

## Sorption Behavior of Volatile Phenols at the Oak Wood/Wine Interface in a Model System

V. DANIELA BARRERA-GARCÍA,<sup>†,‡</sup> RÉGIS D. GOUGEON,<sup>†,‡</sup> ANDRÉE VOILLEY,<sup>‡</sup> AND  
DAVID CHASSAGNE<sup>\*,†,‡</sup>

Institut Universitaire de la Vigne et du Vin "Jules Guyot", Université de Bourgogne,  
Campus Montmuzard, 21078 Dijon France, and Equipe IMSAPS, ENSBANA,  
Université de Bourgogne, 1 Esplanade Erasme, 21079 Dijon France

The sorption in a model system of aroma compounds of enological interest (mixture of the eight derivatives from guaiacol, 4-ethylphenol, and whiskylactone) onto wood was investigated to assess the influence of wood on the concentration of these volatiles during the aging of wine. To evaluate the influence of the solubility of aroma compounds in sorption phenomena, this parameter was determined for each volatile compound in model wine at 10 and 25 °C. The solubility is significantly higher in the model wine than in water and remains constant in the range of temperatures studied, except for guaiacol and vanillin. Kinetic and equilibrium sorptions were investigated. Sorption kinetics showed that the sorption equilibrium for all aroma compounds was reached after 6–7 days. From the study of the individual sorption isotherms, two distinct kinds of sorption behavior were observed depending on the presence or not of an ethylenic para substituent conjugated to the phenyl ring.  $K_{ww}$  partition coefficients between the wood and the model wine were determined, which exhibited an unusual positive variation with temperature.

**KEYWORDS:** Oak wood; model wine; phenolic compounds; sorption; isotherm; solubility

### INTRODUCTION

During aging in oak barrels, wine acquires aromatic complexity as a result of aroma transfer at the interface between wood and wine. Throughout this period, aromas issued from the fermentation lessen, whereas new compounds appear from oak wood and from the evolution of the primary and secondary aromas (1). The volatile compounds extracted from the wood have different impacts on the wine aroma. For instance, eugenol and *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactone are components of oak wood (2, 3) extracted during wine aging (2, 4), which are associated with desired aroma. Alternatively, unpleasant odors can also be generated, caused by the presence of ethylphenol and ethylguaiacol. Although Chatonnet et al. (5, 6) showed that *Brettanomyces* yeasts are involved in the formation of these volatile phenols, their origin is not only microbial. They found that the contents of volatile phenols in wines increase throughout the aging period, and this increase is even more pronounced when the barrels are old.

The extraction of the volatile compounds from oak barrels depends on the amount that is potentially extractable, and the time during which the wine is in contact with the wood. A study of the transfer mechanisms at the interface between wood and wine was recently initiated. Ramirez-Ramirez et al. (7, 8) and

Chassagne et al. (9) highlighted the sorption of wine aroma compounds by oak wood under wine-aging simulation. They showed that the amount sorbed at equilibrium depends on the nature of the aroma compound and on the wine matrix. The capacity of sorption of wood has also been investigated for monoaromatic hydrocarbons (10) and has been related to the hydrophobicity (logP) and the fractional lignin content in the wood.

All of these results indicate that after several years of use, oak barrels will have exchanged aroma compounds with the different wines that they have contained. At this point, a used oak barrel may have sorbed more aroma compounds than it would have initially comprised. The main goal of this work is to study the transfer mechanisms of volatile phenols at the interface between wood and wine through a physicochemical approach, to help in the understanding of the process of wine contaminations by volatile compounds. To that purpose, we have studied the sorption onto wood of different aroma compounds of enological interest: a homologous series of guaiacol, 4-vinylguaiacol, 4-ethylphenol, and the four major aroma components of oak wood (eugenol, isoeugenol, vanillin, and whiskylactone). These compounds were chosen due to their common presence in the wine and exhibit a broad range of phenolic chemical structures.

### MATERIALS AND METHODS

**Materials.** Guaiacol, 4-propylguaiacol, 4-vinylguaiacol, isoeugenol, and a racemic mixture of whiskylactone were supplied from Aldrich-

\* To whom correspondence should be addressed. Tel: +33-380-396392.  
Fax: +33-380-396265. E-mail: david.chassagne@u-bourgogne.fr.

<sup>†</sup> Institut Universitaire de la Vigne et du Vin "Jules Guyot".

<sup>‡</sup> ENSBANA.

Table 1. Physicochemical Characteristics of the Aroma Compounds

aroma compound	CAS number	organoleptic characteristic	developed formula	molar weight (g.mol <sup>-1</sup> )	log P <sup>a</sup>	literature values of log P
guaiacol C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	90-05-1	phenolic		124.14	1.18 ± 0.22	1.33 <sup>b</sup>
4-methylguaiacol C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	93-51-6	leather, spicy		138.16	1.64 ± 0.22	
4-ethylguaiacol C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	2785-89-9	spicy, clove, smoked		152.19	2.17 ± 0.22	
4-propylguaiacol C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	2785-87-7	spicy		166.22	2.7 ± 0.22	
4-vinylguaiacol C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	7786-61-0	carnation, clove, pepper		150.17	1.92 ± 0.25	
4-ethylphenol C <sub>8</sub> H <sub>10</sub> O	123-07-9	ink, horse urine		122.6	2.47 ± 0.19	2.26 <sup>b</sup>
Eugenol C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	97-53-0	clove		164.21	2.2 ± 0.23	2.01 <sup>c</sup>
isoeugenol C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	97-54-1	clove		164.21	2.45 ± 0.24	
Vanillin C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	121-33-5	vanillin		152.15	1.18 ± 0.27	1.14 <sup>c</sup>
Whiskylactone C <sub>9</sub> H <sub>16</sub> O <sub>2</sub>	39212-23-2	coconut		156.22	1.81 ± 0.28	

<sup>a</sup> Estimated by ACD-Lab software. log P, molecule hydrophobicity expressed by the logarithm of the liquid-liquid partition coefficient between 1-octanol and water. <sup>b</sup> Ref 12. <sup>c</sup> Ref 13.

Sigma Co., 4-methylguaiacol, 4-ethylguaiacol, and 4-ethylphenol were bought from TCI-EP, and eugenol and vanillin were purchased from Fluka, each with a minimum purity of 98%. Although they are not phenolic compounds, cis and trans isomers of whiskylactone were added because of their sensorial impact on the aroma of wines elaborated in oak wood aging conditions. The model wine is a 12.5% v/v hydroalcoholic solution of pH 3.5 (7). Volatile compounds (Table 1) were added in mixture to the model wine with initial concentrations between 0.5 and 40 mg/kg. Dichloromethane obtained from Carlo Erba Reactives was used as a solvent for extraction. Small pieces of wood (2 mm × 10 mm × 20 mm) were donated by the Office National des Forêts (ONF, France) and taken from *Quercus robur* (*pedunculata*) oak trees from the Forêt de Cîteaux (France).

**Solubility Measurements.** The solubility of the aroma compounds in water and in model wine was measured by the mutual solubility method (13) under atmospheric pressure and at temperatures of 10 and 25 °C. Classically, volumes of 2 mL of the aqueous solution and 0.5 mL of the pure aroma compound were introduced into a 4 mL airtight flask. A magnetic stirrer allowed a maximum contact between phases. To determine the equilibrium state, concentrations in the aqueous phase

were measured every 6 h until constant values were obtained. For all aroma compounds, the equilibrium between phases was reached between 8 and 12 h. Thus, 24 h was selected as a standard and convenient time of sampling for all of the aroma compounds. Once the equilibrium was reached, the flask was centrifuged for 20 min (5000 rpm) at the temperature of analysis. The amount of soluble aroma compound was then measured by gas chromatography (GC) of the aqueous phase. Measurements were replicated at least three times.

**Sorption Kinetics and Sorption Isotherms.** Sorption isotherms were determined using nine aqueous solutions, which contained between 0.5 and approximately 30 mg/kg of each of the 10 aroma compounds. These concentrations were chosen in order to keep this study within and above (1 order of magnitude) the range of concentrations commonly found in wine. These solutions were prepared from a stock solution containing 500 mg/kg of volatiles dissolved in analytical grade ethyl alcohol. Three kinds of samples were prepared as follows: experimental samples, control samples without wood, and, finally, to estimate the contribution of potentially extractable wood volatiles, control samples without aroma compounds in the liquid phase. Experimental samples consisted of immersing one piece of wood (0.2–0.3 g) into a 25 mL

glass flask completely filled with the model wine (total volume of about 35 mL). Flasks were tightly closed with Teflon caps to prevent losses of the volatile compounds and stored in triplicate at 10 and 25 °C. Two microliters of the solution phase was withdrawn at different intervals of time and subsequently analyzed by GC, with external calibration. This sample volume was considered to be negligible as compared to the total 35 mL. The sorption experiments were stopped when the aroma compounds concentration in the aqueous phase remained constant over three consecutive measurements. For the sorption isotherms, the experimental samples and the control samples were analyzed by liquid–liquid extraction and GC, with 3,4-dimethylphenol added as an internal standard. The amount of aroma 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 aroma compounds in the liquid phase was determined with a GC Trace Ultra (Thermo Electron Corporation) gas chromatograph fitted with a split injector (1/30). A flame ionization detector and capillary column CP-WAX 57CB (Varian) (25 m × 0.25 mm i.d.; 0.2 μm bonded phase) was used. The column temperature was programmed to vary from 130 to 190 °C at a rate of 3 °C/min. The flow rate was 30 mL/min of He for the carrier gas and 35 and 350 mL/min for the H<sub>2</sub> and air detector gases, respectively. The temperature was kept at 250 °C for the detector and at 200 °C for the injector. Two microliters of sample was injected. The acquisition and the processing of the data were carried out under Chrom-card workstation version (Thermo Electron Corporation).

**Statistical Analysis and Physicochemical Values Estimations.** The statistical analysis of the different repetitions was carried out by using the StatBox Microsoft Excel software. All variance analyses were carried out with 95% of confidence. Interactive Laboratory (I-Lab) from ACD Labs (<http://www.acdlabs.com/ilab>) was used for the prediction of the physicochemical properties (logP and water solubility) of the volatile compounds.

## RESULTS AND DISCUSSION

### Physicochemical Properties of the Volatile Compounds.

A physicochemical property such as the hydrophobicity (logP) of the different aroma compounds can bring valuable information for the understanding of their behaviors at the wood–wine interface. The hydrophobicity of an organic compound can be described by the liquid–liquid partition coefficient of this compound between 1-octanol and water (11). This parameter, calculated with ACD-Labs software, is given in **Table 1**, along with experimental values from the literature. **Table 1** shows that all of the volatile compounds used exhibit logP estimated values between 1.18 and 2.7, with the highest value for 4-propylguaiaicol and the lowest value for guaiacol and vanillin. **Table 1** also shows that there is a rather good agreement between our estimated values and the given literature values.

Whatever the aroma compound is, its level of sorption will necessarily be affected by its affinity for the model wine. Therefore, a precise measurement of the solubility in the model wine of each of the aroma compounds is required for a correct description of their behaviors at the wood/wine interface. These solubilities, measured in water and in model wine, are gathered in **Table 2**. Our experimental results (**Table 2**), which are in good agreement with values found in the literature for organic compounds (14–17), show that the aromatic compounds under study are sparingly soluble in water, at 25 °C (less than 20 g/L). It is interesting to observe that for the homologous series of guaiacol, the solubility values are inversely proportional to the calculated logP values (**Table 1**). For example, guaiacol, which is the least hydrophobic, exhibits the higher solubility value both in water and in model wine.

Solubilities of aroma compounds in water were compared to those obtained in the hydroalcoholic solution at 25 °C (**Table**

**Table 2.** Solubility of Aroma Compounds in Water and Model Wine

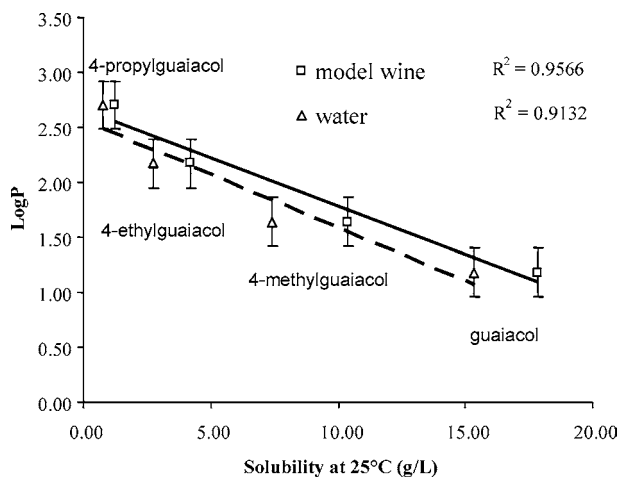
aroma compound	solubility in water at 25 °C (g L <sup>-1</sup> )	solubility in model wine (g L <sup>-1</sup> )	
	experimental <sup>a</sup>	experimental at 25 °C <sup>a</sup>	experimental at 10 °C <sup>a</sup>
guaiacol	15.34 ± 0.30	17.87 ± 0.43 <sup>c</sup>	15.31 ± 0.61 <sup>c</sup>
4-methylguaiaicol	7.42 ± 0.15	10.39 ± 1.01	9.76 ± 0.31
4-ethylguaiaicol	2.75 ± 0.17	4.18 ± 0.17	3.90 ± 0.36
4-propylguaiaicol	0.76 ± 0.15	1.22 ± 0.04	1.44 ± 0.16
4-ethylphenol	5.65 ± 0.39 <sup>b</sup>	5.92 ± 0.22 <sup>b</sup>	6.97 ± 1.69
4-vinylguaiaicol	2.96 ± 0.12	4.19 ± 0.29	4.00 ± 0.08
vanillin	4.33 ± 0.41	9.52 ± 1.37 <sup>d</sup>	3.22 ± 0.07 <sup>d</sup>
eugenol	1.51 ± 0.04	2.15 ± 0.16	2.41 ± 0.23
isoeugenol	1.22 ± 0.05	1.46 ± 0.11	1.36 ± 0.12
<i>trans</i> -whiskylactone	1.67 ± 0.35	2.27 ± 0.14	2.77 ± 0.31
<i>cis</i> -whiskylactone	1.94 ± 0.08	2.97 ± 0.12	3.31 ± 0.34

<sup>a</sup> Results ± standard deviations are the average of three replications. <sup>b</sup> No significant differences ( $p < 0.5$ ) were found by ANOVA;  $F_{crit} > F(7.70864972 > 1.12662861)$ . <sup>c</sup> Significant differences ( $p < 0.5$ ) were found by ANOVA;  $F_{crit} < F(7.70864972 < 35.1146239)$ . <sup>d</sup> Significant differences ( $p < 0.5$ ) were found by ANOVA;  $F_{crit} < F(7.70864972 < 63.5132969)$ .

2). With the exception of 4-ethylphenol, the solubility of aroma compounds is significantly higher [by analysis of variance (ANOVA) test] in the model wine than in water ( $P < 0.05$ ). The highest increase is observed for vanillin, for which the solubility more than doubles when going from water to model wine. This ethanol effect is consistent with results reported by Ramirez-Ramirez et al. (7) and can be explained by the fact that the aroma compounds studied here are weakly polar and consequently more soluble in hydroalcoholic solution than in water (17, 18). Additional arguments in favor of this explanation are brought by the solubilities of the homologous series of guaiacol, for which the solubility gain when alcohol is present in the aqueous medium increases with the length of the hydrophobic para side chain. Indeed, the solubility in model wine is 16, 40, 52, and 60% higher than the one in water for guaiacol, 4-methylguaiaicol, 4-ethylguaiaicol, and 4-propylguaiaicol, respectively. It is also interesting to compare experimental values for aroma compounds with the same number of carbon atoms in the para chain: 4-ethylguaiaicol and 4-vinylguaiaicol exhibit roughly the same solubility in model wine and in water, whereas the solubility of 4-ethylphenol is significantly higher (twice the value in water and nearly 1.5 times higher in model wine). These results suggest that the chemical nature of the ortho substituent has a greater influence on the solubility than the presence of the double bond of the vinyl group in the para position. Finally, **Table 2** shows that when the temperature rises from 10 to 25 °C, the solubility of the aroma compounds in model wine does not vary significantly ( $P < 0.05$ ), except for vanillin and to a lesser extent for guaiacol.

To summarize, although a general rule cannot be proposed for all of the aroma compounds studied, it is clear that there is a good linear correlation between the calculated logP values and the experimental solubilities, both in water and in model wine, for the homologous series of guaiacol (**Figure 1**). According to this correlation, 4-propylguaiaicol, which shows the higher hydrophobic character, is the less soluble in the aqueous solutions. Therefore, among the homologues, 4-propylguaiaicol should have the highest affinity for the hydrophobic oak wood.

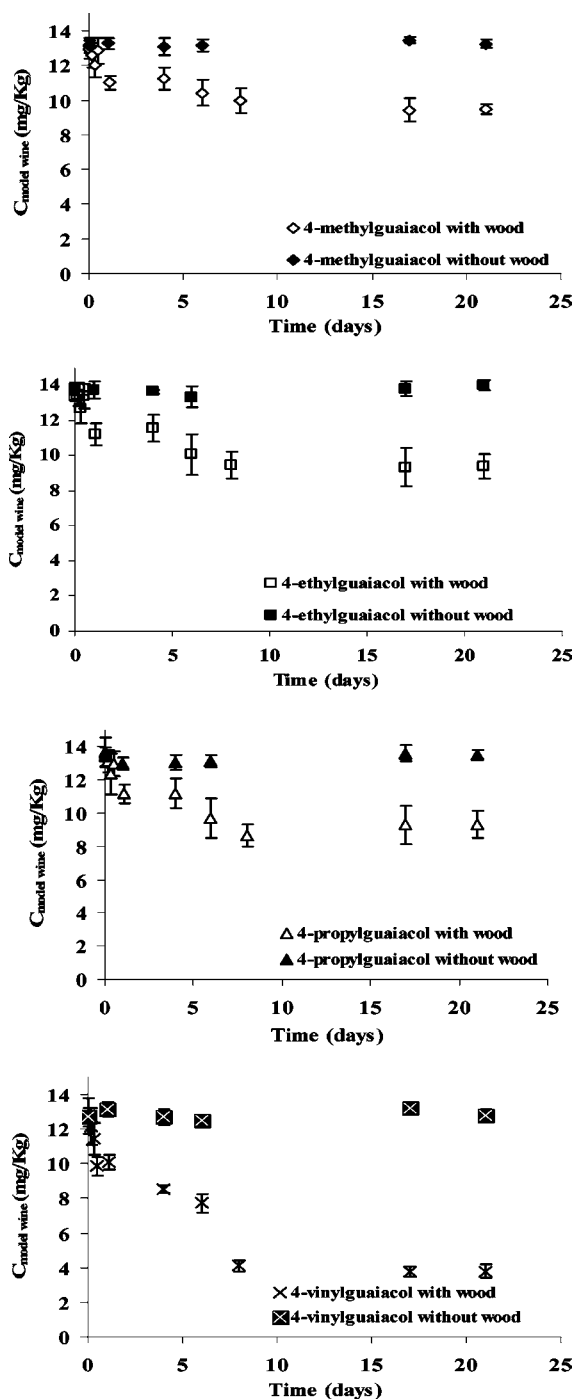
**Evolution of the Concentrations in the Liquid Phase.** The time to reach the sorption equilibrium was determined for each of the aroma compounds. **Figure 2** displays the evolution with time at 25 °C of the concentrations of 4-methylguaiaicol,



**Figure 1.** Correlation between the logP and the solubility of the homologous series of guaiacol.

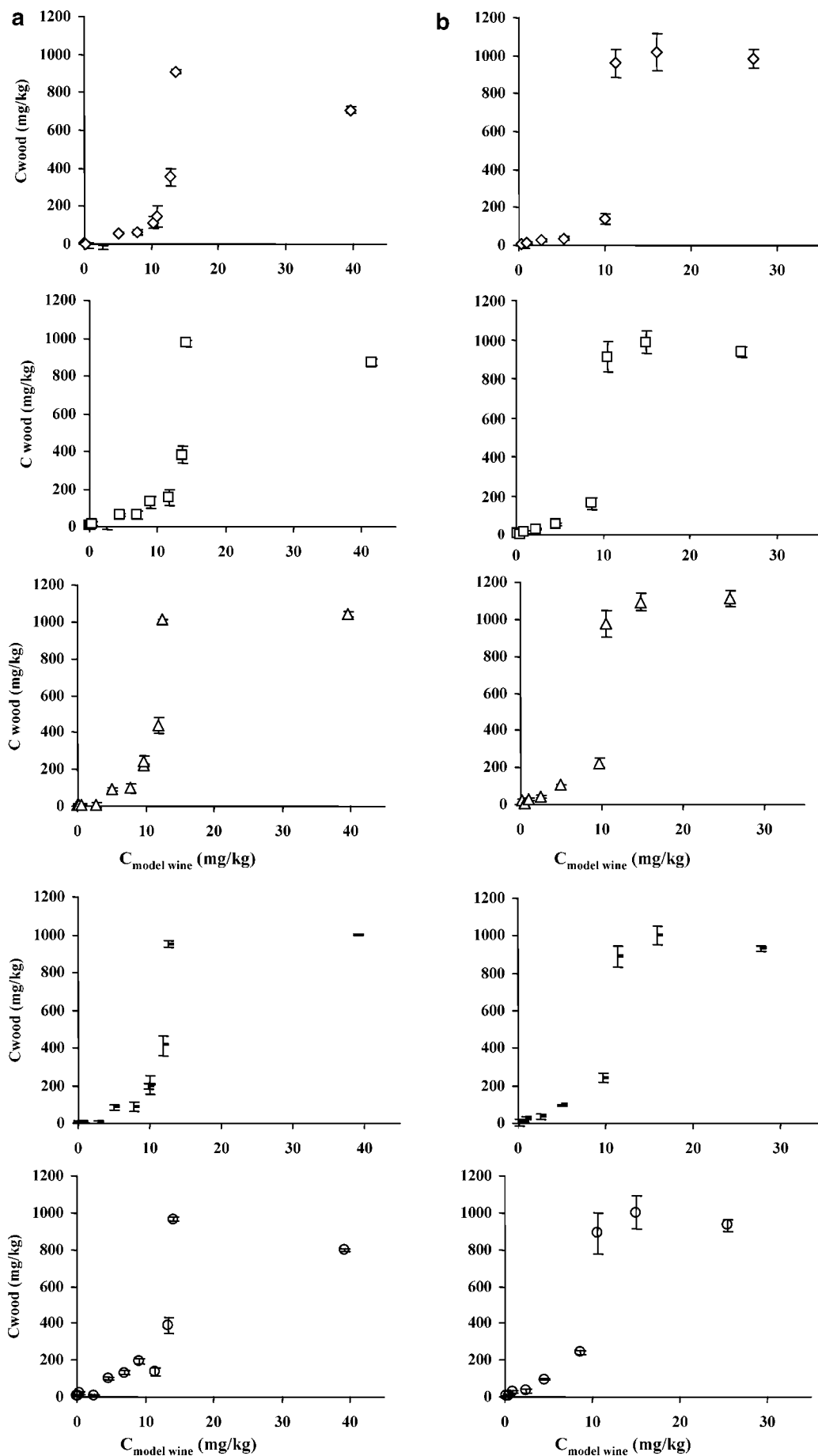
4-ethylguaiacol, 4-propylguaiacol, and 4-vinylguaiacol mixed together with all of the other aroma compounds in model wine, in the presence of *pedunculata* oak wood. Also shown is the evolution of the concentrations of the same compounds in the control samples without wood, which indicate that within experimental errors, the concentrations in the model wine remain constant over the entire period of contact. This indicates that no chemical instability of the volatile compounds in the model wine occurred. Therefore, the observed decrease of the concentrations for the experimental samples can be assumed to be only due to sorption on the oak wood plates. For the control samples without aroma, no extraction of wood volatile compounds in liquid phase was detected. In agreement with previous results (18), the sorption of phenolic compounds seems to follow a two-step process: (i) a fast initial sorption process onto the active sites of the wood surface within the first 26 h and (ii) a slower diffusion process between the second and the eighth day where migration of the phenolic compounds into the wood matrix can be observed. Depending on the aroma compound studied, Figure 2 shows that the sorption equilibrium was reached after 6–7 days, which is comparable to the results reported by Severtson et al. (19) in the case of 2,4,5-trichlorophenol sorbed on wood fiber. At equilibrium, the average rate of disappearance is of the order of 25% for all of the volatile compounds studied, except for 4-vinylguaiacol, for which it is nearly 70%. This observation strongly suggests that the chemical nature of the solute also influences its interaction with the wood plates. As indicated in the next part of the discussion, the structural particularity of 4-vinylguaiacol, which is the presence of a double bond conjugated to the phenyl ring, is likely to be responsible for this behavior.

**Sorption Isotherms.** The sorption isotherms at 10 and 25 °C for 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, eugenol, and 4-ethylphenol on *pedunculata* oak are represented in Figure 3. The sorption isotherms at 25 °C for *cis*- and *trans*-whiskylactone are represented in Figure 4. For each studied volatile, sorption isotherms were plotted using  $C_{\text{wood}}$  (the quantity of aroma sorbed per unit mass of wood) and  $C_{\text{model wine}}$  (the concentration of aroma in the liquid phase at equilibrium). The same sorption behavior is observed for all of these volatile compounds: a linear variation for low concentrations (below 10 ppm) and a sharp increase above. This S type isotherm suggests that, in the range of concentrations studied, a two-step uptake process is involved. During the first step, the aroma compounds are apparently sorbed without competition via weak interactions with the wood surface, thus forming a first layer



**Figure 2.** Evolution of the concentration of 4-methylguaiacol ( $\diamond$ ), 4-ethylguaiacol ( $\square$ ), 4-propylguaiacol ( $\triangle$ ), and 4-vinylguaiacol ( $\times$ ) in model wine stored for 30 days at 25 °C with (open symbols) and without (filled symbols) *pedunculata* oak wood.

on the solid surface. This interpretation is in good agreement with the linear sorption isotherms of chlorophenols to wood fibers, where it was shown that, within the same range of concentrations, there is no competition between cosolutes (20). It can be explained by the fact that there are enough sorption sites at the wood interface for all of the different phenol compounds to weakly interact without competition. Above 10 mg/kg, the sorption increases dramatically, from around 100 mg/kg up to about 1000 mg/kg ( $C_{\text{wood}}$ ). This sharp increase indicates that the volatile compounds are now sorbed via a different mechanism, which can be sorbate/sorbate hydrophobic interactions between volatile molecules, which form additional



**Figure 3.** Sorption isotherms of 4-methylguaiacol ( $\diamond$ ), 4-ethylguaiacol ( $\square$ ), 4-propylguaiacol ( $\triangle$ ), eugenol ( $-$ ), and 4-ethylphenol ( $\circ$ ) by *pedunculata* oak wood at 10 (a) and 25 °C (b).

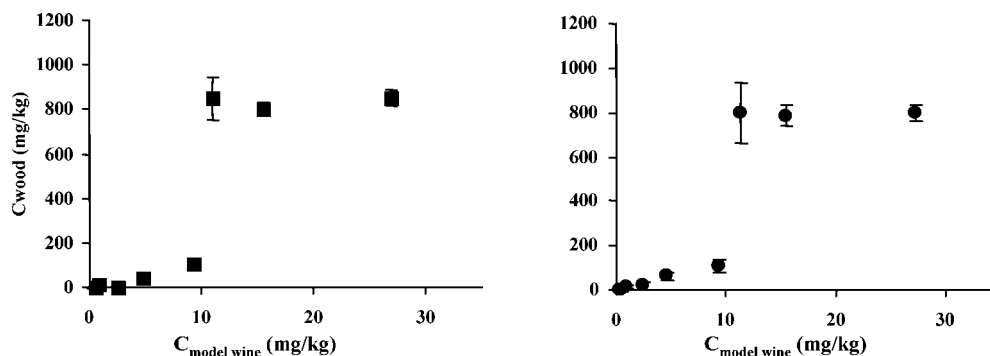


Figure 4. Sorption isotherms of *cis*- (■) and *trans*-whiskylactone (●) by *pedunculata* oak wood at 25 °C.

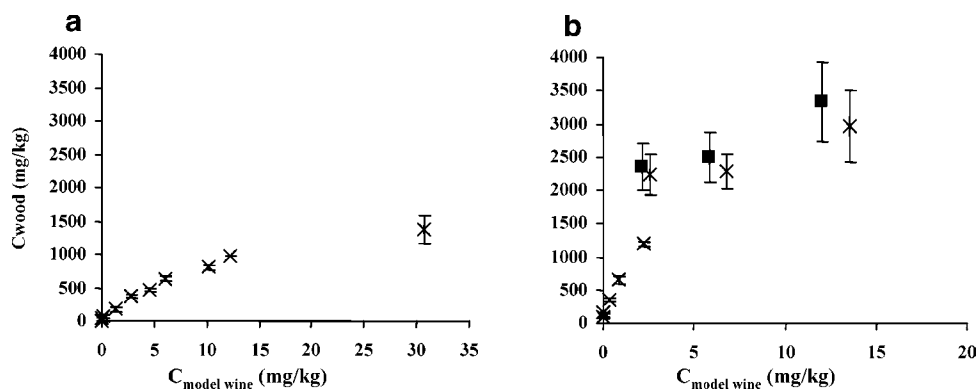


Figure 5. Sorption isotherms of 4-vinylguaiaicol by *pedunculata* oak wood at 10 (a) and 25 °C (b) and values measured for isoeugenol (■).

layers (21). Such a two-step mechanism of sorption can be compared to that proposed by Leng et al. (22) where the sorption of phenol on activated carbons has been found to be a combination of physisorption and surface polymerization. However, for the low initial concentrations studied here, the plateau of sorption for *pedunculata* oak wood is about 1000 mg/kg for all volatile compounds (Figures 3 and 4), which is a relatively low value as compared to the sorption capacities of activated carbons, where concentrations of up to 200 g/kg were measured (23, 24). Clearly, this difference relies on the fact that the thermal activation of carbon provides a higher porosity, whereas our oak wood samples probably exhibit a very low micro- and mesoporosity. Different equations can be used to model sorption isotherms, among which Langmuir and Freundlich equations are the most reported in the literature (25, 26). However, they are valid for a monolayer adsorption of single solute systems and/or often describe isotherms on broad ranges of concentrations. For our system with a mixture of diluted cosolutes, none of these equations can reliably be used to describe individual isotherms. Furthermore, concentrations above 10 mg/kg correspond to a range where sorption competition between cosolutes cannot be excluded. Therefore, we only considered the initial shape of these sorption isotherms, which agree with the fact that partitioning is the major sorption mechanism over this low-concentration range (7).

Within the low concentration region, the sorption of aroma compounds can be described by the partition coefficient ( $K_{ww}$ ) between the wood and the model wine solution. The different values of  $K_{ww}$  were calculated from the slope of the linear part of the isotherms (below 10 mg/kg) and are presented for *pedunculata* oak at 10 and 25 °C in Table 3. These results show that  $K_{ww}$  increases with temperature for most of the compounds studied. Such increase of sorption with temperature has also been observed for sorption of other phenols on activated carbons (25) and has been explained in terms of hydrophobic interactions: The thermal motion brought by the temperature increase

Table 3. Wood–Model Wine Partition Coefficients after 30 Days of Contact<sup>a</sup>

aroma compound	$K_{ww}$ for <i>pedunculata</i> oak wood	
	at 10 °C	at 25 °C
guaiaicol	ND	ND
4-methylguaiaicol	9.7 ± 1.3	13.5 ± 2.0
4-ethylguaiaicol	13.5 ± 0.7	16.4 ± 0.9
4-propylguaiaicol	21.7 ± 1.2	22.8 ± 1.3
4-vinylguaiaicol	75.1 ± 7.8	484.6 ± 33.5
4-ethylphenol	19.4 ± 1.0	27.3 ± 2.5
vanillin	ND	ND
eugenol	19.4 ± 1.3	18.9 ± 1.9
isoeugenol	ND	ND
<i>trans</i> -whiskylactone	ND	12.2 ± 0.9
<i>cis</i> -whiskylactone	ND	11.7 ± 1.7

<sup>a</sup> ND, not determined.

favors the hydrophobic interactions between the volatile compounds in solution and the wood surface. For the homologous series of guaiaicol and for a given temperature, the sorption increases with an increase of the length of the para aliphatic chain. Therefore, there is a linear correlation ( $R^2 = 0.9553$ ) between the sorption capacity of oak wood and the hydrophobic character of the volatile compound (Tables 1 and 3); that is, the higher the number of hydrophobic carbons in the aliphatic substituent is, the higher the possibility of establishing weak interactions with the wood surface is (27).

The sorption isotherms of 4-vinylguaiaicol at 10 and 25 °C (Figure 5) clearly show a significantly different shape from that of the other volatile compounds studied. These isotherms display a shape that could be more suitably fitted to the initial part of the theoretical Langmuir or Freundlich models corresponding to monolayer adsorption behavior (18). However, as indicated before, because 4-vinylguaiaicol was part of a mixture of cosolutes, these models cannot be applied unambiguously. As already suggested, a possible reason for this different sorption

behavior could be the C=C double bond conjugated to the phenyl ring for 4-vinylguaiacol. As shown in **Figure 5**, this hypothesis is supported by the data obtained for isoeugenol, which also has a double bond conjugated to the phenyl ring (**Table 1**). On the basis of electronic resonance processes allowed by this double bond conjugated to the phenyl ring, it is likely that a chemical mechanism of interaction is involved for the sorption of 4-vinylguaiacol and isoeugenol, which is different from the sorption mechanism of the other volatile compounds studied.

To compare the partition coefficient of 4-vinylguaiacol to that of the other volatile compounds, we applied the same linear model for the low concentrations at equilibrium (**Table 3**). As indicated in **Table 3**, the increase of temperature leads to the same increase of  $K_{ww}$  but at a much higher level. These results show that the sorption behaviors of volatile compounds in wine medium and at diluted concentrations do not follow the general rule for the sorption behaviors of organic compounds in aqueous medium, for which sorption typically decreases with temperature (28). According to Chiou et al. (29), increased sorption at higher temperatures can be expected for compounds for which the solubility decreases at higher temperatures. From our results in **Table 2** and except for vanillin, the solubility in model wine of the different compounds studied does not vary significantly with an increase of temperature from 10 to 25 °C. Therefore, within this temperature range, the particular chemical composition of the model wine along with its pH and ionic strength characteristics seems to be responsible for an unusual partitioning behavior of volatile compounds between oak wood and wine.

To summarize, we have shown that among the different volatile compounds studied, two families of chemical structures can be distinguished in terms of sorption behavior to oak wood. With or without -OCH<sub>3</sub> ortho substituent, the phenolic structures with aliphatic or unconjugated ethylenic para substituents display similar linear sorption behaviors for diluted concentrations and similar logarithm type behaviors above individual equilibrium concentrations of about 10 ppm. The  $K_{ww}$  partition coefficients extracted from the linear part of the isotherms are moderate and slightly increase from 10 to 25 °C. The two isomers of whiskylactone show the same behavior. Alternatively, the phenolic structures with conjugated ethylenic para substituents are much more sorbed already for diluted concentrations and display type I or possibly type II like isotherms (30). Their  $K_{ww}$  partition coefficients are 3–4 times higher than those of the other compounds, and they increase significantly from 10 to 25 °C. Together, these results bring new insights for the understanding of the sorption equilibria and the fate of volatile phenolic compounds in wine aged in oak barrels.

#### ACKNOWLEDGMENT

Prof. J. P. Bellat is warmly thanked for helpful discussions, and J. Guerreau is thanked for technical assistance.

#### LITERATURE CITED

- Rapp, A.; Mandery, H. Wine aroma. *Experientia* **1986**, *42*, 873–884.
- Chatonnet, P.; Dubourdieu, D.; Boidron, J.-N.; Pons, M. Elevage des vins rouges en fûts de chêne: Évolution de certains composés volatils et de leur impact aromatique. *Sci. Aliments* **1990**, *10*, 565–587.
- Sefton, M. A.; Francis, I. L.; Pocok, K. F.; Williams, P. J. The influence of natural seasoning on the concentration of eugenol, and cis and trans- $\beta$ -methyl- $\gamma$ -octalactone extracted from French and American oak wood. *Sci. Aliments* **1993**, *13*, 629–643.
- Towey, J. P.; Waterhouse, A. L. The extraction of volatile compounds from French and American oak barrels in Chardonnay during three successive vintages. *Am. J. Enol. Vitic.* **1996**, *47*, 163–172.
- Chatonnet, P.; Dubourdieu, D.; Boidron, J.-N.; Pons, M. The origin of ethylphenols in wines. *J. Sci. Food Agric.* **1992**, *60*, 165–178.
- Chatonnet, P.; Dubourdieu, D.; Boidron, J.-N. Incidence des conditions de fermentation et d'élevage de vins blancs secs en barriques sur leur composition en substances cédées par le bois de chêne. *Sci. Aliments* **1992**, *12*, 665–685.
- Ramirez-Ramirez, G.; Lubbers, S.; Voilley, A.; Charpentier, C.; Feuillat, M.; Chassagne, D. Aroma compound sorption by oak wood in model wine. *J. Agric. Food Chem.* **2001**, *49*, 3893–3897.
- Ramirez-Ramirez, G.; Chassagne, D.; Feuillat, M.; Voilley, A.; Charpentier, C. Effect of wine constituents on aroma compound sorption by oak wood in a model system. *Am. J. Enol. Vitic.* **2004**, *55*, 22–26.
- Chassagne, D.; Ramirez, G.; Lubbers, S.; Charpentier, C.; Feuillat, M.; Voilley, A. Sorption of aroma compounds to oak wood in wine aging conditions. In *Flavour Research at the Dawn of the Twenty-First Century*; Le Quére, J. L., Etievant, P. X., Eds.; Lavoisier: Cachan, France, 2003; pp 63–66.
- Trapp, S.; Miglioranza, K. S.; Mosbaek, H. Sorption of lipophilic organic compounds to wood and implications for the environmental fate. *Environ. Sci. Technol.* **2001**, *25*, 1561–1566.
- Rekker, W. T.; Nauta, R. F. The hydrophobic fragmental constant. Its derivation and application. *Farmacochimistry Library*; Elsevier: Amsterdam, 1977; Vol. 1, p 389.
- Piraprez, G.; Hérent, M. F.; Collin, S. Determination of the lipophilicity of aroma compounds by RP-HPLC. *Flavour Fragrance J.* **1998**, *13*, 400–408.
- Voilley, A.; Loncin, M. Une méthode simple pour la détermination des coefficients d'activité de substances d'arômes modèle peu solubles dans l'eau. *Ind. Aliment. Agric.* **1976**, 1417–1418.
- Roberts, W.; Kenneth, B. Correlation of aqueous and lipid solubilities with flux for prodrugs of 5-fluorouracil, theophylline, and 6-mercaptopurine: A potts-Guy approach. *J. Pharm. Sci.* **1999**, *88*, 515–522.
- Dohanyosova, P.; Fenclova, D.; Vrbka, P.; Dohnal, V. Measurement of aqueous solubility of hydrophobic volatile organic compounds by solute vapor absorption technique: Toluene, ethylbenzene, propylbenzene, and butylbenzene at temperatures from 273 to 328 K. *J. Chem. Eng.* **2001**, *46*, 1533–1539.
- Garde, S.; Garcia, A. E.; Pratt, L. R.; Hummer, G. Temperature dependence of the solubility of non polar gases in water. *Biophys. Chem.* **1999**, *78*, 21–32.
- Tolls, J.; van Dijk, J.; Verbruggen, E. J. M.; Hermes, J. L. M.; Loeprecht, B.; Schüürmann, G. Aqueous solubility-molecular size relationships: A mechanistic case study using C<sub>10</sub>- to C<sub>19</sub>-alkanes. *J. Phys. Chem. A* **2002**, *106*, 2760–2765.
- Streat, M.; Patrick, J. W.; Camporro, P. Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbons. *Water Res.* **1995**, *29*, 467–472.
- Severtson, S.; Banerjee, S. Dual reactive domain model for sorption of aqueous organics by wood fiber. *J. Colloid Interface Sci.* **2001**, *236*, 362–368.
- Severtson, S.; Banerjee, S. Sorption of chlorophenols to wood pulp. *Environ. Sci. Technol.* **1996**, *30*, 1961–1969.
- Huang, H.-C.; Lee, J.-F.; Chao, H.-P.; Yeh, P.-W.; Yang, Y.-F.; Liao, W. L. The influences of solid-phase organic constituents on the partition of aliphatic and aromatic organic contaminants. *J. Colloid Interface Sci.* **2005**, *286*, 127–133.
- Leng, C. C.; Pinto, N. G. Effects of surface properties of activated carbons on adsorption behaviour of selected aromatics. *Carbon* **1997**, *35*, 1375–1385.
- Moreno-Castilla, C.; Rivera-Utrilla, J.; Lopez-Ramon, M. V.; Carrasco-Marin, F. Adsorption of some substituted phenols on activated carbons from a bituminous coal. *Carbon* **1995**, *33*, 845–851.

- (24) Salame, I. I.; Bandosz, J. T. Role of surface chemistry in adsorption of phenol of activated carbons. *J. Colloid Interface Sci.* **2003**, *264*, 307–312.
- (25) Tancredi, N.; Medero, N.; Möller, F.; Píriz, J.; Plada, C.; Cordero, T. Phenol adsorption onto powdered and granular activated carbon, prepared from *Eucalyptus* wood. *J. Colloid Interface Sci.* **2004**, *279*, 357–363.
- (26) Boving, T.; Zhang, W. Removal of aqueous-phase polynuclear aromatic hydrocarbons using aspen wood fibers. *Chemosphere* **2004**, *54*, 831–839.
- (27) Trapp, S.; Miglioranza, K. S.; Mosbaek, H. Sorption of lipophilic organic compounds to wood and implications for the environmental fate. *Environ. Sci. Technol.* **2001**, *25*, 1561–1566.
- (28) ten Hulscher, Th. E. M.; Cornelissen, G. Effect of temperature on sorption equilibrium and sorption kinetics on organic micropollutants—A review. *Chemosphere* **1996**, *32*, 609–625.
- (29) Chiou, C. T.; Peters, L. J.; Freed, V. H. A physical concept of soil–water equilibria for nonionic organic compounds. *Science* **1979**, *206*, 831–832.
- (30) Rouquerol, J.; Rouquero, F.; Sing, K. W. *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*; Academic Press: London, San Diego, 1999; p 18.

---

**Received for review December 6, 2005. Revised manuscript received March 9, 2006. Accepted March 14, 2006. This work was financially supported by the Region Bourgogne (Project 04 516 AA 011 591) and the AROBOIS Company (France). V.D.B.-G. is grateful to CONACyT-Mexico for financial support.**

JF053043D