

Cosorption of Sulfur Dioxide and Water on Cork

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Abstract: The cosorption of gaseous sulfur dioxide (SO₂) and water vapor (H₂O) on raw cork powder by using calorimetry coupled with manometry at 298 K was studied. Sorption isotherms of single components confirm the previous results obtained by thermogravimetry: SO₂ is well chemisorbed on cork surface while H₂O is only physisorbed. Moreover, the interaction of SO₂ and H₂O with cork appears more like an absorption process than an adsorption process. Competitive sorption of SO₂ and H₂O first occurs in favor of SO₂ chemisorption. After all chemisorption sites are saturated by SO₂, the cosorption process becomes selective for H₂O. The amount of SO₂ sorbed on cork is rather low compared to H₂O. Results indicate that the sorption of SO₂ on cork cannot explain the decrease in SO₂ content observed during wine aging in bottle.

Key words: cosorption, sulfur dioxide, water, cork, calorimetry, selectivity

Wine production has long been affected by premature oxidation reactions occurring in wine stored in bottle (Ribéreau-Gayon 1963, Singleton 1987, Wildenradt and Singleton 1974). The main molecules responsible for oxidation are oxygen (O₂) and its derived species, which react with wine polyphenols (Rossi and Singleton 1966, Waterhouse and Laurie 2006). Oxidation can eventually lead to sensory defaults (off flavors, browning), resulting in rejection by consumers (Escudero et al. 2002). Oxygen is essentially brought to wine during wine-making and also during storage by oxygen transfer through the bottle stopper (Karbowiak et al. 2010, Valade et al. 2007, Vidal et al. 2004). The choice of the sealing material is therefore important.

Natural cork stopper has been the most common material used for bottling, given its low permeability to liquids and gases. Cork is constituted by alveolar cells arranged without intercellular spaces (Gibson et al. 1981). These cells are mainly composed of suberin (~50% m/m), a rather hydrophobic compound with long aliphatic chains of fatty acid and some aromatic domains. The other major compounds present in cork are lignin (~30% m/m) and cellulose (~20% m/m) (Pereira 2007, Silva et al. 2005). Such structure and chemical composition provide cork with good barrier properties. How-

ever, oxidation reactions can randomly occur in wine during bottle aging. In order to reduce this phenomenon, sulfur dioxide (SO₂) is generally added before bottling as an antioxidant. However, it has been shown that SO₂ concentration can abnormally decrease after four months of storage (Brajkovich et al. 2005) and thus wine becomes less protected against oxidation. The question arises as to whether this decrease results from the sorption of SO₂ on cork or from the diffusion of SO₂ through cork. Moreover, in real conditions of wine storage, either in vertical or horizontal bottles, cork is highly hydrated. Thus, a second question arises concerning the possibility of hydration to favor the sorption and reactivity of cork with other molecules, such as SO₂. Although cork has been used as stopper material for several centuries, interactions of SO₂ and H₂O with cork are not yet fully understood. To our knowledge, no data are reported on cork and SO₂ interactions and only limited data on cork and water (Abdulla et al. 2009, Adrados and Haro 1994, Gil and Cortiço 1998). Thus, over the past few years, we have undertaken basic research on the interaction of these molecules on natural cork. Previous work used thermogravimetry and differential calorimetry to study the sorption of SO₂ and H₂O molecules individually in the gas state on crude cork, either dry or partially hydrated, and showed that SO₂ is chemisorbed on cork while H₂O is only physisorbed (Lequin et al. 2009, 2010). Surprisingly, we demonstrated that SO₂ is sorbed to a lesser extent when H₂O is previously sorbed on cork. To explain this decrease of the sorption capacity of SO₂ in the presence of H₂O, we suggested a competitive sorption between water and SO₂.

The aim of the present paper is to confirm that SO₂ is selectively sorbed on cork in the presence of H₂O. To that purpose, we report here a complete thermodynamic study of the cosorption of H₂O and SO₂ in the gas phase on cork by using manometry coupled with calorimetry, which is more appropriate than thermogravimetry for studying cosorption. The sorption of single components was studied first, and then the sorption of a binary mixture was realized to investigate the competitive sorption between water and sulfur dioxide and to determine the sorption selectivity and cosorption enthalpy

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as a function of the sorbed amount. Results obtained here should help to elucidate the interaction mechanisms of some wine active compounds with cork and to confirm whether the sorption on this material is or is not responsible for the decrease in SO₂ content observed during wine aging in bottle.

Materials and Methods

Materials. Raw cork stoppers, from *Quercus suber* L. in the Mora (Portugal) production area, were supplied by the Bouchons Trescases S.A. (Boulou, France). Stoppers were neither washed nor treated on surface (with paraffin or silicone) prior to use. Powder was made by grating cork stopper with a rasp. After sieving, the mean particle size was less than 500 µm. Nitrogen as well as krypton adsorptions at 77 K indicated that cork did not exhibit any specific surface area.

Experimental technique. The sorption of single components and binary mixture was studied by using a homemade manometric apparatus coupled with a heat-flow Setaram C80 differential calorimeter (Setaram, Caluire, France). This setup was connected to a HP 4890 gas-phase chromatograph (Agilent Technologies, Santa Clara, CA) equipped with a TCD detector and a Chrompack Bentone 34 packed column (Supelco, Saint-Germain-en-Laye, France). A bypass system connected to the vacuum line (turbomolecular pump) and composed of a six-way gas injection valve with sample loop allowed collection of a small amount of gas under low pressure for chromatographic analysis. This device has been described in detail in previous studies (Moise and Bellat 2005, Weber et al. 2008).

The sorption isotherms of single components were measured step-by-step by placing small successive doses of gas in contact with the sample. For each pressure step, measurement of the pressure before and after sorption allowed calculation of the amount sorbed. Two consecutive sorption isotherms were performed on the same sample (outgassing under vacuum was applied before the second sorption isotherm without changing the temperature) to determine whether chemisorption occurred on the material.

Cosorption isotherms were obtained by following the same procedure. However, in this case, in addition to measuring the pressure, the composition of the gas was also analyzed by gas chromatography before and after each sorption step. The initial molar fraction in the gas mixture was 0.67 for SO₂ and 0.33 for H₂O. The sorbed amount (n_i^s) and the molar fraction in the sorbate (x_i) were calculated for each component i by performing a mass balance in the gas phase from the total pressure (p) and the molar fraction of component i in the gas phase (y_i), measured at equilibrium. Thus, it was possible to calculate the sorption selectivity of sulfur dioxide with respect to water, as defined by the following relation:

$$\alpha_{\text{SO}_2/\text{H}_2\text{O}} = \frac{x_{\text{SO}_2} \cdot y_{\text{H}_2\text{O}}}{x_{\text{H}_2\text{O}} \cdot y_{\text{SO}_2}}$$

The mass of cork powder was ~640 mg. Before each experiment, cork powder was outgassed in situ under vacuum (10⁻⁵ hPa) at 298 K for 72 hr. For all experiments, the pressure

ranged from 0.1 hPa to a maximum of 25 hPa in order to avoid the condensation of water vapor.

Results and Discussion

Sorption of single components. Sorption isotherms of water (Figure 1) and sulfur dioxide (Figure 2) were determined and given in mmol per gram of dry cork activated under vacuum. Values are similar to those measured previously by thermogravimetry, which is a more accurate technique for studying sorption of gases on solids (Lequin et al. 2009, 2010). In both cases, the isotherms show a shape similar to the type II of the IUPAC classification (Sing et al. 1985). The same isotherm shape has been observed for sorption of water in hydrophilic polymers (Toribio et al. 2004). For H₂O,

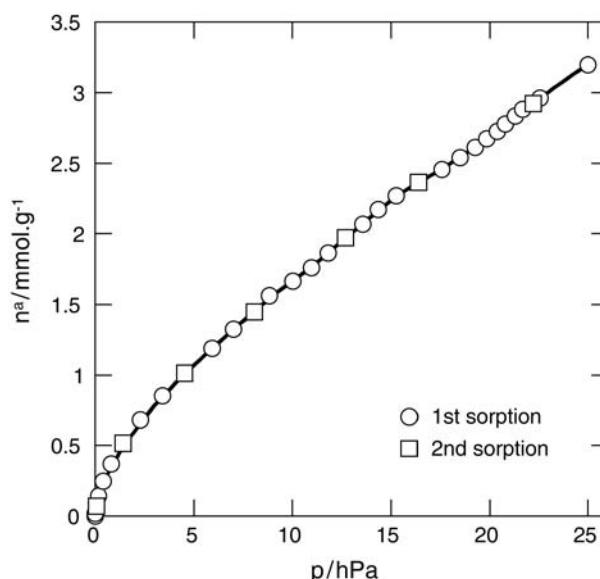


Figure 1 Sorption isotherm of water vapor (H₂O) on dry cork powder at 298 K.

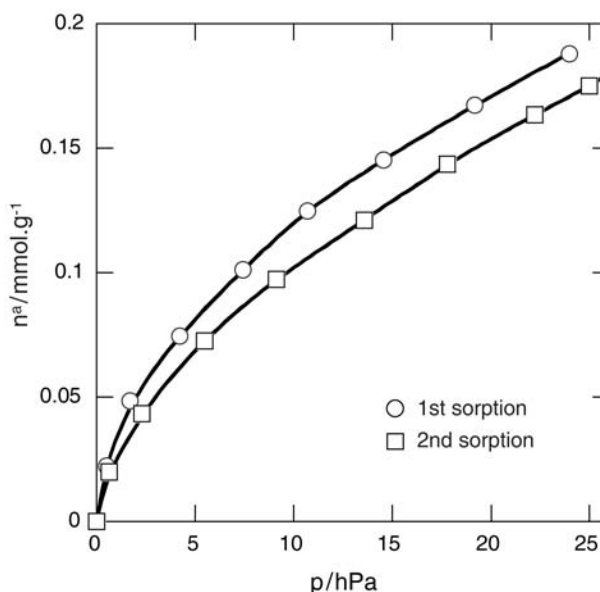


Figure 2 Sorption isotherm of sulfur dioxide (SO₂) on dry cork powder at 298 K.

first and second sorption isotherms were indistinguishable (Figure 1), indicating that no water remained sorbed after outgassing under vacuum. That was not the case with SO₂ (Figure 2), in that the second sorption was lower than the first sorption. Moreover, SO₂ was not completely removed by pumping under dynamic vacuum after the first sorption, indicating that SO₂ was chemisorbed on the surface, as was previously determined by thermogravimetry (Lequin et al. 2009). The difference between first and second sorption allowed for calculating the chemisorbed quantity, which was ~0.024 mol.g⁻¹.

It is also important to note that previous experiments performed by thermogravimetry using SO₂ or H₂O did not show much difference in sorbed quantities between massive cork slices and cork powder (Lequin et al. 2009, 2010). Thus, studying sorption on powder gives valuable results. Cork powder was used in this work to obtain more precise accuracy in the thermal transfers measured by calorimetry.

The sorption capacities and the Henry constants of sorption are reported (Table 1). Under 25 hPa, the molar sorption capacity was 17 times higher for H₂O than for SO₂. The number of sorption sites is thus very different for these two molecules. SO₂ molecules are likely chemisorbed on specific sites, which do not interact with H₂O. Henry constants are calculated from the slope of the sorption isotherms when the pressure tends to zero and from the saturated vapor pressure (p_s) of the gas at 298 K according to the relation:

$$n_{p \rightarrow 0}^a = K_H \frac{p}{p_s}$$

Such a calculation allows for comparison of the Henry constants of the two gases. Results show that K_H was approximately eight times higher for SO₂ than for H₂O, revealing a stronger sorption affinity of cork for SO₂ than for H₂O. Therefore, for sorption of the binary mixture SO₂+H₂O, we can expect that the sorption will be in favor of SO₂ at low pressure. However, as the sorption capacity of H₂O largely exceeds that of SO₂, it is possible that the sorption process becomes selective for H₂O when the pressure increases.

Calorimetric sorption enthalpies of water and sulfur dioxide individually on cork powder are given as absolute values (Table 1). These sorption enthalpies are also represented versus loading (Figure 3). For water, only values at very low loading are represented. The sorption enthalpy of water at zero loading was ~60 kJ.mol⁻¹, typical of a physisorption process. A detailed study of this sorption mechanism has been demonstrated previously (Lequin et al. 2010). For sulfur dioxide,

the sorption enthalpy at zero loading was 90 kJ.mol⁻¹ for the first sorption and did not exceed 50 kJ.mol⁻¹ for the second sorption, confirming that SO₂ was chemisorbed on the surface. Then, as loading increased, the sorption enthalpy decreased to the liquefaction enthalpy. No important sorbate-sorbate (SO₂-SO₂) interactions were observed at high loading. The SO₂ molecules sorbed on cork were likely too far apart to interact. According to calorimetric results, sorbate-sorbent interactions were stronger for SO₂ than for H₂O at low loading, whereas sorbate-sorbate interactions become predominant for H₂O at high loading (Lequin et al. 2010), reinforcing the conclusion deduced from the Henry constants. In the case of the cosorption of SO₂ and H₂O, we can expect to have a sorption process selective for SO₂ at low loading and for H₂O at high loading.

Sorption of binary mixture. Total and partial sorption isotherms of sulfur dioxide and water are shown (Figure 4). The major component in the sorbed phase was SO₂. The composition of the sorbed phase was not very different than the composition of the initial gas mixture. However, that does not indicate that the sorption process is obviously in favor of SO₂. As the initial mixture is very rich in this compound, it is not abnormal to retrieve it in majority in the sorbed phase. Only the sorption selectivity, which takes into account the molar fractions of each component in the sorbed and gas phases, can give information on the preferential sorption of SO₂ or H₂O.

The dependence of the total loading on the sorption selectivity of SO₂ with respect to H₂O ($\alpha_{\text{SO}_2/\text{H}_2\text{O}}$) is shown (Figure 5), and the curve exhibits three distinct regions, or steps. At the beginning of the sorption, α is >1 and increases with loading to reach a maximal value of 2.4 at a total loading of 0.033 mmol.g⁻¹. The partial amount of SO₂ sorbed at this total loading is equal to 0.028 mmol.g⁻¹, which is very close to the amount of the single SO₂ chemisorbed on cork. Moreover, the

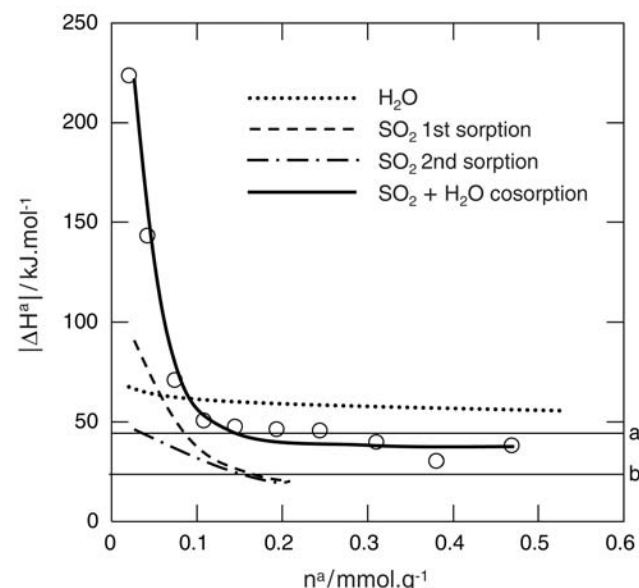


Figure 3 Cosorption enthalpy (absolute value) of H₂O and SO₂ on cork powder at 298 K versus loading (open symbols). Initial composition of the mixture: 0.67 SO₂ + 0.33 H₂O. Sorption enthalpy of single components are also reported (a: liquefaction enthalpy of water = 44 kJ.mol⁻¹; b: liquefaction enthalpy of SO₂ = 22.9 kJ.mol⁻¹).

Table 1 Henry constants, sorption capacities, and sorption enthalpies of SO₂ and H₂O on dry cork at 298 K.

	SO ₂	H ₂ O
K_H (mmol.g ⁻¹)	160	19
n_{\max}^a at 25 hPa (mmol.g ⁻¹)	0.19	3.2
$ \Delta H_{n^a \rightarrow 0}^a $ (kJ.mol ⁻¹)	>90 (1 st sorption) ~50 (2 nd sorption)	~60

cosorption enthalpy is very high in this region, with values decreasing from 225 to 100 kJ.mol⁻¹ (Figure 3). These energies are typical of chemical bonds. Therefore, this first cosorption step can be unambiguously attributed to the selective chemisorption of SO₂. For loading between 0.033 and 0.15 mmol.g⁻¹, the sorption selectivity sharply decreases; above 0.1 mmol.g⁻¹, the selectivity becomes less than 1. The cosorption heat continues to decrease to the liquefaction enthalpy of water (44 kJ.mol⁻¹). In this second cosorption step, all chemisorption sites for SO₂ are saturated and the cosorption process, which is now only a physisorption of SO₂ and H₂O, turns in favor

of the sorption of H₂O. Above 0.15 mmol.g⁻¹, the sorption selectivity still decreases with loading, but to a lesser extent (Figure 5). The selectivity tends to ~0.15 at high loading. In this range, the cosorption heat remains constant and equal to the liquefaction enthalpy of water (Figure 3), suggesting that in this third cosorption step only water molecules are sorbed on cork. There is a significant change in the slopes of total and partial sorption isotherms above this total loading of 0.15 mmol.g⁻¹ (Figure 4).

In a recent work devoted to the sorption of SO₂ on partially hydrated cork studied by calorimetry (Lequin et al. 2009), we obtained, for the sorption enthalpy of SO₂ as a function of the loading, a bell curve shape, as for the selectivity shown in Figure 5. At that time, we suspected that the increase of the sorption enthalpy of SO₂ at low loading was due to the chemisorption of SO₂ on cork. The results obtained here unambiguously confirm this assumption.

Conclusion

This work reports a thermodynamic study of cosorption of water and sulfur dioxide on raw cork at 298 K by using an original technique that combines manometry and calorimetry. Sorption of single components confirms the conclusions from previous thermogravimetric studies: SO₂ is chemisorbed on cork whereas H₂O is only physisorbed. Nevertheless, the amounts sorbed are higher for H₂O than for SO₂. Moreover, we have considered in our previous articles that SO₂ and H₂O are adsorbed on cork (Lequin et al. 2009, 2010). In light of the present results, the term adsorption now seems inappropriate. Cork exhibits neither micro- and mesoporosity nor specific surface area, measurable by nitrogen or krypton adsorption and the interaction of SO₂ and H₂O with cork is more like a gas solubility in a polymer rather than a gas adsorption on a solid surface. Thus, the interaction process of the molecules with cork is more likely absorption rather than adsorption, even though the interaction of the first molecules (probably on specific sites located on the external surface of cork) is very similar to an adsorption process. However, without solid experimental proof, we prefer now to label this kind of interaction as *sorption*.

Concerning the sorption of the binary mixture, the cosorption process is firstly in favor of SO₂. As this compound is chemisorbed, it strongly interacts with cork, compared to water. After all chemisorption sites are saturated with SO₂, the cosorption process becomes selective to H₂O. This study shows that, even in the presence of water, the partial amount of SO₂ sorbed on cork is very low.

In terms of mean sulfur dioxide in a wine bottle, free SO₂ may range from 20 to 30 mg.L⁻¹, and total SO₂ may be ~100 mg.L⁻¹. The Henry constant for the equilibrium of SO₂ between the gas phase and the liquid phase is equal to 0.768 mg.L⁻¹.Pa⁻¹ at 298 K. Therefore, considering the mean free SO₂ concentration, the partial pressure of SO₂ in the headspace of a wine bottle is 0.33 hPa. Under this pressure, the amount of SO₂ sorbed by cork partially hydrated (sorption isotherm given in Lequin et al. 2009) is ~0.1 mg.g⁻¹. In the worst-case scenario, the full cork stopper—not simply the

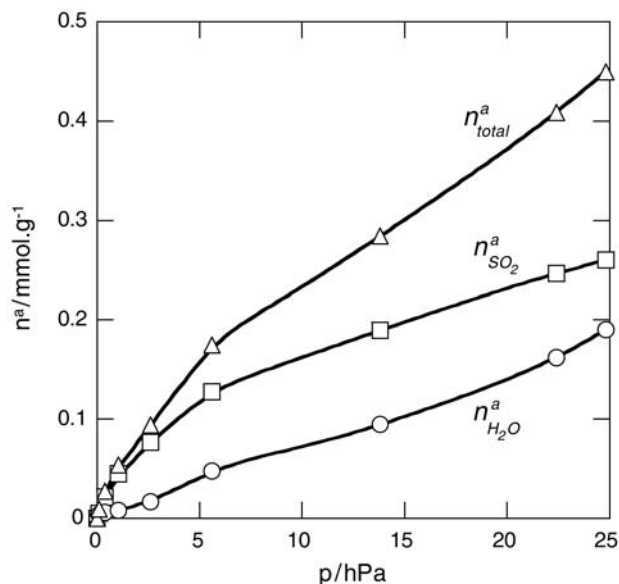


Figure 4 Total and partial sorption isotherms of water and sulfur dioxide for the binary mixture composed of 0.33 molar water and 0.67 molar sulfur dioxide.

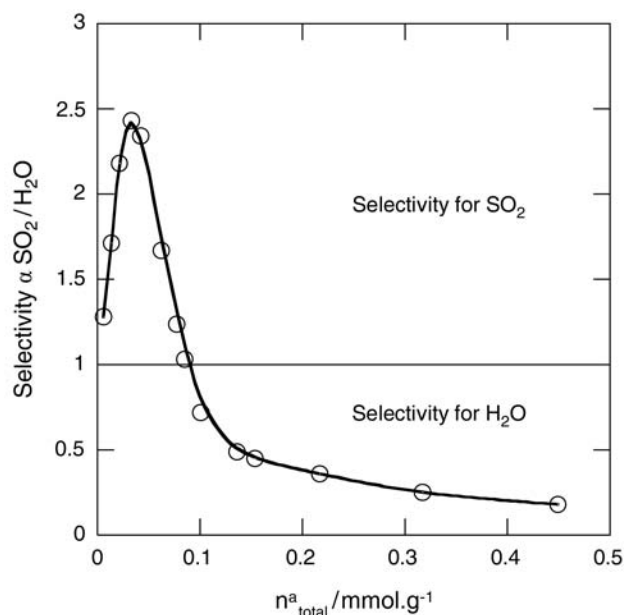


Figure 5 Dependence of the total loading on the sorption selectivity of SO₂ with respect to H₂O at 298 K. Initial molar composition of the mixture: 0.67 SO₂ + 0.33 H₂O.

surface in contact with wine—will contribute to the sorption of SO₂. The mass of SO₂ sorbed by a standard cork stopper weighing ~3 g would be equal to 0.3 mg, representing ~1.6% of the free SO₂ in a bottle of wine. Consequently, the decrease in the SO₂ content observed by several authors (Keenan et al. 1999, Brajkovich et al. 2005, Godden et al. 2001, 2005, Skouroumounis et al. 2005, Kwiatkowski et al. 2007) during aging of wine stored in bottle cannot be attributed to its sorption on cork. For some of these studies, the sharp decrease in SO₂ concentration in wine during the first three months of storage can be attributed to the presence of oxygen in the bottle headspace at bottling (if air has not been withdrawn) and its subsequent dissolution in wine and reaction with SO₂. During that time it can also be due to the release of oxygen initially present in the closure (Brajkovich et al. 2005, Lopes et al. 2007). Then the more gradual loss of SO₂ observed in subsequent months in those studies can unambiguously be attributed to mass transfer mechanisms of oxygen or SO₂ through the closure. According to the chemical potential gradient of these diffusing molecules between the two sides of the closure, oxygen can diffuse from the outside to the inside of the bottle, while SO₂ diffusion will occur in the opposite way. Therefore, the study of this kinetic aspect would be of relevant interest.

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