molecules are considered to interact in the same way with the adsorbent, with no distribution of site strength and no lateral interaction. In the same way, all “free” sorbate is considered to be in one energy state, intermediate between the “monolayer” and the external fluid. In a material as complex and compliant as wood, the model cannot consider the way in which sorption modifies the sorbent, with a continuous variability of the accessibility of hydroxyls with swelling and the competition of interaction with several wood components. In these conditions, it is maybe surprising that the GAB model provides a quite correct fit of experimental sorption isotherms. This is at the basis of its widespread use and its valour in the comparison of isotherms on different materials and as a descriptor of the curves, allowing to pinpoint similarity and differences. If a parallel with a different field of adsorption is allowed, the use of the GAB equation in biomass sorption corresponds to the use of BET surface area in adsorption on zeolites, where the monolayer–multilayer model, albeit with no physical meaning in microporous sorbents, is currently used to compare properties at an industrial scale (Thommes et al. 2015). The comparison of the GAB parameter values is indeed useful, as the BET surface area is for gas adsorption on zeolites, although their absolute values do not represent a reliable evaluation of specific physical properties (Thybring et al. 2021), as the C_{BET} values in the BET model.

The values of the GAB constants for the four specimens in the presence of water and ethanol vapours are reported in Tables 3 and 4. In the case of water sorption (Table 3), the GAB parameters are representative of the similarity of the isotherms of the four samples (Fig. 1). All samples presented a monolayer capacity of $54 \pm 6\%$ mg g⁻¹ and a C_{GAB} parameter of $7.32 \pm 10\%$. The similarity of the C_{GAB}

Table 3 GAB parameters for water sorption on the four specimens

	C_{GAB}	K_{GAB}	$W_m/\text{mg g}^{-1}$	r^2	$S_{GAB}/\text{m}^2 \text{g}^{-1}$
Chestnut	6.46	0.79	58	0.9999	206
Walnut	8.32	0.85	51	0.9999	179
Oak	7.18	0.84	52	0.9999	182
Poplar	7.32	0.84	53	0.9999	187

The specific surface area was determined, taking the cross-sectional area of water as 0.105 nm^2 (Trens et al. 1996; Rouquerol et al. 2013)

Table 4 GAB parameters for ethanol sorption on the four specimens

	C_{GAB}	K_{GAB}	$W_m/\text{mg g}^{-1}$	r^2	$S_{GAB}/\text{m}^2 \text{g}^{-1}$
Chestnut	10.74	0.53	81	0.9999	153
Walnut	2.02	0.44	140	0.9983	–
Oak	2.52	0.37	143	0.9998	–
Poplar	11.47	0.57	67	0.9998	127

The specific surface area was determined, taking the cross-sectional area of ethanol as 0.145 nm^2 (Tang et al. 2019)

values suggests that, in our experimental setting, the water/specimen interaction is nearly independent of the nature of the wood. The K_{GAB} parameters are in the range $0.83 \pm 3\%$. We already reminded the fact that the K_{GAB} parameter is essentially of entropic nature. Its low value (< 1) regardless of the nature of the specimen suggests here that secondary water molecules are clearly more structured than they are in the liquid water phase.

Compared to water sorption, several comments can be put forward, considering the description of the ethanol sorption through the GAB model. Concerning the derivation of the specific surface area, the model failed when applied to walnut and oak, the most adsorptive-rich specimens. Indeed, any BET-related model attempts to define a monolayer volume on the basis of the decrease of slope of the isotherm after an initial more energetic sorption. The anomalous linear ethanol isotherms of walnut and oak (Fig. 2) presented a minimal decrease of slope only beyond $p/p^\circ = 0.6$, suggesting an unreliable calculated monolayer uptake at relative pressure above 1, which is the indication that this model cannot be used in a correct fashion. In the case of chestnut and poplar, the specific surface areas could be derived. They are lower than those derived using water as sorbate. A reason for this discrepancy can be found in the cross-sectional area taken for ethanol which is less common than that used for water and therefore less robust. It can be also argued that specific interactions of ethanol with the surface can affect the orientation of the molecule. The GAB parameters obtained for chestnut and poplar are consistent with the conclusions drawn from calculated Henry's constant. Indeed, the C_{GAB} parameters are higher compared to those obtained from water sorption, which is the indication that ethanol has a higher affinity for these specimens. This affinity could be related to the interaction of ethanol with the macromolecules of the walls which are more accessible when less extractives are present. As discussed above, the irreversibility would be related to the presence of extractives, which is more visible in the case of oak and

chestnut. Additionally, the K_{GAB} is lower, which shows that, for all the specimens, the mobility of the secondary ethanol sorbate is less different from the bulk liquid than in the case of water.

Mixed vapours

In the liquid phase, mixed solvents are known to induce specific behaviours towards wood swelling compared to pure solvents. It can be assumed that the sorption properties of wood samples do result from synergistic effects. Water/ethanol vapour mixtures were therefore tested, and for these experiments, two different compositions were chosen (33.3% and 66.6% molar mass ratio of water). A comparison of the mixed vapours sorbed on the four wood samples is shown in Fig. 3.

The sorption isotherms shapes were observed to be similar, regardless of the water/ethanol ratio and wood sample, indicating that the solvent mixtures average the interactions ruling governing the sorption process. Compared to pure systems, this observation is reminiscent of the case of pure water with which very similar sorption isotherms were obtained for all tested species (see Fig. 1). However, in the case of mixed vapours, for both ethanol concentrations, the sorption isotherms exhibit a well-defined curvature of the low-pressure part of the isotherm and wide hysteresis loops which have only been found in the case of pure ethanol sorption isotherms. Additionally, differences can also be distinguished at $p/p^\circ = 0$ on the desorption branches where the data are more scattered for 66.6% ethanol.

These observations could be interpreted as intermediate situations between pure water and pure ethanol sorption isotherms. Indeed, the large hysteresis loops can be related to ethanol whereas the similarity of the shape of the adsorption branches is more reminiscent of pure water sorption. To obtain more insight into these results, the sorption isotherms were gathered for each wood specimen and solvent mixture in Fig. 4.

For all the woods tested, it can be observed that the mass uptake at high p/p° is lower for mixtures compared to pure solvents. This observation tends to indicate

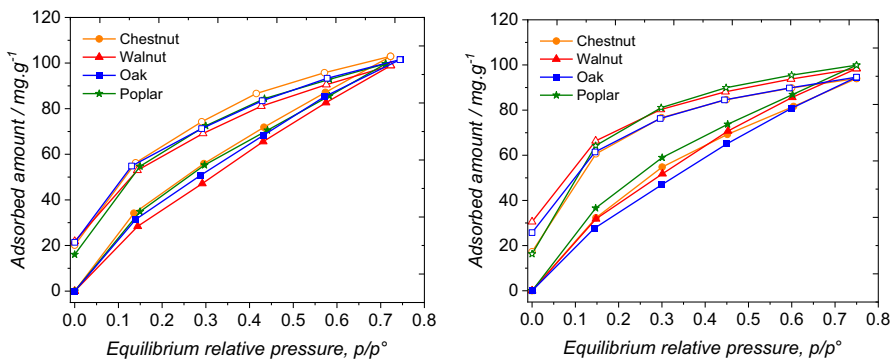


Fig. 3 Sorption isotherms of the four hardwoods using water/ethanol mixtures. (Left) 66.6% water, (right) 33.3% water

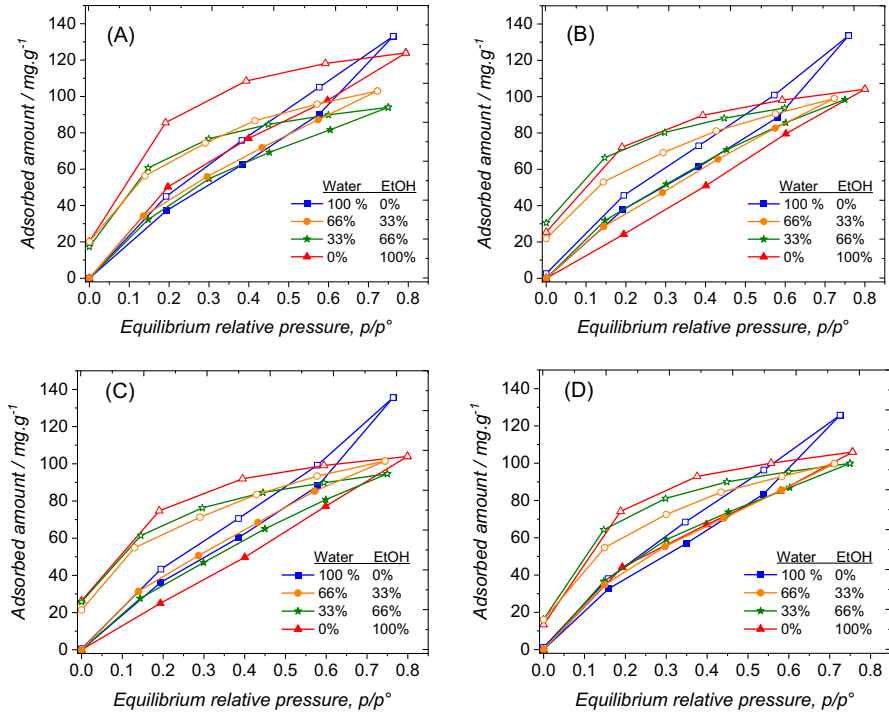


Fig. 4 Sorption isotherms of solvents mixtures by **a** chestnut, **b** walnut, **c** oak and **d** poplar. All these sorption isotherms have been determined at 25 °C

that the phenomenon of wood hyperswelling in mixed solvents is not resulting from a higher quantity of sorbed solvent but rather related to the enhancement of wood cell wall swelling ability after they have been modified by ethanol molecules. Such hypothesis is consistent with Bossu et al. (2018) who already observed this synergistic effect, in the case of poplar veneers in water/ethanol mixed solvents.

Interestingly, except in the case of chestnut, the maximum mass uptakes of the mixtures are very close to that obtained using pure ethanol. Despite the relative amount of adsorbed water and ethanol cannot be determined by gravimetry, this trend is significant and could be tentatively explained either by a competition mechanism through which ethanol co-adsorption limits the accessibility of water to hydrophilic sites or by a specific volume of secondary ethanol higher than water in the presence of a similar swelling. Furthermore, in the case of chestnut, despite a higher ethanol sorption, the ethanol/water mixtures do not adsorb more than in the other wood specimens. It is also interesting to observe that the sorbate retention at the end of desorption process, also observed in the presence of ethanol, is independent of the ethanol concentration in the vapour. This seems coherent with the absence of retention at $p/p^\circ = 0$ in the case of water sorption and supports the attribution of delayed desorption to ethanol chemisorption.

The evolution of the sorption isotherm shape can also be discussed, even though the saturation pressure of the pure sorbates is different. This is the reason

why the Raoult's law was used to determine a saturation pressure for the mixture. It can be observed that the peculiar linear isotherm of ethanol on extractive-rich oak and walnut is never observed when any water is present in the vapour phase. This allows to limit any explanation of the phenomenon to a specific interaction of ethanol with the adsorbent. For all specimens, the adsorption branches of the sorption isotherms obtained in the case of vapour mixtures are very close to that of water on all specimens or of ethanol on extractive-poor chestnut and poplar up to a relative pressure of $p/p^0 = 0.5$. No further information can be drawn from the Henry's constant, as it is related to a specific surface site/sorbate interaction and cannot be derived for mixtures. At higher relative pressure on the adsorption branches and also on the desorption branches, the shape of the sorption isotherms is similar to that of the pure ethanol sorption isotherms, suggesting that the ethanol is responsible for the hysteresis loop obtained in the case of mixed solvents. Indeed, the amount of ethanol in the mixture seems to have a direct impact on the size of the hysteresis loop. In other words, the amount retained in the hysteresis loop increases with increasing molar fraction of ethanol (Aguilera-Segura et al. 2019).

The maximum mass uptakes are better shown in Fig. 5a for each specimen and water/ethanol mixture. The results presented are as near to the thermodynamic equilibrium as allowed by the equilibrium criterion indicated in the method section, viz. the value of the slope of the mass variation versus time. However, the time to reach the equilibrium is relevant for any practical sorption process involving complex structures such as woods. We therefore also focused on the equilibration times recorded for each sorption isotherm, which provide information on the kinetics of adsorption and desorption. The results are presented in Fig. 5b–d.

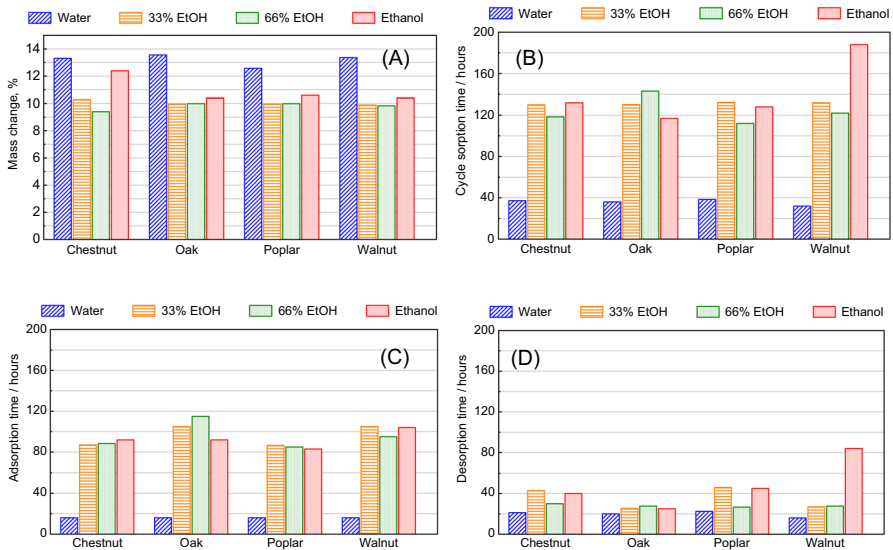


Fig. 5 a Maximum mass change of each wood with increasing molar mass fraction (%) of ethanol, b sorption cycle time, c full adsorption time and d full desorption time

When looking at the full sorption cycle times, clear differences can be observed (Fig. 5b). The sorption cycle time in the case of pure water is the shortest, regardless of the wood concerned (around 40 h). When ethanol is adsorbed, pure or in water/ethanol mixtures, the sorption duration is much longer, around 120 h reaching up to 185 h in the case of walnut when pure ethanol is adsorbed. The results are consistent with the lower values obtained for constant K_{GAB} in the GAB model obtained in the case of ethanol, despite the fact that the GAB model failed in the case of walnut and oak. Indeed, as ethanol sorbed during the multilayer mechanism is less structured than in the case of water, it can be deduced that it takes much longer time to reach equilibrium.

When studying adsorption and desorption kinetics of water, these two processes require similar durations, which is consistent with the reversibility of the sorption processes already discussed. In the case of mixtures and pure ethanol, adsorption processes were two to four times longer than desorption processes. However, in the case of pure ethanol sorption by walnut, adsorption and desorption times were quite similar, making this sorption process the longest observed in this study, which may be related to the highest extractives content (11.5%) found in walnut. In all other cases, the differences in equilibration time observed between adsorption and desorption of ethanol or water–ethanol mixtures can be rationalized by taking into account the shape of the isotherms. The presence of an important hysteresis loop in the presence of ethanol implies that the first steps of desorption correspond to small losses of mass. In these conditions, the mass stability criteria is reached faster, leading to a lower equilibration time and a shorter total time for the desorption than the adsorption process.

Conclusion

This study was conducted to interrogate the sorption behaviour of four hardwood species in pure water and ethanol vapours and their mixtures in different proportions. Dynamic vapour sorption was employed to assess whether literature modifications of wood swelling properties could be related to the sorption behaviour of different hardwoods as the result of wood/vapour and wood biopolymers interactions. The four hardwood species showed synergistic effects in mixed vapours, as the amount of mixed vapours uptake at high partial pressures was found to be lower than for pure vapours. It was also shown that part of the sorbed ethanol molecules remains chemisorbed in the wood structures at the end of the desorption process. These results are related to different behaviour of wood species towards sorption/desorption process in relation to their specific microstructure and biochemical composition, higher contents of extractives affecting the interactions with ethanol. More specifically, it is shown that ethanol has a higher affinity compared to water, which could be related to the interaction with the macromolecules of the cell walls. The extractives clearly play a prominent role in these vapour sorption processes, in the sense that their presence hinders ethanol sorption, as shown for oak and walnut, and slows down the desorption of ethanol. The retention observed at the end of the desorption is not correlated by the Henry's constants as these parameters do not refer to

the same processes. Additionally, it has been shown that the ethanol absorbed after saturation of the stronger sites is less structured than in the case of water. In terms of kinetics, walnut exhibited the longest time of full desorption of ethanol, which can be related to its higher extractive contents leading to a higher ethanol retention.

Investigations on the impact of the selective interactions of pure vapours or vapour mixtures towards wood microstructures during static and dynamic mechanical measurements are in progress.

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Availability of data and materials The raw data to reproduce the results are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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Consent for publication All authors read and approved the final manuscript.

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