

## Sorption Equilibria of Ethanol on Cork

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**ABSTRACT:** We report here for the first time a thermodynamic study of gaseous ethanol sorption on raw cork powder and plate. Our study aims at a better understanding of the reactivity of this material when used as a stopper under enological conditions, thus in close contact with a hydroethanolic solution, wine. Sorption–desorption isotherms were accurately measured by thermogravimetry at 298 K in a large range of relative pressures. Sorption enthalpies were determined by calorimetry as a function of loading. Sorption–desorption isotherms exhibit a hysteresis loop probably due to the swelling of the material and the absorption of ethanol. Surprisingly, the sorption enthalpy of ethanol becomes lower than the liquefaction enthalpy as the filling increases. This result could be attributed to the swelling of the material, which would generate endothermic effects. Sorption of SO<sub>2</sub> on cork containing ethanol was also studied. When the ethanol content in cork is 2 wt %, the amount of SO<sub>2</sub> sorbed is divided by 2. Thus, ethanol does not enhance the sorption rate for SO<sub>2</sub> but, on the contrary, decreases the SO<sub>2</sub> sorption activity onto cork, probably because of competitive sorption mechanisms.

**KEYWORDS:** wine, cork, ethanol, sulfur dioxide, sorption, calorimetry

### ■ INTRODUCTION

Our work lies in the frame of a large study concerning the sorption, in the gas phase, of wine active compounds on cork. The aim of this research work is to help clarify the oxidation phenomena that take place during wine aging in the bottle and to elucidate the exact role the closure plays.<sup>1</sup> To prevent oxidation, sulfur dioxide (SO<sub>2</sub>) is added as an exogenous antioxidant to wine at pressing and before bottling. However, in some cases, the SO<sub>2</sub> concentration was found to abnormally decrease during wine storage in the bottle.<sup>2</sup> This decrease could result not only from reactivity with some wine constituents but also from sorption or diffusion through the cork stopper. Also, cork is not an inert material. Its physicochemical properties are well described by Pereira.<sup>3</sup> It is known that it can interact with some molecules such as pollutants,<sup>4</sup> pesticides,<sup>5</sup> or trichloro-anisoles that are responsible for cork taint.<sup>6</sup> So, it seems to us particularly relevant to study, from a thermodynamic point of view, the interaction with cork stoppers of the two major molecules present in wine, water and ethanol, along with a third one used as an antioxidant, sulfur dioxide. In previous works, sorption of water vapor and sulfur dioxide on raw cork (as plate or powder) was studied.<sup>7,8</sup> Surprisingly, although cork has been used since antiquity for sealing ethanolic beverages, particularly wine, the sorption of ethanol on cork has never been studied in detail. To our knowledge, no data on the sorption of ethanol on cork are reported in the literature. This is the reason why we now report a complete thermodynamic study on the sorption of gaseous ethanol on raw cork. Sorption–desorption isotherms and sorption enthalpy were accurately measured to understand the mechanism of the interaction of ethanol with cork. In addition, special attention was paid to the effect of the presence of ethanol previously sorbed in cork on the further sorption of SO<sub>2</sub>. This was dictated by a recent work devoted to

the competitive sorption of water with sulfur dioxide which showed that the presence of H<sub>2</sub>O is not favorable to the sorption of SO<sub>2</sub>.<sup>9</sup> So, we assess here this sorption behavior in the presence of ethanol, the second major component of wine. Sorption of ethanol was also studied on cork previously subjected to extraction with various solvents to know the role that the free extractives play in the sorption process.

### ■ EXPERIMENTAL SECTION

**Material.** Raw cork planks, from *Quercus suber* L. oak trees in the Mora (Portugal) production area, were supplied by the Bouchons Trescases S.A. company (Boulou, France). Planks were neither washed nor surface-treated (with paraffin or silicone) prior to use. For gravimetric study of ethanol sorption, cork pieces in plate geometry (35 mm long, 10 mm wide and 1 mm thick) were manually cut from the planks. This geometry mimics the gas–solid contact existing in the headspace of a wine bottle: the largest surface area available has the same cellular orientation. Cork powder was also used to increase the surface area available for sorption. Powder was made by grating cork stopper or cork plate with a rasp. After sieving, the mean particle size was lower than 500 μm. Part of this powder was subjected to extraction using the Soxhlet method with different solvents (dichloro-methane, ethanol, and finally water) followed by methanolysis, as proposed by Pereira,<sup>10</sup> to remove free extractives and to isolate suberin present in cork. Lignin was extracted from oak wood *Quercus robur* (Forest of Cîteaux, Côte d'or, France) according to the method developed by Barrera Garcia et al.<sup>11</sup> High purity cellulose powder (medium fibrous) from cotton was supplied from Sigma-Aldrich Co.

**Thermogravimetry.** Sorption of gaseous ethanol on natural cork, suberin, lignin, and cellulose was investigated by thermogravimetry with a homemade McBain balance at 298 K. The pressure lay between

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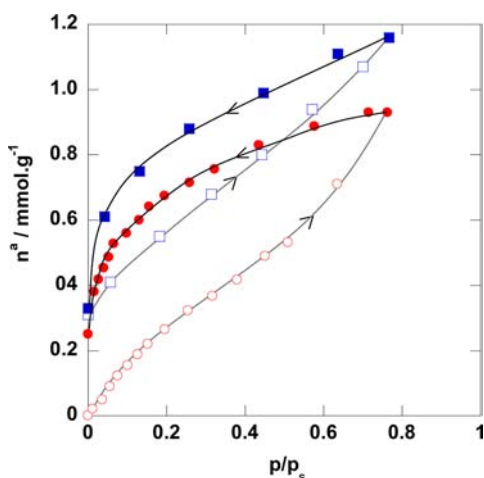
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$10^{-5}$  and 60 hPa at maximum to avoid any liquefaction of ethanol in the apparatus. As the saturated vapor pressure of ethanol is equal to 78.2 hPa at 298 K, the relative pressure  $p/p_s$  ranged from 0.005 to 0.78. Cork samples with different geometries were studied: cork plate and cork powder. The mass of the cork sample was around 40 mg for cork plate and 25 mg for cork powder. Considering cork main macromolecules, the sample mass was around 16 mg for suberin, 25 mg for cellulose, and 16 mg for lignin. The sorption–desorption isotherms were measured following the same procedure as detailed in a previous work.<sup>8</sup> Prior to experiment, the sample was outgassed under dynamic vacuum ( $10^{-5}$  hPa) for one night. Several sorption–desorption cycles were performed on the same sample. Between each cycle, the sample was put under vacuum without changing the temperature for evacuating the species physisorbed on the material. Thus, it was possible to observe if chemisorption occurred on the material. The experimental accuracy is  $\pm 0.01$  mmol·g<sup>-1</sup> for the sorbed amount,  $\pm 0.5$  K for the temperature, and  $\pm 0.01$  hPa for the pressure.

**Differential Calorimetry Coupled with Manometry.** Sorption enthalpy of ethanol on cork was measured with a differential calorimeter (Thian-Calvet Setaram C80) coupled with a manometric apparatus constructed in-house. This device has been described in detail in previous studies.<sup>12–14</sup> It allows the measurement of the molar sorption enthalpy  $\Delta H^{\text{F}}(n^{\text{a}})$  of ethanol, the so-called the sorption heat, as a function of the sorbed amount  $n^{\text{a}}$ . Sorption was realized at 298 K on about 640 mg of cork powder with or without extractives, previously outgassed in situ under vacuum at  $10^{-5}$  hPa for 72 h. Cork with or without extractives refers here to raw cork material and raw cork material after extractives extraction (liquid/solid extraction in a Soxhlet system with dichloromethane (8 h), ethanol (8 h), and water (8 h), respectively). The ethanol pressure ranged from 0.2 to 60 hPa. Before the SO<sub>2</sub> sorption measurements by manometry coupled to calorimetry, a presorption of ethanol was performed by subjecting the outgassed sample to a pressure of ethanol equal to 12 hPa. It corresponds to the partial pressure that can be calculated in the headspace of a wine bottle by considering an ethanol concentration in wine of 2 mol·L<sup>-1</sup> (ethanolic degree of 12°) and a Henry constant of solubility equal to 2.10<sup>-3</sup> mol·L<sup>-1</sup>·Pa<sup>-1</sup> at 298 K. Sulfur dioxide sorption was then performed by putting successive and calibrated doses of gas, ranging from 0.2 to 45 hPa, in contact with the sample.

## RESULTS AND DISCUSSION

**Sorption Capacity of Raw Cork for Ethanol. 1. Cork Plate.** The sorption–desorption isotherms of ethanol on raw cork plate are shown in Figure 1. Two sorption–desorption cycles were performed. For the first sorption–desorption cycle,



**Figure 1.** Sorption–desorption isotherms of gaseous ethanol on raw cork plate at 298 K. Open symbols: sorption; closed symbols: desorption. Dots: first cycle. Squares: second cycle.

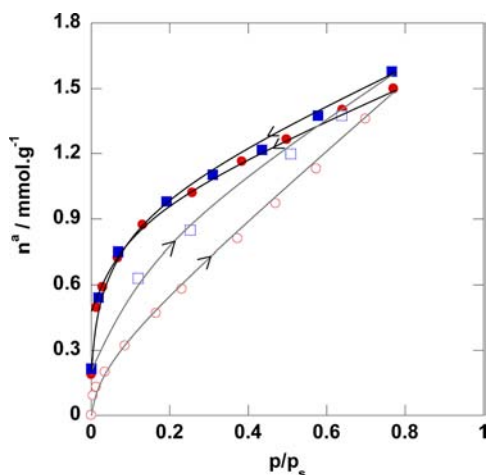
the isotherm exhibits a large hysteresis with a first sorption branch obtained from the outgassed cork and a second desorption branch obtained from the saturated cork. The first sorption branch presents a shape close to the type II isotherm of the IUPAC classification<sup>15</sup> that is usually found when adsorption occurs on nonporous or macroporous solids. The slope of the isotherm at low relative pressure ( $p/p_s < 0.1$ ) is rather low. This indicates a weak sorption affinity of cork for ethanol. The Henry constant given by this slope ( $K_H = n^{\text{a}}/(p/p_s)$ ) is about 1.5 mmol·g<sup>-1</sup>. This value is 10 times lower than those reported for ethanol adsorption on silicalite-1 membrane and Na-ZSM5 zeolite (about 30 and 50 mmol·g<sup>-1</sup>, respectively),<sup>16,17</sup> and 50 times lower than that found for activated carbon (about 168 mmol·g<sup>-1</sup>),<sup>18</sup> which are all three known as stronger organophilic materials. However, our value is higher than those found for cellulose triacetate film (about 0.05 mmol·g<sup>-1</sup>) which has a microporous structure<sup>19</sup> and for chitosan (about  $1.5 \times 10^{-4}$  mmol·g<sup>-1</sup>) which is a hydrophilic polysaccharidic biopolymer.<sup>20</sup>

At the relative pressure of 0.7, the sorbed amount is around 1 mmol·g<sup>-1</sup>. This corresponds to 4 wt %. This sorption capacity is rather low compared to mesoporous adsorbent carbons (MCM-41) which can adsorb up to 18 mmol·g<sup>-1</sup>.<sup>21,22</sup> Activated carbons can adsorb from 5 to 9 mmol·g<sup>-1</sup>.<sup>18,21</sup> Microporous FAU and MFI zeolites<sup>17,21</sup> have an adsorption capacity of around 4 mmol·g<sup>-1</sup>. The sorption capacity of cork is of the same order of magnitude as that observed for silicalite-1 (2 mmol·g<sup>-1</sup>)<sup>16</sup> and for cellulose triacetate film (around 1 mmol·g<sup>-1</sup>).<sup>19</sup> However, it is much higher than that measured on chitosan (about  $1 \times 10^{-5}$  mmol·g<sup>-1</sup>).

As displayed in Figure 1, desorption is not complete at the end of the first sorption–desorption cycle, even after pumping under dynamic vacuum during four days. The ethanol amount that remains sorbed in cork is equal to 0.25 mmol·g<sup>-1</sup>, which represents as much as 25% of the total sorbed quantity. This result suggests that ethanol could be chemisorbed on cork as it has been observed on cellulose acetate films.<sup>19</sup> This chemisorption significantly contributes to the hysteresis observed between sorption and desorption. Nevertheless, this irreversibility can also be attributed to an absorption of ethanol accompanied by a swelling of the material as in the case of some polymers.<sup>19,23</sup>

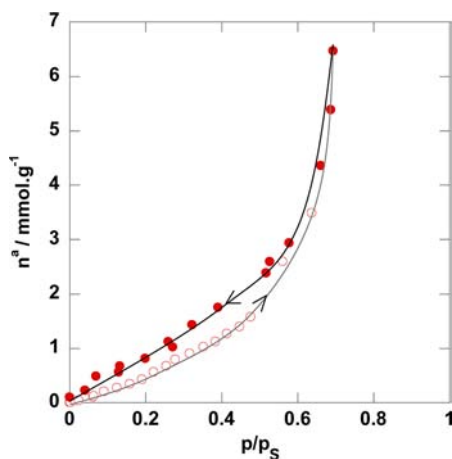
When a second sorption–desorption cycle is performed, a hysteresis is again observed between sorption and desorption. However, desorption returns back to the initial value, which corresponds in that case to the starting level of the second cycle. This means that no more chemisorption of ethanol occurs after the first sorption–desorption cycle. Thereafter, this hysteresis is only due to swelling of the material.

**2. Cork Powder.** The sorption–desorption isotherms of ethanol on raw cork powder are shown in Figure 2. They are very similar to those obtained with cork plate, displaying in particular the same incomplete desorption after the first cycle and hysteresis between sorption and desorption. However, the sorption capacity close to saturation is slightly higher (1.5 mol·g<sup>-1</sup>). Moreover, the difference between the first sorption–desorption cycle and the second cycle is reduced. This is due to a surface effect. As the surface in contact with the gas phase is higher with powder than with plate, the number of accessible sorption sites is higher. We have observed exactly the same hysteresis phenomenon when recently studying the sorption of ethanol on oak wood (results not shown).



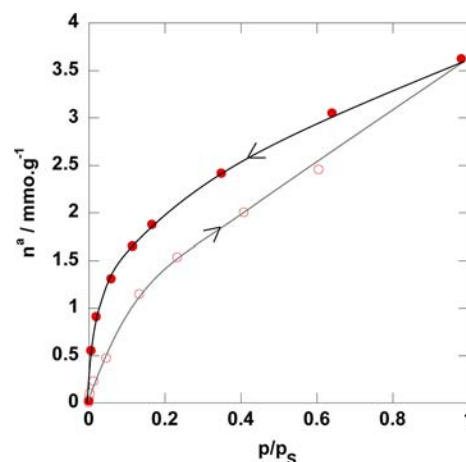
**Figure 2.** Sorption–desorption isotherms of gaseous ethanol on raw cork powder at 298 K. Open symbols: sorption; closed symbols: desorption. Dots: first cycle. Squares: second cycle.

**Affinity of the Three Major Macromolecules of Cork for Ethanol.** It is also interesting to consider separately the different constituents of cork to better understand their respective role in the sorption mechanism of ethanol. Cork is composed of three major macromolecules: suberin (33 to 50 wt %), lignin (13 to 29 wt %), and polysaccharides (cellulose and hemicellulose, 6% to 25 wt %).<sup>24</sup> Figure 3 displays the sorption

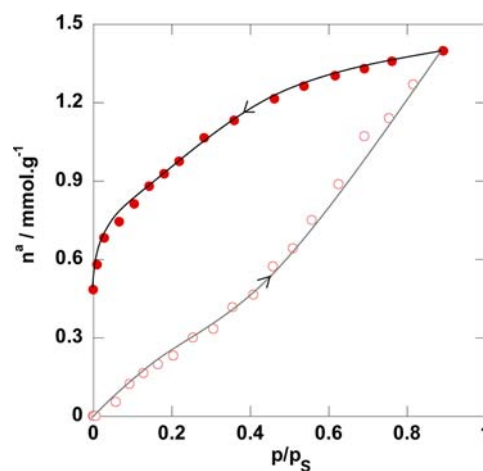


**Figure 3.** Sorption–desorption isotherm of gaseous ethanol on suberin extracted from cork at 298 K. Open symbols: sorption; closed symbols: desorption.

isotherm of ethanol on suberin extracted from cork. First, the sorption isotherm exhibits a type III shape typical of weak sorbate–sorbent interactions. Second, contrary to previous sorption isotherms on cork as shown in Figures 1 and 2, it does not show any chemisorption: all sorbed ethanol molecules are totally desorbed at the end of the desorption cycle. So, we can reasonably assume that suberin is not involved in the chemisorption of ethanol by cork. Despite this, it is noteworthy that a higher amount of ethanol is sorbed on suberin in comparison to cork. Figure 4 shows the sorption isotherm of ethanol on lignin<sup>25</sup> which is also one of the major chemical components of wood. Similarly to suberin, desorption of ethanol is complete; only physisorption occurs. Therefore, we can reasonably assume that ethanol is rather chemisorbed on



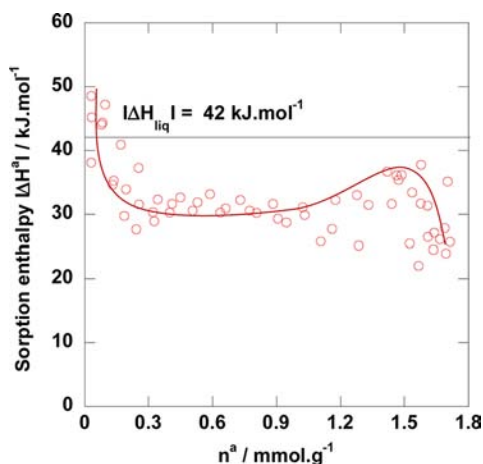
**Figure 4.** Sorption–desorption isotherm of gaseous ethanol on lignin at 298 K. Open symbols: sorption; closed symbols: desorption.



**Figure 5.** Sorption–desorption isotherm of gaseous ethanol on commercial cellulose at 298 K. Open symbols: sorption; closed symbols: desorption.

cellulose. To support this hypothesis, the sorption isotherm of ethanol on commercial cellulose was determined. Figure 5 shows that sorption isotherm on cellulose is very similar to those obtain on cork. Therefore, it is conceivable that the cellulosic fraction of cork (cellulose and probably hemicellulose) is essentially responsible for chemisorption of ethanol on cork.

**Sorption Energy of Ethanol on Raw Cork.** Sorption enthalpies of ethanol on raw cork powder (thus containing free extractives) are given in absolute value versus loading in Figure 6. The shape of the calorimetric curve indicates that the sorption process is energetically heterogeneous. It can be divided into three parts. First, the sorption enthalpy sharply decreases from 50 to 30 kJ·mol<sup>-1</sup>. This part could correspond to the chemisorption of ethanol in cork, even if the energy involved is not so high. Then, the sorption enthalpy is constant (about 30 kJ·mol<sup>-1</sup>). This region corresponds to the physisorption of ethanol. Absorption of ethanol in cork is also not excluded. Finally, the sorption enthalpy increases, passes through a maximum, and then decreases when saturation is approaching. This phenomenon is due to sorbate–sorbate interactions. Considering the whole curve, it is noteworthy that the sorption enthalpy quickly becomes lower than the



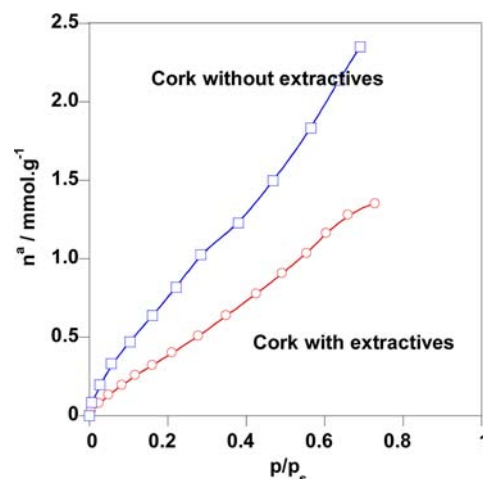
**Figure 6.** Sorption enthalpy (absolute value) of gaseous ethanol on cork powder with extractives measured by calorimetry at 298 K versus loading.  $\Delta H_{\text{liq}}$  is the liquefaction enthalpy of ethanol.

liquefaction enthalpy of ethanol ( $42 \text{ kJ}\cdot\text{mol}^{-1}$ ), which is rather surprising. The adsorption enthalpy of a gas on a solid is generally higher than the liquefaction enthalpy. This suggests that some endothermic effects exist, which counterbalance the exothermic sorption effects. These endothermic effects could be caused by cork swelling or other structural modifications. Tazhbaev et al.<sup>23</sup> have already demonstrated that interactions of ethanol with copolymers of acrylic acids give rise to an endothermic effect due to the swelling of the copolymer. According to the copolymer composition, they indicate that swelling enthalpy can vary from 20 to  $100 \text{ J}\cdot\text{g}^{-1}$ . It is highly probable that the same phenomenon occurs in cork. Let us consider a physisorption enthalpy of ethanol on cork close to the liquefaction enthalpy ( $42 \text{ kJ}\cdot\text{mol}^{-1}$ ). In such a case, for loadings ranging from 0.25 to  $1.2 \text{ mmol}\cdot\text{g}^{-1}$ , the swelling enthalpy would be of  $12 \text{ kJ}\cdot\text{mol}^{-1}$  (corresponding to the difference observed with the experimental value of around  $30 \text{ kJ}\cdot\text{mol}^{-1}$ ). This value corresponds to  $4 \text{ J}\cdot\text{g}^{-1}$  of cork. It is lower than the values found for previous polymers, but it does not seem abnormal. It is interesting to note that the same effect was also observed during the sorption of *n*-hexane on cork in the same experimental conditions (results not shown). It is well-known that ethanol and *n*-hexane are good solvents to extract the extractives (phenolic and aliphatic compounds) present in cork.<sup>3</sup> Therefore, the fact that the sorption enthalpy is lower than the liquefaction enthalpy could also be due to chemical reactions of ethanol with cork extractives. To confirm this second hypothesis, ethanol sorption was thus performed on cork without extractives.

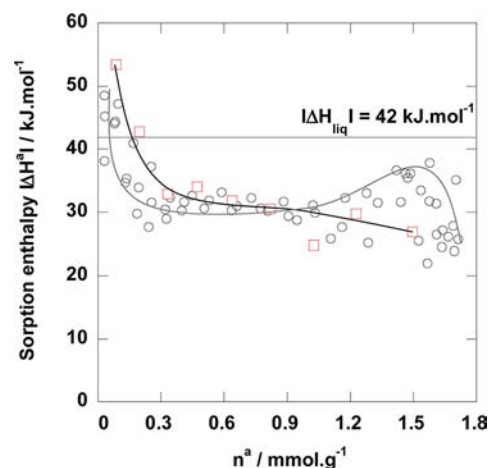
#### Role of Extractives from Cork in the Ethanol Sorption.

Sorption isotherms of ethanol on dry cork powder without extractives (obtained after solvent extraction) were determined by manometry. They are displayed in Figure 7. Desorption was not studied in that case. For comparison, the sorption isotherm on cork before extraction is also reported. The isotherm shape is the same for the two cork samples. However, the Henry constant and the sorption capacity are about two times higher for cork without extractives than for cork with extractives.

Calorimetric sorption enthalpies of ethanol on cork powder with and without extractives are given in absolute value versus loading in Figure 8. No significant change is observed after extraction. The sorption enthalpy of ethanol is still lower than the liquefaction enthalpy. Therefore, the hypothesis of



**Figure 7.** Sorption isotherms obtained by manometry, at 298 K, of ethanol on cork with (O) and without extractives (□).

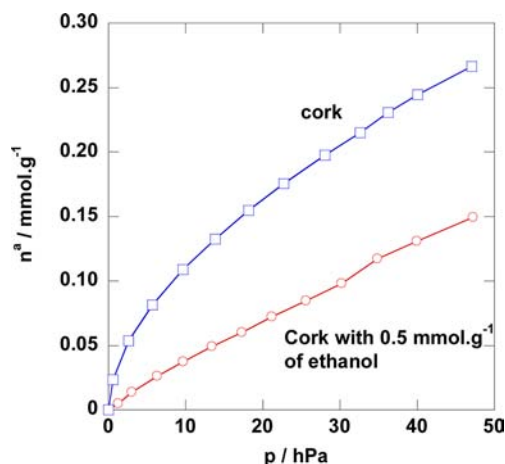


**Figure 8.** Sorption enthalpy (absolute value) of gaseous ethanol on cork powder measured by calorimetry at 298 K versus loading. (O) Cork with extractives; (□) cork without extractives.  $\Delta H_{\text{liq}}$  is the liquefaction enthalpy of ethanol.

endothermic effects consecutive to chemical reactions of ethanol with cork extractives can be rejected. Moreover, the hypothesis of an interaction of ethanol with cork following an absorption process with a swelling of the material is reinforced.

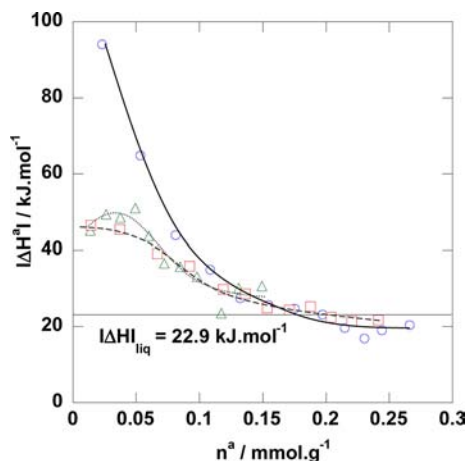
**Influence of Ethanol on the Sorption of Sulfur Dioxide.** Sorption isotherms of  $\text{SO}_2$  on cork and on dry cork already having sorbed ethanol are displayed in Figure 9. The figure clearly shows that the isotherm is significantly modified when  $\text{SO}_2$  is sorbed on cork having previously sorbed  $0.5 \text{ mmol}\cdot\text{g}^{-1}$  of ethanol. This value corresponds to the quantity sorbed by cork at a pressure of ethanol of 12 hPa, which is close to the ethanol partial pressure in the headspace of a bottle of wine (considering an alcoholic strength by volume of  $12^\circ$ ). In the presence of ethanol, the sorption capacity of cork for  $\text{SO}_2$  is divided by two. Thus, we suspect here a competitive sorption between ethanol and sulfur dioxide. This phenomenon has already been observed when  $\text{SO}_2$  was sorbed in the presence of  $\text{H}_2\text{O}$ . When cork contains 5 wt % of water, its sorption capacity for  $\text{SO}_2$  is divided by a factor of 3.<sup>7</sup>

Sorption enthalpy of  $\text{SO}_2$  on cork powder having previously sorbed ethanol is shown in Figure 10. Sorption enthalpy of  $\text{SO}_2$  on dry cork powder for two consecutive sorptions on a same



**Figure 9.** Sorption isotherms of sulfur dioxide at 298 K on dry cork ( $\square$ ) and on cork having previously sorbed  $0.50 \text{ mmol}\cdot\text{g}^{-1}$  of ethanol ( $\circ$ ).

sample (the sample being outgassed after the first sorption) is also reported for comparison.



**Figure 10.** Sorption enthalpies of gaseous  $\text{SO}_2$  at 298 K by cork powder containing  $0.5 \text{ mmol}\cdot\text{g}^{-1}$  of ethanol and by dry cork for two consecutive sorptions, as a function of the loading. Also indicated is the enthalpy of liquefaction of  $\text{SO}_2$ . (— $\circ$ —) First sorption on dry cork. (--- $\square$ ---) Second sorption on dry cork. (··· $\triangle$ ···) Sorption on cork containing ethanol.

When  $\text{SO}_2$  sorption is realized on dry cork, for the first sorption, a high sorption enthalpy is observed (about  $100 \text{ kJ}\cdot\text{mol}^{-1}$ ) at low loading. For the second sorption, the sorption enthalpy is reduced to  $50 \text{ kJ}\cdot\text{mol}^{-1}$ . This is typical of a chemisorption process of  $\text{SO}_2$  molecules on the cork surface. During the first sorption, the sulfur dioxide molecules are first chemisorbed and then physisorbed on cork. During the second sorption, after outgassing under vacuum, the sulfur dioxide is only physisorbed.<sup>7</sup>

When  $\text{SO}_2$  sorption is performed on cork containing ethanol previously sorbed, the sorption enthalpy of  $\text{SO}_2$  is exactly the same as that measured during the second sorption of  $\text{SO}_2$  on cork. This means that  $\text{SO}_2$  is only physisorbed. It cannot be chemisorbed on the cork surface probably because the sites for chemisorption are already saturated by ethanol. This result again reinforces the hypothesis of a chemisorption of the first ethanol molecules on cork. It also reinforces the fact that cork is

not implied in the sorption of  $\text{SO}_2$  molecules to high enough levels that can lead to a decrease of its concentration in wine. Not only are sorbed quantities very low but also their sorption process presents competitive mechanisms with the sorption of the other two major molecules in wine, water and ethanol.

To conclude this complete thermodynamic study of ethanol sorption on cork, we show that the sorption process of ethanol on cork is irreversible. The large hysteresis loop observed on the sorption–desorption isotherms could be the consequence of a chemisorption of ethanol and/or to structural modifications of cork such as swelling. These structural changes lead to an endothermic effect, estimated at about  $12 \text{ kJ}\cdot\text{mol}^{-1}$ , which makes the sorption enthalpy of ethanol lower than the liquefaction enthalpy. The sorption process is then essentially driven by entropic effects. As loading is increasing, the adsorption process of ethanol is probably replaced by an absorption process. The amount of ethanol retained by cork after desorption corresponds to molecules either chemisorbed and/or physically trapped by entropic confinement in the cork during the sorption process. In addition, presorption of ethanol, as well as water, on cork is not in favor of further sorption of sulfur dioxide. As a consequence, the sulfur dioxide concentration decrease in hydroethanolic media cannot be attributed to the sorption process of sulfur dioxide on cork. This first study on the interaction of ethanol with cork constitutes a good basis for further investigations on the permeation by other molecules such as  $\text{O}_2$  and  $\text{CO}_2$  through cork. It will also be useful to better understand the aging of the material in contact with wine.

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### Notes

The authors declare no competing financial interest.

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## DEDICATION

We dedicate this paper to the memory of Professor David Chassagne.

## REFERENCES

- (1) Karbowski, T.; Gougeon, R. D.; Alinc, J.-B.; Brachais, L.; Debeaufort, F.; Voilley, A.; Chassagne, D. Wine oxidation and the role of cork. *Crit. Rev. Food Sci. Nutr.* **2010**, *49*, 1–33.
- (2) Brajkovich, M.; Tibbits, N.; Peron, G.; Lund, C. M.; Dykes, S. I.; Kilmartin, P. A.; Nicolau, L. Effect of screwcap and cork closures on  $\text{SO}_2$  levels and aromas in a sauvignon blanc wine. *J. Agric. Food Chem.* **2005**, *53* (26), 10006–10011.
- (3) Pereira, H. *Cork: Biology, Production and Uses*, 1st ed.; Elsevier: Oxford, 2007; p 336.
- (4) Chubar, N.; Carvalho, J. R.; Correia, M. J. N. Cork biomass as biosorbent for  $\text{Cu(II)}$ ,  $\text{Zn(II)}$  and  $\text{Ni(II)}$ . *Colloids Surf, A* **2003**, *230* (1–3), 57–65.

(5) Domingues, V.; Alves, A.; Cabral, M.; Delerue-Matos, C. Sorption behaviour of bifenthrin on cork. *J. Chromatogr., A* **2005**, *1069* (1), 127–132.

(6) Buser, H. R.; Zanier, C.; Tanner, H. Identification of 2,4,6-trichloroanisole as a potent compound causing cork taint in wine. *J. Agric. Food Chem.* **1982**, *30* (2), 359–362.

(7) Lequin, S.; Karbowiak, T.; Brachais, L.; Chassagne, D.; Bellat, J. P. Adsorption equilibria of sulphur dioxide on cork. *Am. J. Enol. Vitic.* **2009**, *60* (2), 138–144.

(8) Lequin, S.; Chassagne, D.; Karbowiak, T.; Gougeon, R. G.; Brachais, L.; Bellat, J.-P. Adsorption equilibria of water vapor on cork. *J. Agric. Food Chem.* **2010**, *58* (6), 3438–3445.

(9) Lequin, S.; Chassagne, D.; Karbowiak, T.; Bellat, J.-P. Cosorption of sulfur dioxide and water on cork. *Am. J. Enol. Vitic.* **2011**, *63*, 127–131.

(10) Pereira, H. The chemical composition of cork. *Cork*; Elsevier Science B.V.: Amsterdam, 2007; pp 55–99.

(11) Barrera-Garcia, V. D.; Gougeon, R. G. D.; Karbowiak, T.; Voilley, A.; Chassagne, D. Role of wood macromolecules on selective sorption of phenolic compounds by wood. *J. Agric. Food Chem.* **2008**, *56* (18), 8498–8506.

(12) Moise, J.-C.; Bellat, J.-P. Effect of preadsorbed water on the adsorption of *p*-xylene and *m*-xylene mixtures on BaX and BaY zeolites. *J. Phys. Chem. B* **2005**, *109* (36), 17239–17244.

(13) Weber, G.; Benoit, F.; Bellat, J.-P.; Paulin, C.; Mougin, P.; Thomas, M. Selective adsorption of ethyl mercaptan on NaX zeolite. *Microporous Mesoporous Mater.* **2008**, *109* (1–3), 184–192.

(14) Simonot-Grange, M. H.; Bertrand, O.; Pilverdier, E.; Bellat, J.-P.; Paulin, C. Differential calorimetric enthalpies of adsorption of *p*-xylene and *m*-xylene on  $\gamma$  faujasites at 25°C. *J. Therm. Anal. Calorim.* **1997**, *48* (4), 741–754.

(15) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouqu  rol, J.; Siemieni  wska, T. Reporting physisorption data for gas/solid systems. *Pure Appl. Chem.* **1985**, *57* (4), 603–619.

(16) Yang, J. Z.; Liu, Q. L.; Wang, H. T. Analyzing adsorption and diffusion behaviors of ethanol/water through silicalite membranes by molecular simulation. *J. Membr. Sci.* **2007**, *291* (1–2), 1–9.

(17) Boddenberg, B.; Rakhmatkariev, G. U.; Greth, R. Statistical thermodynamics of methanol and ethanol adsorption in zeolite NaZSM5. *J. Phys. Chem. B* **1997**, *101* (9), 1634–1640.

(18) Gon  alves da Silva, A. M.; Soares, V. A. M.; Calado, J. C.; Brotas de Carvalho, M. Adsorption of pure vapours of ethanol and *n*-heptane and their liquid mixtures on activated carbon. *J. Chem. Soc., Faraday Trans.* **1991**, *87* (23), 3799–3804.

(19) Bolton, B. A.; Kint, S.; Bailey, G. F.; Scherer, J. R. Ethanol sorption and partial molar volume in cellulose acetate films. *J. Phys. Chem.* **1986**, *90* (6), 1207–1211.

(20) Kotel'nikova, T.; Kuznetsov, B. The isotherms of ethanol sorption on chitosan. *Russ. J. Phys. Chem. A* **2007**, *81* (3), 378–382.

(21) Nguyen, C.; Do, D. D. Adsorption of benzene and ethanol on activated carbon, MCM-41 and zeolite Y. *Adsorpt. Sci. Technol.* **1998**, *16* (6), 439–452.

(22) Nguyen, C.; Sonwane, C. G.; Bhatia, S. K.; Do, D. D. Adsorption of benzene and ethanol on MCM-41 material. *Langmuir* **1998**, *14* (17), 4950–4952.

(23) Tazhbaev, E.; Mustafin, E.; Burkeev, M.; Kasenov, B. Enthalpy of swelling of crosslinked copolymers of acrylic acid  $\beta$ -vinyl-oxethylamide in water and ethanol. *Russ. J. Phys. Chem. A* **2006**, *80* (8), 1300–1304.

(24) Silva, S. P.; Sabino, M. A.; Fernandes, E. M.; Correl  o, V. M.; Boesel, L. F.; Reis, R. L. Cork: properties, capabilities and applications. *Int. Mater. Rev.* **2005**, *50*, 345–365.

(25) Barrera-Garcia, V. D.; Chassagne, D.; Paulin, C.; Raya, J.; Hirschinger, J.; Voilley, A.; Bellat, J.-P.; Gougeon, R. D. Interaction mechanisms between guaiacols and lignin: The conjugated double bond makes the difference. *Langmuir* **2011**, *27* (3), 1038–1043.