

Role of Wood Macromolecules on Selective Sorption of Phenolic Compounds by Wood

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Wood is a complex structure of various macromolecules, mainly cellulose, hemicellulose, and lignin. Although the sorption process of some organic compounds by wood has been elucidated, the relative contribution of its different fractions in the sorption mechanism is not clearly determined. Certain works predict the amount of organic compounds sorbed on wood as a direct relationship to its lignin fraction. All wood macromolecules, however, seem to have the capacity to sorb organic compounds. Sorption of phenolic compounds on individual wood macromolecules has been studied and compared to that on wood. Wood–water partition coefficients (K_{wood}) for phenolic volatiles and their sorption rates in the presence of lignin display a linear relationship. Results show that cellulose and hemicellulose sorb all phenolic compounds without apparent distinction, whereas lignin is a selective sorbent of these compounds. Sorbent availability and sorbate chemical structure seem to be the key factors governing the sorption mechanism. Sorption kinetics study gives apparent diffusion coefficient values of aroma compounds, bringing new kinetic data for understanding the ternary system of wood, hydroalcoholic solution, and phenolic compounds.

KEYWORDS: Wood macromolecules; phenolic compounds; sorption; diffusion

INTRODUCTION

Many studies show that wood is a good adsorbent of various organic compounds, such as organochlorine pesticides (1), monoaromatic and polyaromatic hydrocarbons (2, 3), lipophilic organic compounds (4), wine aroma compounds (5–7), and stilbene derivatives (8). This sorption capacity is thought to be related to its chemical nature and, therefore, its composition (2, 3). Wood is indeed a complex natural material mainly composed of three major polymeric components: cellulose, hemicellulose, and lignin, which, respectively, represent around 40, 25, and 25% of hardwood dry mass (9, 10). The chemical differences between these three main biomacromolecules result in significant variability in their abilities to interact with organic compounds in solution. The polyhydroxyl structure of cellulose and hemicellulose provides numerous hydrogen bonding possibilities, whereas lignin's phenylpropane units give rise to relatively high hydrophobic regions (11). Wood macromolecules also contain sites that are able to donate or accept electrons. In the case of cellulose and hemicellulose, the most likely electron donors are the oxygen atoms in hydroxyl groups. For lignin, the most likely electron donor sites are the phenyl rings. Thus, as a whole, wood

is considered to be a basic material according to the Lewis definition (12).

The sorption level of a compound (sorbate) in solution by a solid material (sorbent) can be described by its partition coefficient ($K_{S/L}$). This thermodynamic parameter is defined by the ratio between the concentration of sorbate in the liquid phase and its concentration in the solid phase at equilibrium:

$$K_{S/L} = C_{\text{solid phase}} / C_{\text{liquid phase}} \quad (1)$$

Garbarini and Lion (13) observed that, among various soil organic matter macromolecules, lignin is a molecule with great capacity to sorb individual hydrocarbons. These authors studied in particular the sorption capacity of isolated soil organic matter macromolecules (humic acid, corn protein zein, lignin, and cellulose). They showed that the $K_{S/L}$ values of toluene and trichloroethylene, in a sodium phosphate buffer solution, are around 100 times greater in the presence of lignin than in the presence of cellulose. A few years later, another study investigating the retention of 2,4-dichlorophenol and 2,4,5-trichlorophenol by pulped wood fibers also indicated that sorption is directly related to the lignin fraction (11), as

$$K_{\text{wood}} = f_{\text{lignin}} K_{\text{lignin}} \quad (2)$$

where f_{lignin} is the lignin mass fraction and K_{lignin} is the lignin–water partition coefficient. Thus, wood–water partition coefficients, K_{wood} , have been hypothesized to be controlled by

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the wood lignin content (2, 3). Nevertheless, the presence of the two other macromolecules, cellulose and hemicellulose, cannot be neglected. They could also take part in the sorption phenomena of small organic molecules. It is well-known in particular that cellulose has a good affinity for water (14), for organic compounds in aqueous solution (15), and even for nicotine (16).

Considering the diffusivity of the sorbate into the studied material, the transient state of the sorption kinetics can also be used to determine the diffusion coefficient assuming a Fickian mechanism with imposed boundary conditions (17). This obviously gives an apparent diffusion coefficient, as it often includes other phenomena due to convection, capillary forces, chemical reactions, or transport obstruction (18). It represents, however, an important parameter to characterize the kinetics of the phenomenon in a ternary system composed of the sorbent (wood or constituent), the sorbate (diffusing molecule), and the surrounding medium (containing the sorbate). In this respect, wood could be considered as a type of packaging with specific permeability characteristics, especially for its use as barrels for wine aging.

The purpose of this research was to investigate the sorption and diffusion properties of phenolic compounds diluted in hydroalcoholic solution (using a homologous series of guaiacol, 4-vinylguaiacol, 4-ethylphenol, eugenol, and isoeugenol) by individual wood macromolecules (cellulose, hemicellulose, and lignin), to compare these properties with those of oak wood, and to identify the respective roles and contributions of each macromolecule.

MATERIALS AND METHODS

Material. Guaiacol, 4-propylguaiacol, 4-vinylguaiacol, 3,4-dimethylphenol, and isoeugenol were supplied from Aldrich-Sigma Co.; 4-methylguaiacol, 4-ethylguaiacol, and 4-ethylphenol were bought from TCI-EP, and eugenol was purchased from Fluka, each with a minimum purity of 98%. All solvents used were purchased from Carlo Erba Reactives. Small pieces of wood (2 × 10 × 20 mm) were given by the Office National des Forêts (ONF, France) and taken from *Quercus robur* (*pedunculata*) oak trees from the Forêt de Cîteaux (France).

Cellulose (long fibrous) and hemicellulose (xylan, from birchwood) were supplied from Aldrich-Sigma Co. Lignin was extracted from *pedunculata* oak wood.

Lignin Extraction from Pedunculata Oak Wood. *Pedunculata* oak wood sawdusts were initially purified and then extracted with HCl-acidified dioxane, incorporating some minor modifications (19). Ten grams of *pedunculata* oak wood sawdust (size particle = 0.25–0.315 nm) were placed in a cellulosic cartridge (28 × 100 mm, Macherey-Nagel) in a Soxhlet system for 24 h, with an ethyl alcohol/benzene (1:2) mixture as the solvent. The purified sawdust was placed in a 1000 mL round-bottom flask, and 500 mL of acidic dioxane (90 mL of dioxane + 10 mL of 2 N HCl solution) was added; the flask was connected to a reflux condenser for 6 h. After cooling, the solution was filtered through a filter paper (110 mm, Whatman Inc.) and collected in an Erlenmeyer flask. Twenty milliliters of 96% dioxane was used to wash the residue collected on the filter, and the wash was combined with the original filtrate. The obtained liquor was poured in a 2000 mL glass flask and doubled in volume with distilled water. Lignin immediately formed a fine precipitate. The solution was added to a 250 mL centrifuge bottle. The precipitate was pelleted by centrifugation (3000g, 20 min), and the supernatant was removed. The pellet was partially air-dried and then washed by ethylic ether during 48 h. The lignin residue was stored in a glass flask at ambient temperature prior to use.

Measurements of Sorption Kinetics of Phenolic Compounds onto Wood Macromolecules. Sorption kinetics of the different phenolic compounds on wood macromolecules were determined in hydroalcoholic acidic solutions (12.5% v/v ethanol and pH 3.5). Phenolic

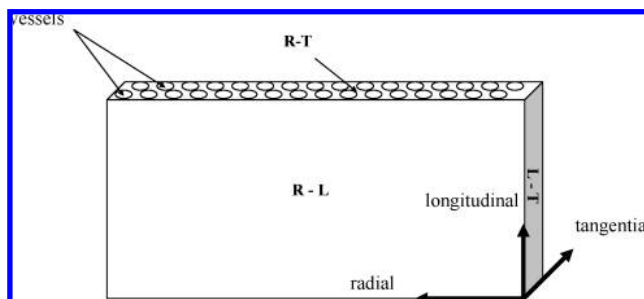


Figure 1. Schematic representation of wood plates denoting the three distinct surfaces, the radial–longitudinal (R-L), the radial–tangential (R-T), and the longitudinal–tangential (L-T), and showing the macroporous openings of the longitudinal vessels.

compounds were used in mixture to compare with previous results observed on wood (7). Solutions were prepared from a stock solution containing 500 mg/kg of all volatiles dissolved in analytical-grade ethyl alcohol, in order to obtain an initial concentration of about 10 mg/kg. Each wood macromolecule was weighed and added to 25 mL glass flasks completely filled with the hydroalcoholic acidic solution (total volume of about 35 mL). Final concentrations of solid materials in solutions were 2.8, 2.8, and 1.4 g/L, respectively, for cellulose, hemicellulose, and lignin. Hemicellulose and lignin concentrations in solution were chosen according to their ratio in wood (40 and 25%, respectively). For cellulose, in order to be able to compare the behavior of two wood polysaccharides, its concentration in model system was fixed to the same value as that of hemicellulose. Control samples were prepared without any wood macromolecules. Flasks were tightly closed with Teflon caps to prevent the loss of volatile compounds and stored, in triplicate, at 10 °C. Two microliter aliquots of the solution phase were withdrawn at different times and subsequently analyzed by GC, using an external calibration. Removal of this sample volume for analysis was considered to be negligible compared to the total volume.

Stability of Phenolic Compounds in a Model Wine Containing Extractables of Lignin. To take into account reactions that could occur between lignin extractables and wine phenolic compounds, the lignin sample was put in contact with the model wine during 7 days at 10 °C. After removal of the lignin sample, all of the polyphenolic compounds studied were added to this model wine having extracted lignin extractables, and the evolution of their concentrations was followed with time.

We have observed that for all phenolic compounds, the concentration remains constant in the presence of lignin extractables (not shown).

Sorption Kinetics Measurements as a Function of Wood Surface Accessibility. To study the effect of the wood surface exposed to the solution on sorption kinetics, concentrations of volatiles were measured in solutions in contact with wood plates and compared to those measured with wood plates having their radial–tangential (R-T) surface (Figure 1) sealed with epoxy resin (Araldite Cristal). Experimental samples were prepared by immersing one piece of wood (0.25–0.35 g) in the hydroalcoholic acidic solution containing individual phenolic volatiles. Control samples were prepared with epoxy resin alone (0.05 g). Dependency of sorption kinetics on the wood shape has also been studied by immersing sawdust (0.25–0.35 g) in the hydroalcoholic acidic solution containing individual volatiles. Sorption kinetics were followed as indicated above.

Construction of Sorption Isotherms of 4-Ethylguaiacol and 4-Vinylguaiacol by Lignin and by Unsealed Wood Plates. Sorption isotherms were determined using 10 hydroalcoholic acidic solutions, which contained between 5 and approximately 40 mg/kg of either 4-ethylguaiacol or 4-vinylguaiacol. Sorption isotherm experiments were carried out on oak wood lignin and on unsealed wood plates. The experimental and control samples were analyzed by liquid–liquid extraction and GC. Samples were prepared as described above. Aliquots of 10 g of sample solutions from sorption experiments were extracted two times with 2 mL of dichloromethane. Before extraction, 50 µg of 3,4-dimethylphenol was added as an internal standard.

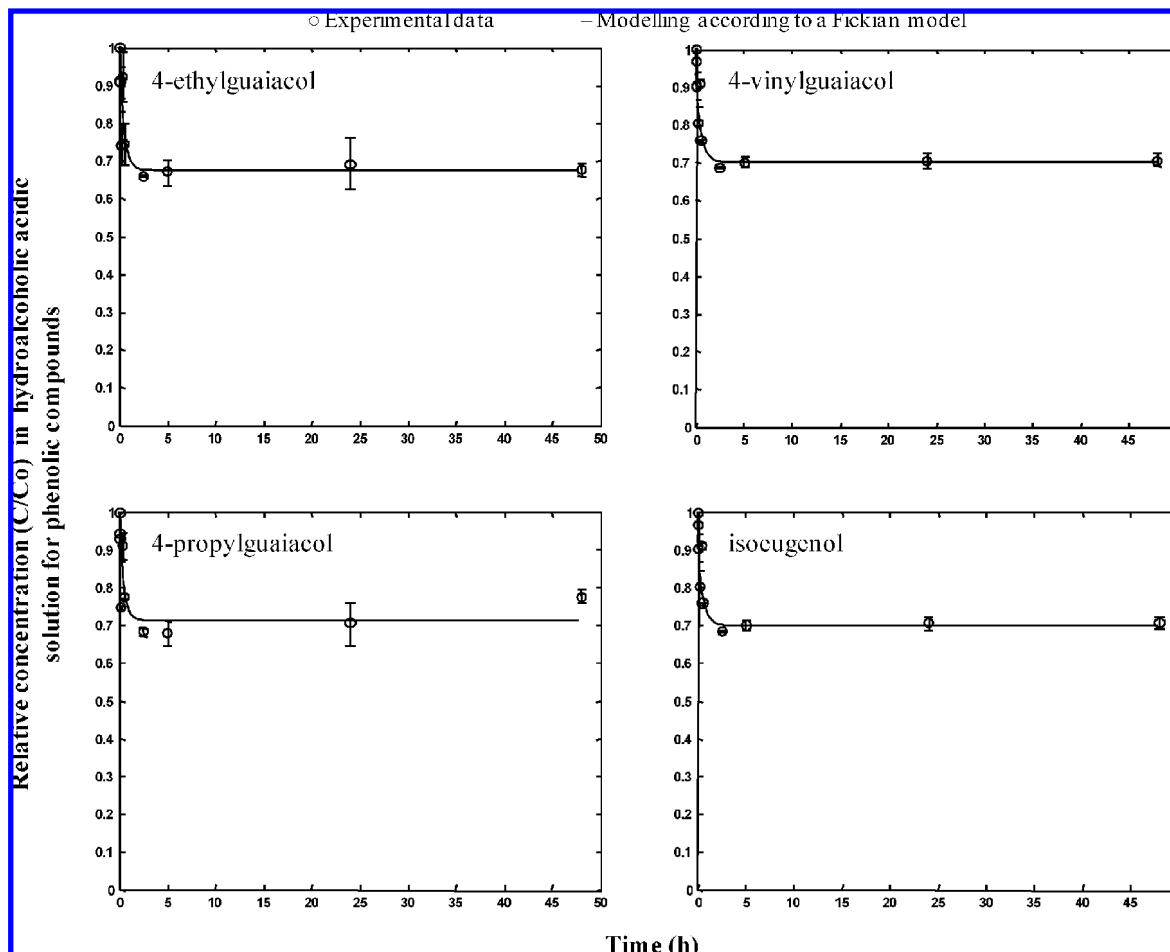


Figure 2. Evolution of the concentrations of 4-ethylguaiaicol, 4-propylguaiaicol, 4-vinylguaicol, and isoeugenol in hydroalcoholic solution stored at 10 °C in contact with cellulose.

The amount of phenolic compounds sorbed was calculated from the difference in concentration between control samples and experimental samples at equilibrium in the liquid phase.

GC Analysis. The concentration of phenolic compounds in the liquid phase was determined with a GC TRACE ULTRA (Thermo Electron Corp.) gas chromatograph fitted with a split injector (1/30). A flame ionization detector and a capillary column CP-WAX 57CB (Varian) (25 m × 0.25 id; 0.2 μm bonded phase) were used. The column temperature was programmed to vary from 130 to 190 °C at a rate of 3 °C/min. The flow rates were 30 mL/min for He, the carrier gas, and 35 and 350 mL/min, respectively, for H₂ and air detector gas. The temperature was kept at 250 °C for the detector and at 200 °C for the injector. Two microliters of sample were injected. The acquisition and processing of the data were carried out with Chrom-card workstation version (Thermo Electron Corp.).

Sorption Kinetics Model To Estimate Diffusion Coefficients. The sorption kinetics of phenolic compounds by wood can be described by the classical Fickian diffusion equation through a membrane of L thickness, with a uniform initial distribution and different surface concentrations. In the hypothesis of a unidirectional mass transfer, this can be solved using an analytic solution (20) to Fick's law applied to the transient state ($\delta C/\delta t = D\delta C/\delta x$):

$$\frac{m_t}{m_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D_{app}(2n+1)^2\pi^2 t}{4L^2}\right] \quad (3)$$

m_t = mass of the diffusing substance at time t (g), m_∞ = mass of the diffusing substance at time equilibrium (g), D_{app} = apparent diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), L = half-thickness of the wood sample for our experimental conditions (m), and x = distance (m).

In this case, the concentration ratio C/C_∞ , obtained from the integration of the corresponding chromatograms, could also be used in place of the mass ratio.

This model was thus applied to experimental values to determine the apparent diffusion coefficient of the aroma compound, D_{app} , and its sorption coefficient, S , that is to say, the kinetic and thermodynamic parameters of the sorption process. The values of the unknown parameters were determined by minimizing the sum of the square of the differences between measured and predicted values, using a Levenberg–Marquardt algorithm and taking D_{app} and m_∞ as adjustable parameters. Data treatment was performed using Matlab software (version 7.01, The Mathworks, Natick, MA).

RESULTS AND DISCUSSION

Sorption Kinetics of Phenolic Compounds onto Wood Macromolecules. As an example, Figures 2, 3, and 4 display the evolution with time at 10 °C of the normalized concentrations of 4-ethylguaiaicol, 4-propylguaiaicol, 4-vinylguaicol, and isoeugenol, mixed together with all other volatiles in the presence of cellulose, hemicellulose, and oak wood lignin, respectively. The evolution of phenolic concentrations in hydroalcoholic acidic solution was charted over time. To assess the chemical stability of volatiles due to possible reactions under experimental conditions, the evolution of their concentrations with time in solution were also monitored and, for all compounds, no significant variations of concentration were observed (results not shown). These results confirm a stability of phenolic compounds in a hydroalcoholic acidic solution under experimental conditions (7). Therefore, the observed decrease of the concentrations for the experimental samples can be assumed to be due only to sorption onto the wood macromolecules.

Figures 2–4 show that the time to reach the sorption equilibrium in the presence of wood polysaccharides is a few

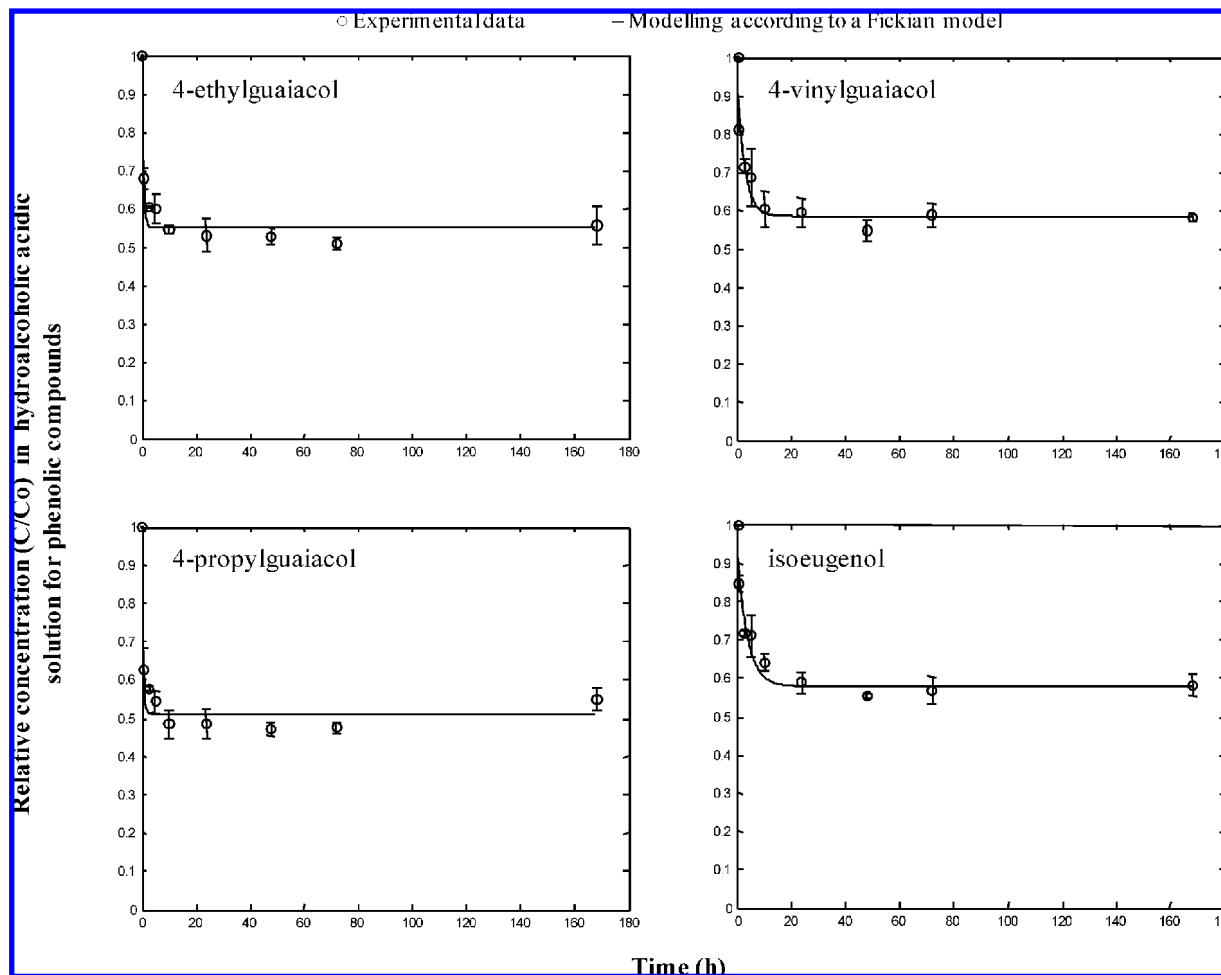


Figure 3. Evolution of the concentrations of 4-ethylguaiacol, 4-propylguaiacol, 4-vinylguaiacol, and isoeugenol in hydroalcoholic solution stored at 10 °C in contact with hemicellulose.

hours and between 5 and 7 days for that in the presence of lignin. Except for lignin, equilibration times of volatiles were significantly shorter than the approximately 7–10 days it took to reach the sorption equilibrium for the same phenolic compounds in the presence of oak wood plate (7). This difference in equilibration times is probably due to a faster diffusion toward the polysaccharide sorption sites. The use of pure biopolymers could indeed increase the accessibility of the active sites for sorption. In contrast, sorption kinetics of 4-vinylguaiacol and isoeugenol in the presence of lignin indicate that the sorption equilibrium was reached after 7 days.

As shown in **Figures 2–4**, the application of a diffusion model based on an analytic solution of Fick's law applied to the transient state provides a good adjustment to the experimental points. However, diffusion coefficient values are not presented here. Indeed, using an analytical solution in the case of an equivalent geometry to a sphere that corresponds to the characteristic dimension of the particles (polymer powder) did not give a true representation of the system, as these particles lie as a thin sheet, because experiments were not carried out under stirring. This means that the characteristic geometry of the system is between small spheres and a thin sheet, conferred by upright spheres, with a decreasing accessibility for diffusant from top (toward solution) to bottom.

Sorption Equilibrium of Phenolic Compounds onto Wood Macromolecules. **Table 1** shows the rates of disappearance of each volatile at equilibrium calculated by the difference between their initial and final concentrations in solution. The sorption level of all of the volatiles ranged between 20 and 30% in the

presence of cellulose and between 30 and 40% in the presence of hemicellulose. In the presence of lignin, sorption levels ranged from 14% for guaiacol to 60% for 4-vinylguaiacol. Sorption levels at equilibrium in the presence of lignin appear very similar to those observed in the presence of wood (7). **Figure 5** displays the linear correlation ($R^2 = 0.87$) observed between K_{wood} for phenolic volatiles (7) and their sorption rates in the presence of lignin. As it can be seen from **Figures 4 and 5** and from **Table 1** for both the wood and the lignin, the more sorbed molecules are the chemical structures that have a C=C double bond conjugated to the phenyl ring, that is, 4-vinylguaiacol and isoeugenol. These results suggest that lignin governs not only sorption kinetics as shown above but also sorption levels at equilibrium, indicating that the three wood polymers have a different capacity to sorb volatile phenolic compounds. For polysaccharides sorption occurs in homogenous proportions, whereas proportions are much more variable for lignin, the most hydrophobic polymer. This small difference in the sorption levels observed for volatile molecules in the presence of cellulose and hemicellulose testifies to a nonselective retention process of organic compounds by these sorbents of polysaccharidic nature. In the presence of lignin, the range of measured values for sorption is broader, showing the existence of different interactions between the macromolecules and the phenolic compounds according to the nature of the sorbed molecule. The calculated hydrophobicity ($\log P$) and the solubility for the studied compounds are also summarized in **Table 1**. For the homologous series of guaiacol, the sorption rates in the presence of lignin seem to be directly related to the physicochemical

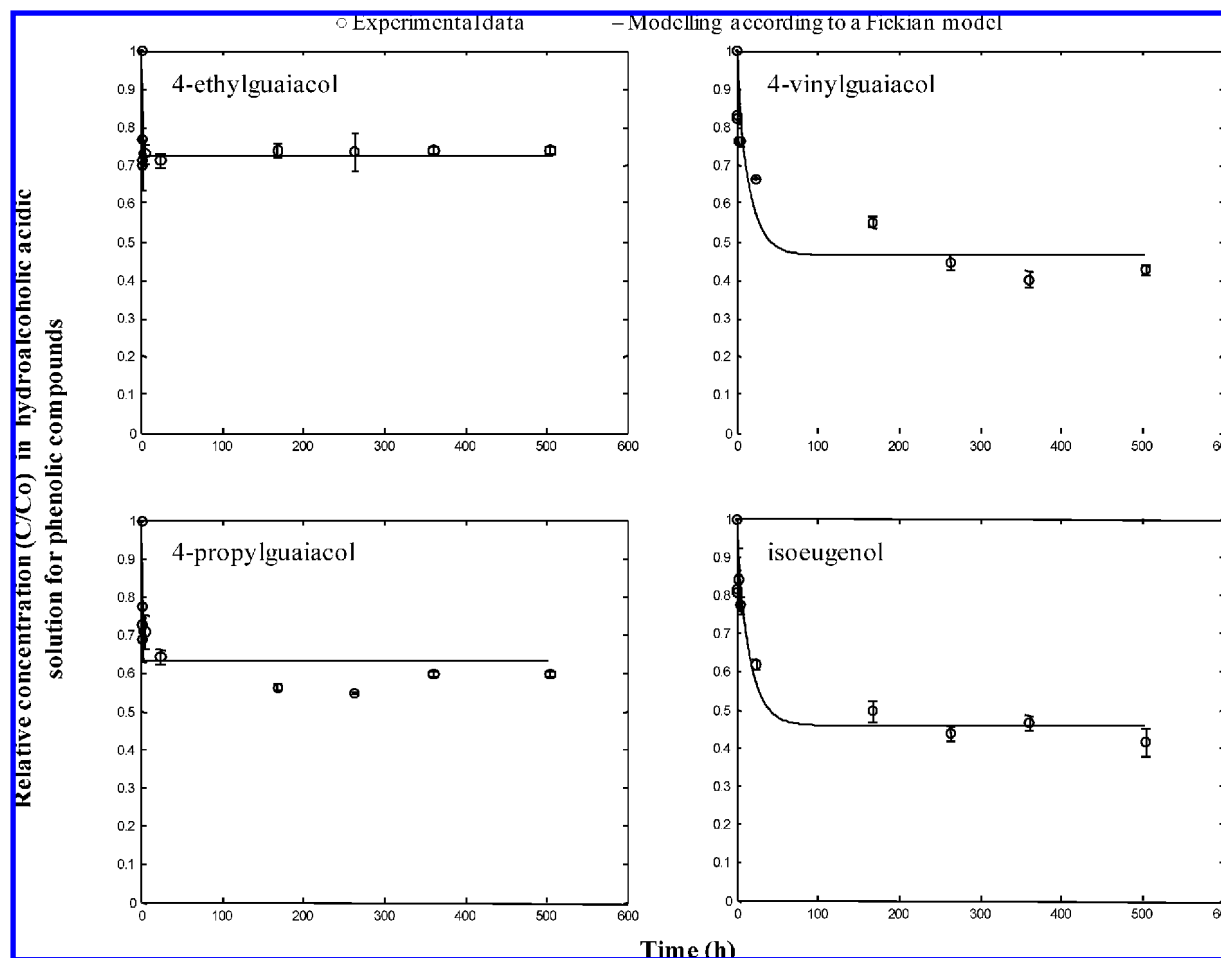


Figure 4. Evolution of the concentrations of 4-ethylguaiacol, 4-propylguaiacol, 4-vinylguaiacol, and isoeugenol in hydroalcoholic solution stored at 10 °C in contact with lignin.

Table 1. Physicochemical Characteristics of the Phenolic Compounds and Sorption Levels by Wood Macromolecules, Expressed in Percent of the Initial Concentration in Solution

phenolic compound	physicochemical characteristics		sorption levels (%) by wood macromolecules		
	log P^a	solubility in model wine (g/L) at 10 °C ^b	cellulose (2.8 g/L)	hemicellulose (2.8 g/L)	lignin (1.4 g/L)
guaiacol	1.18 ± 0.22	15.31 ± 0.61	26.64 ± 1.12	38.95 ± 0.99	14.16 ± 1.31
4-methylguaiacol	1.64 ± 0.22	9.76 ± 0.31	27.99 ± 0.12	40.76 ± 3.71	16.42 ± 3.10
4-ethylguaiacol	2.17 ± 0.22	3.90 ± 0.36	22.30 ± 1.68	42.69 ± 5.03	26.20 ± 0.92
4-propylguaiacol	2.70 ± 0.22	1.44 ± 0.16	22.31 ± 1.93	45.26 ± 2.94	40.15 ± 0.61
eugenol	2.20 ± 0.23	2.41 ± 0.23	22.80 ± 2.15	32.49 ± 1.61	33.80 ± 3.52
4-ethylphenol	2.47 ± 0.19	6.97 ± 1.69	21.61 ± 2.32	33.73 ± 3.52	25.76 ± 3.19
4-vinylguaiacol	1.92 ± 0.25	4.00 ± 0.08	24.27 ± 1.64	36.64 ± 0.89	59.86 ± 2.11
isoeugenol	2.45 ± 0.24	1.36 ± 0.12	17.54 ± 0.12	41.94 ± 2.77	53.48 ± 1.94

^a Estimated hydrophobicity by ACD-Labs software. ^b Reference 7.

properties of the compounds. Indeed, there is a positive linear correlation between their sorption rates and their hydrophobicity ($R^2 = 0.93$) and a negative linear correlation between their sorption rates and their solubilities in hydroalcoholic acidic solution ($R^2 = 0.82$). These results are in agreement with previous results, which displayed a linear relationship between sorption rates and the physicochemical properties of organic compounds (3, 4). In summary, all of these results show that among the biopolymers of wood, lignin has the strongest capacity of selective sorption of volatile compounds of phenolic nature.

Wood and Lignin Sorption Isotherms. To compare the sorption capacities of wood and lignin in simplified conditions, sorption isotherms were built only for 4-ethylguaiacol and 4-vinylguaiacol, added individually to the hydroalcoholic acidic

solution. These compounds were chosen because of their close chemical structures and, in contrast, their significantly different sorption levels at equilibrium.

Sorption isotherms were plotted using C_{wood} or C_{lignin} (the quantity of aroma sorbed per unit mass of wood or lignin at equilibrium) and C_{liquid} (the concentration of the aroma in the liquid phase at equilibrium). The individual sorption isotherms at 10 °C for 4-ethylguaiacol and 4-vinylguaiacol on *pedunculata* oak wood and on *pedunculata* oak wood lignin are displayed in **Figure 6**.

For 4-ethylguaiacol the same sorption behavior is observed for wood or lignin: a linear correlation between C_{wood} or C_{lignin} and C_{liquid} is found ($R^2 = 0.98$ and 0.96 for wood and lignin, respectively). For 4-vinylguaiacol a similar sorption behavior is also observed for wood and lignin, but contrary to 4-ethylguai-

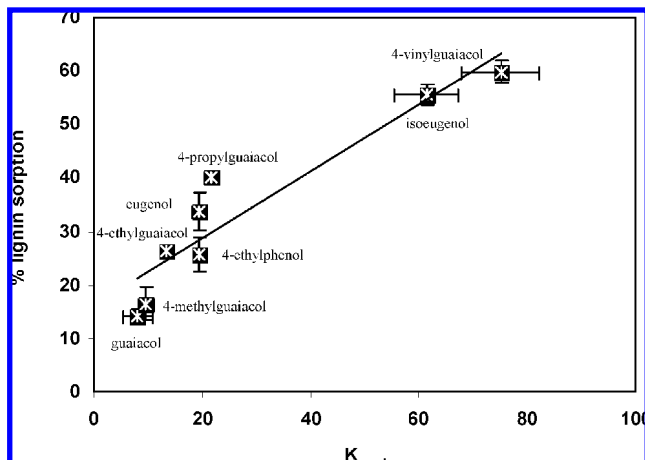


Figure 5. Correlation between lignin sorption, expressed in percent of the initial concentration in solution, and K_{wood}^* .

Table 2. Partition Coefficients of Phenolic Volatiles Alone or in Mixture with Other Volatiles in Hydroalcoholic Acidic Solution at 10 °C^a

	K_{lignin} alone	K_{wood}	
		alone	in combination ^b
4-ethylguaiacol	193.8 ± 30.0	24.4 ± 4.4	13.5 ± 0.7
4-vinylguaiacol	779.8 ± 89.3	54.0 ± 9.0	75.1 ± 7.8

^a K_{wood} and K_{lignin} are calculated within the low concentration region of sorption isotherms. ^b Reference 7.

acol, the relationship between C_{wood} or C_{lignin} and C_{liquid} seems to be nonlinear, although no particular model could reliably fit the data in this range of concentration. These results show two different sorption behaviors for two volatiles with closely related chemical structures. However, considering the observed sorption phenomena, isolated lignin displays a sorption behavior very similar to that of wood, regardless of the studied volatile. These data demonstrate again the importance of lignin in the sorption process. In a previous work we studied the sorption isotherms of 4-ethylguaiacol and 4-vinylguaiacol in combination with other phenolic compounds (7). We observed that, within the same range of concentrations, and when in mixture, 4-ethylguaiacol produces a nonlinear sigmoid-shape sorption isotherm, whereas 4-vinylguaiacol produces a shape similar to that observed in this study (**Figure 6**). Linear isotherms have also been observed for other phenolic compounds individually present in aqueous solution sorbed to pine and fir wood (2). Therefore, these results suggest that the presence of cosolutes in solution has a significant impact on the 4-ethylguaiacol sorption behavior, whereas the sorption of 4-vinylguaiacol does not seem to be affected by the presence of other cosolutes.

The different values of partition coefficients between wood or lignin and the hydroalcoholic acidic solution, referred to as K_{wood} and K_{lignin} , respectively, were calculated from the slope of the linear part of the isotherms (below 10 mg/kg) according to eq 1. They are presented in **Table 2** and compared with K_{wood} reported in the literature (7). Clearly, results in **Table 2** indicate that two distinct sorption behaviors are observed for these two phenolic compounds, which only differ by the para double bond. As proposed by Moreno-Castilla et al. for substituted phenols on activated carbons (21), a possible sorption mechanism that could explain these two behaviors is the electron donor/acceptor character of the sorbent and the sorbate. In fact, a vinyl substituent acts as a stronger electron acceptor group than does the more acid ethyl substituent. Also, lignin phenyl rings are electron donors, so interactions between 4-vinylguaiacol and

lignin should be favored. These interactions between 4-vinylguaiacol and lignin should therefore be investigated in more detail, and their study is already considered for future work.

In another line of thought, an increase in K_{wood} is found when 4-ethylguaiacol is alone in hydroalcoholic acidic solution, compared to previous K_{wood} values reported for 4-ethylguaiacol in combination, with other phenolic compounds in solution. Values of K_{wood} for 4-vinylguaiacol, alone or in combination, remain more or less in the same range. These observations support our hypothesis that a competitive sorption between 4-ethylguaiacol and other phenolic compounds occurs for sorption sites, whereas for 4-vinylguaiacol, the sorption by wood does not seem to be affected by the presence of other cosolutes. Consequently, sorption sites, mainly provided by lignin, could be specific for this compound.

Table 2 also shows that sorption onto lignin (K_{lignin}) is 7 and 14 times greater than that observed onto wood plates (K_{wood}) for 4-ethylguaiacol and 4-vinylguaiacol, respectively. Because lignin represents approximately 25% of the wood plate (f_{lignin}) in our system, the quantity of lignin in contact with the hydroalcoholic solution should be equal to 25% of the mass of one wood plate. Thus, according to eq 2, K_{wood} should be 4 times smaller than K_{lignin} . This discrepancy could be explained by the fact that all of the lignin is not accessible in wood plates, either because it is hidden by the presence of other wood polymers or because it interacts with the structure of the molecular network by chemical bonds or simply because it is a nonporous polymeric network that offers only an external surface for adsorption. According to Mackay et al. (2) and Persson et al. (22), lignin is located intercellularly, between adjoining fibers within the wood particles. Thus, the sorption level of phenolic compounds should increase when the lignin sites are more accessible in wood.

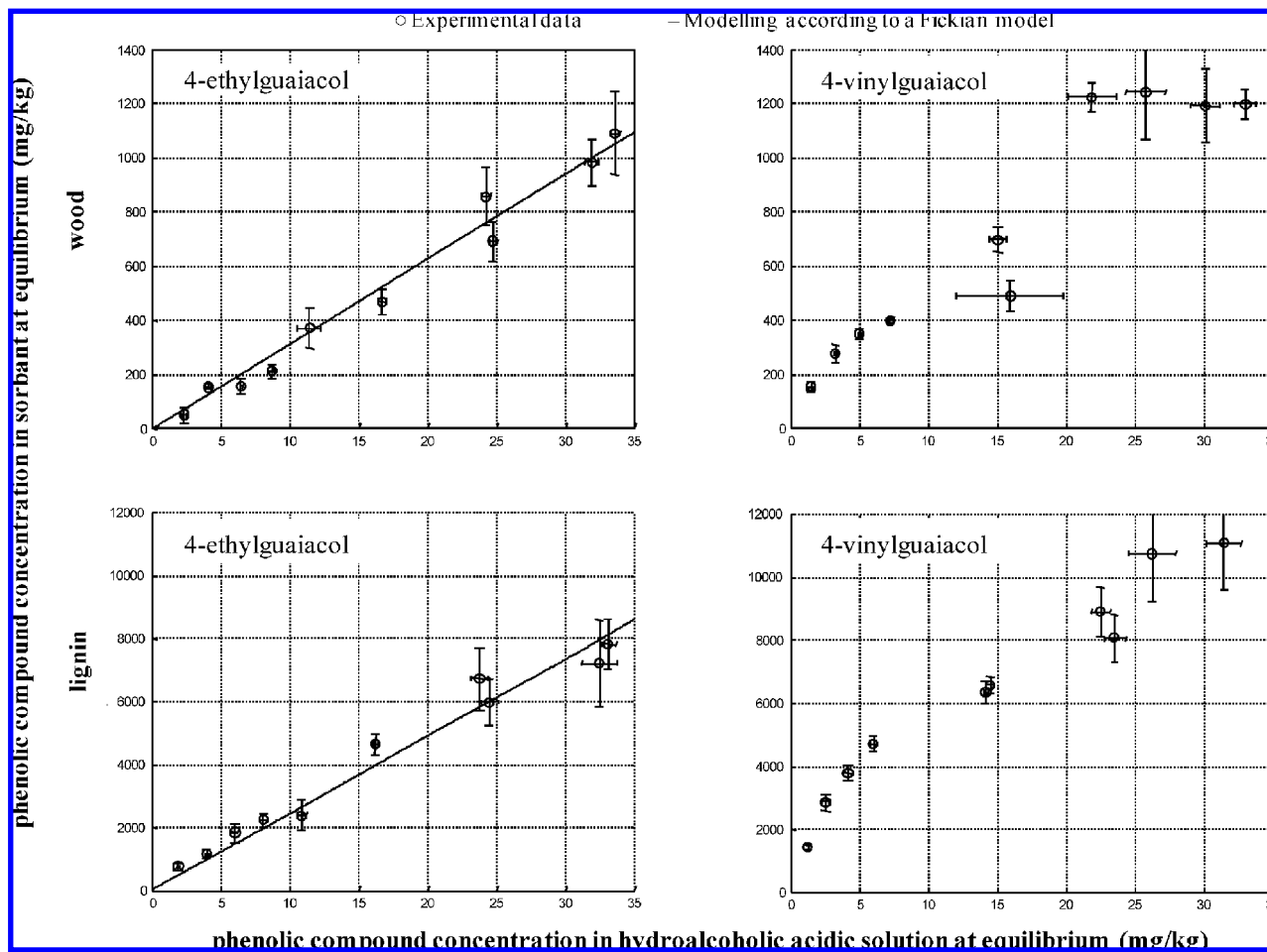
Dependency of Sorption Equilibrium and Sorption Kinetics on the Wood Surface Accessibility. To study the sorption capacity of wood as a function of lignin accessibility, we studied the influence of both the accessibility of sorbates to the radial–tangential (R-T) surface and that of the granulometry on the sorption equilibrium and sorption kinetics. To that purpose, three wood geometries were used in contact with hydroalcoholic solution: oak wood plates, oak wood plates with the R-T surface sealed, and oak wood sawdust. As shown in **Figure 1**, the R-T surface of the plates offers the easiest and highest accessibility to the macroporous surface of wood and, as such, we assumed that preventing this accessibility would be a good assessment of the lignin accessibility. In contrast, we assumed that sawdust would put a significantly higher surface in contact with the hydroalcoholic solution and, therefore, would provide significantly higher lignin accessibility. For simplicity, these wood geometries are named R-T face opened, R-T face sealed, and sawdust, respectively.

Figures 7, 8, and 9 display the evolution with time at 10 °C of the normalized concentrations of 4-ethylguaiacol and 4-vinylguaiacol separately in hydroalcoholic acidic solution, in the presence of R-T face opened, R-T face sealed, and sawdust, respectively.

For all wood geometries, a decrease in concentration was observed. After 35 h of contact, in the presence of R-T face opened (**Figure 7**), sorption rates were 15% for 4-ethylguaiacol and 33% for 4-vinylguaiacol. For R-T face sealed (**Figure 8**) sorption rates were 7 and 16% for 4-ethylguaiacol and 4-vinylguaiacol, respectively. Finally, for the system containing sawdust, sorption rates were 20 and 37% for 4-ethylguaiacol and 4-vinylguaiacol, respectively. These results, therefore, support

Table 3. Apparent Diffusion Coefficient (D_{app}) and Sorption Coefficient (S) of Phenolic Compounds, Determined from the Fitting of Experimental Curves to the Fick's Second Law

compound	$D_{app} \times 10^{-13} \text{ (m}^2 \text{ s}^{-1}\text{)}$			$S \text{ (mg kg}^{-1} \text{ of dry wood)}$		
	R-T faces sealed	R-T faces opened	sawdust	R-T faces sealed	R-T faces opened	sawdust
4-ethylguaiaicol	3.00 ± 1.2	5.1 ± 1.6	nd ^a	388.1 ± 81.0	433.4 ± 61.1	618.8 ± 25.8
4-vinylguaiaicol	3.7 ± 1.0	2.9 ± 0.5	nd	735.2 ± 130.7	751 ± 46.5	812.3 ± 24.5

^a Not determined.**Figure 6.** Sorption isotherms of 4-ethylguaiaicol and 4-vinylguaiaicol by *pedunculata* oak wood (above) and by *pedunculata* oak lignin (below) at 10 °C.

our hypothesis concerning the accessibility of lignin. If we consider the R-T face opened system as a control sample, we observed that in the R-T face sealed system, wood vessels were not so quickly accessible; thus, a large amount of intercellular tissue rich in lignin could not be in direct contact with the liquid phase. Consequently, sorption rates decreased. In the case of sawdust, the particle size and the surface exposed favor the accessibility and the number of lignin sorption sites. Thus, sorption rates were significantly higher. Nevertheless, our results are in disagreement with those observed by Mackay et al. (2). These authors studied the dependency of sorption kinetics on wood shapes (shavings, sticks, and chips) for monoaromatic hydrocarbons and showed that, at equilibrium, similar sorption rates were observed, regardless of the shape. This discrepancy is probably explained by the fact that our experimental values did not reach complete equilibrium.

For each sorption kinetic, a Fickian model was plotted. A rather good agreement with experimental values was observed for the three systems under study. From these adjustments an apparent diffusion coefficient (D_{app}) and a sorption coefficient

(S) are given (Table 3). These results show that, as previously observed, there is a difference in sorption between 4-ethylguaiaicol and 4-vinylguaiaicol, but contrary to observed experimental sorption rates, for the R-T face opened system and the R-T face sealed system; close S values are predicted for the same compound, regardless of the accessibility to the wood surface. Because the mathematical model takes into account the experimental points and predicts an S value at infinite times, our results are, ultimately in agreement with the literature (2). It is reasonable to suppose that, at infinite time, even the surface of the vessels of the R-T sealed sample will have become accessible to hydroalcoholic solution, thus leading to the same sorption rate as that observed for the R-T face opened sample. Concerning 4-ethylguaiaicol in the sawdust system, the S value (Table 3) was significantly higher than in the two other systems, suggesting that more sorption sites were offered by this wood geometry. Although less significant, a similar increase was also observed for 4-vinylguaiaicol.

Figures 7–9 also indicate that the sorption kinetics for the sawdust system seemed to be higher than those for the two other

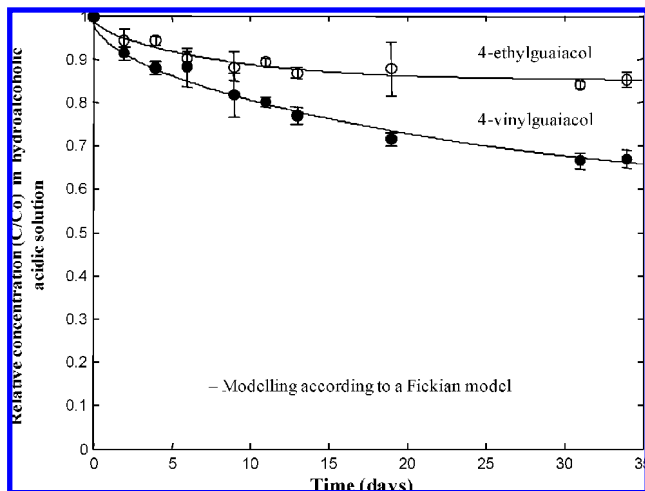


Figure 7. Evolution of the concentrations of 4-ethylguaiaicol and 4-vinylguaiaicol in hydroalcoholic acidic solution stored for 35 days at 10 °C with R-T faces opened.

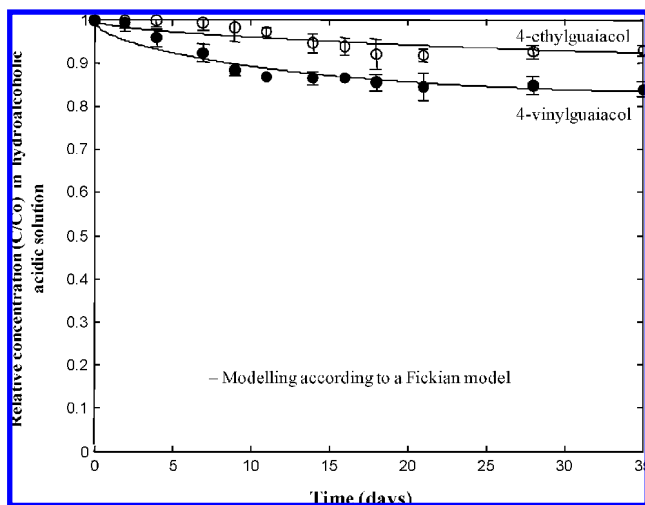


Figure 8. Evolution of the concentrations of 4-ethylguaiaicol and 4-vinylguaiaicol in hydroalcoholic acidic solution stored for 35 days at 10 °C with R-T faces sealed.

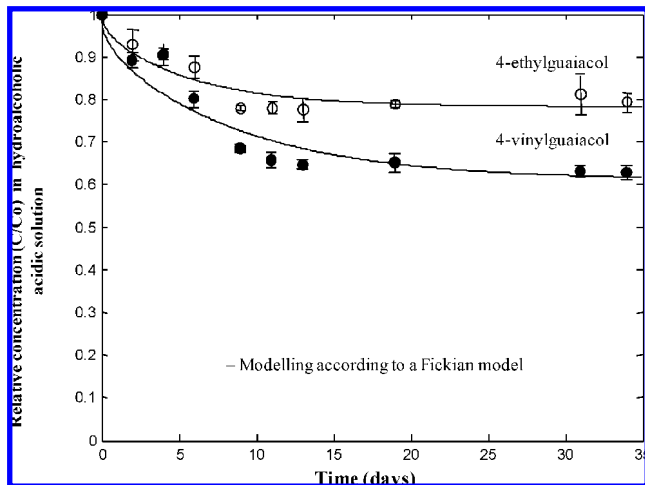


Figure 9. Evolution of the concentrations of 4-ethylguaiaicol and 4-vinylguaiaicol in hydroalcoholic acidic solution stored for 35 days at 10 °C with sawdust.

systems. Indeed, for the former, equilibrium is already reached after 11 days of contact. This is further corroborated by values

in **Table 3**, which also indicate that the diffusion coefficients (D_{app}) were in the same range for R-T face opened and R-T sealed. However, D_{app} values of volatiles in contact with sawdust could not be estimated because of the wood geometry, as explained previously. These results show that sorption kinetics of phenolic compounds are not significantly affected by the wood face exposed to the solution. Consequently, there is no preferential pathway for diffusion of these compounds to lignin tissues through large wood vessels.

The D_{app} values for phenolic compounds correspond to those found for other aroma compounds sorbed by plastic polymers (23). In contrast, the diffusion values of these phenolic molecules are much weaker than those reported for water (24) (about $10^{-10} \text{ m}^2 \text{ s}^{-1}$). Such lower diffusion coefficients compared to that of water can indicate that water may not be the direct carrier of these volatiles in the system or that the molecular size of these compounds in this hydrated medium could limit their diffusion through the narrow pathways offered by wood sections.

In addition, the polarity of the sorbent could also play a role in the sorption and diffusion process. In the case of cellulose and hemicellulose (**Figures 2 and 3**), which exhibit hydrophilic characters, water could quickly carry sorbates toward the solid surface of the sorbent, and the measured rate of sorption could actually correspond to the amount of sorbate retained by the surface-adsorbed water fraction (11). This would explain why sorption rates are the same regardless of sorbate type. In contrast, in the case of lignin, which exhibits a marked hydrophobic character with selective sorption sites, the diffusion at the lignin interface could be governed by specific sorbent–sorbate interactions, even when water acts as carrier.

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