

Adsorption equilibria of sulphur dioxide on cork

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Abstract

We report for the first time a study on the adsorption of sulphur dioxide in the gas phase on crude cork. The understanding of the interaction of this sulphur compound with cork is of a relevant interest because this biomaterial is largely used as stopper in the conservation of wine in bottles. In this case, a close contact between sulphur dioxide and cork occurs either by the liquid phase or by the vapour phase from the headspace. So, it is crucial to know the behaviour of cork with SO₂ from a thermodynamic point of view. Adsorption of gaseous sulphur dioxide has been studied by thermogravimetry and calorimetry at 298 K and for pressures ranging from 10⁻⁵ to 40 hPa on cork sample previously outgassed under vacuum. Amounts of SO₂ adsorbed on dry cork are rather low. They correspond to negligible quantities when extrapolated to an entire cork stopper. The presence of a hysteresis loop on the isotherm and the high adsorption heats measured at low loading (around 100 kJ·mol⁻¹) indicate that a reactive adsorption occurs between SO₂ and cork. Nevertheless the chemisorbed amount is very low and the main adsorption mechanism for SO₂ on cork corresponds to a physisorption process. Adsorption of sulphur dioxide on partially hydrated cork has also been studied. When the water content in cork is of 5 wt %, the amount of SO₂ adsorbed is divided by a factor 3. Thus, water does not enhance the adsorption rate for sulphur dioxide, but yields to a decrease of the SO₂ adsorption activity onto cork, probably because of competitive adsorption mechanisms.

Keywords: cork, wine, sulphur dioxide, adsorption, thermogravimetry, calorimetry.

1. Introduction

Sulphur dioxide (SO₂) represents an anthropogenic global atmospheric pollutant produced by various industrial processes. It is mainly generated by the combustion of fossil fuels and by incineration of solid waste, which contain sulphur compounds. As a precursor to sulphuric acid (H₂SO₄), formed by atmospheric oxidation of sulphur dioxide in the presence of water, it can then lead to acid rains, sulphuric acid being extremely soluble in water. Amazingly, sulphur dioxide is also widely used as preservative and antioxidant in foods, in particular in winemaking. In this empiric use, reported since several centuries, it generally serves for both its antiseptic properties and its antioxidant effects to protect musts and wines at pressing and bottling, in concentrations from several tens to hundreds milligrams per litre.

The study of sulphur dioxide adsorption by solid adsorbents has been firstly reported by Shiels on activated carbons (Shiels, 1929), which have been proved to be excellent absorbents for SO₂ (Arunov et al., 1977, Zhang et al., 2007). This adsorption process has also been studied for zeolites, which exhibit good potentiality as adsorbents for sulphur dioxide due to their high microporosity (Garcia-Martinez et al., 2002, Kopac, 1999). Adsorption of SO₂ by activated carbons has also been shown to be mainly governed by the microporosity of the adsorbent (Bagreev et al., 2002, DeBarr et al., 1997). The adsorption phenomenon of sulphur dioxide on these adsorbents may be of two types: either physisorption by weak bonds (Arunov et al., 1977), such as hydrogen bonds or ion-dipole bonds (interaction SO₂-Na⁺) in zeolites for example (Garcia-Martinez et al., 2002), or/and chemisorption by strong bonds (Arunov et al., 1977, Furmaniak et al., 2006, Moreno-Castilla et al., 1993). Therefore the chemical nature and the structure of the surface layer are both determining factors for the adsorption process of SO₂, through the adsorption ability of the adsorbent and the accessibility of the adsorbate for the adsorption sites of the adsorbent. In particular, certain surface oxygen groups, such as pyrone structures, could play an important role by increasing the surface basicity of the adsorbents (Kisamori et al., 1994, Moreno-Castilla et al., 1993). Oxidative adsorption in the presence of oxygen and water can

also lead to the formation of new adsorbed chemical species derived from SO₂, such as SO₃ and H₂SO₄ (Arunov et al., 1977, Bagreev et al., 2002, Furmaniak et al., 2006, Kisamori et al., 1994, Zhang et al., 2007).

Cork, from *Quercus suber L.*, displays a good impermeability to liquids and gases and is traditionally used as stopper for closing wine bottles, in which SO₂ is present (Karbowiak et al., 2009). The chemical composition of cork as described in literature remains relatively variable and can be found different within the tree and between trees (Pereira, 1988). Cork is mainly constituted by suberin (33-50% w/w), lignin (13-29%) and polysaccharides which are cellulose and hemicellulose (6-25%). Lignin is thought to be the main constituent of the thin internal primary cork cell wall, which is surrounded by alternating suberin and wax lamella in the thick secondary wall, which is in turn contained by the thin tertiary wall composed of polysaccharides (Silva et al., 2005). It contains also smaller percentages of waxes (2-8%), tannins (6-7%), extractable (8-24%), ash (2-3%) and others (6-7%) (Silva et al., 2005). The chemical structure of suberin and lignin in cork has not yet been fully elucidated. Suberin is thought to be a macromolecular network of aliphatic polyesters, with various long-chain fatty acids and phenolic moieties, these two domains being spatially distinct (Cordeiro et al., 1998). Due to its specific physical and mechanical properties (Gibson et al., 1981), cork biomaterial also recovers various other application fields. These products made of cork granules, or waste cork from the stopper industry, can be used in particular in civil construction as floor and wall covering or as insulation corkboard for thermal insulation, acoustical absorption and vibration insulation (Silva et al., 2005). In addition, adsorption properties of cork begin also to be considered. Since recently, this aspect is mostly studied from the point of view of the use of cork powder waste as a biosorbent of pollutants from wastewater as it can be easily incinerated afterwards. Moreover, it can be physically or chemically activated in order to obtain activated carbons with molecular sieve properties (Carvalho et al., 2006, Mourao et al., 2006). Cork powder waste has been shown to adsorb various metallic cations from the liquid phase, such as chromium (Cr³⁺) (Machado et al., 2002), copper (Cu²⁺) (Chubar et al., 2003, Villaescusa et al., 2002), nickel (Ni²⁺) (Chubar et al., 2003, Villaescusa et al., 2002), zinc (Zn²⁺) (Chubar et al., 2003), biphentrin

(a pyrethroid) (Domingues et al., 2005), and phenolic compounds (Mourao et al., 2006). Cork can also adsorb various volatile organic compounds (Carvalho et al., 2006). 2,4,6-trichloroanisole, a wine contaminant known for cork taste, has been shown to be easily absorbed by cork stopper via the vapour phase, mainly confined in the outer 2 mm of the cork cylinder with also some migration in the inside after 24 hours of exposure to this contaminant (Barker et al., 2001).

This natural organic material therefore displays rather good adsorption capacities for various adsorbates. The adsorption capacity of cork for sulphur dioxide has however never been studied, and could be of interest both for its oenological use as stopper and its potential application as biosorbent. The present study therefore focuses for the first time on the adsorption of gaseous sulphur dioxide by cork at the equilibrium. A special attention has been paid on the effect of the hydration degree of cork on the adsorption properties of gaseous sulphur dioxide.

2. Materials and methods

2.1. Material

Raw cork planks, from *Quercus suber L.* oak trees in the Mora (Portugal) production area, were supplied by the society Bouchons Trescases S.A. (Boulou, France). Planks were neither washed nor surface treated (with paraffin or silicone) prior to use. Uniform cork pieces in plate geometry, 35 mm long, 10 mm wide and 1 mm thick for gravimetric study of SO₂ in gas phase, were manually cut from the planks. In this geometry the axial plane has the largest contact area with wine. Cork powder with a granulometry $\leq 500 \mu\text{m}$ has also been used.

Sulphur dioxide has been used in the gas state (purity 99.9 %, molar mass 64.1 g·mol⁻¹, Air Liquide, France).

2.2. Scanning electronic microscopy

Scanning Electronic Microscopy (SEM) observations of the cellular cork structure has been performed on a JEOL-JSM, 6400 F, with an acceleration voltage of 15 kV and a preliminary carbon metallization of cork plate samples.

2.3. Thermogravimetry

Adsorption of gaseous SO₂ on natural cork was investigated by thermogravimetry with a home-made McBain balance, under controlled conditions of temperature (298 K) and H₂O or SO₂ gas pressure (controlled with a MKS Baratron absolute pressure transducer). In this closed glass system, the cork is hanged to a quartz helicoidal spring, the elongation of which gives a mass variation of the sample as a function of the gas pressure at equilibrium. The experimental accuracy is ± 0.01 mg for the mass of adsorbate, ± 0.5 K for the temperature, and ± 1 Pa for the pressure. The adsorption-desorption isotherm is measured step by step using a static method. Once a plateau of mass is recorded, the next equilibrium is reached by changing the pressure of the gaseous adsorbate. Two different geometries of the sample have

been studied: cork plate and cork powder. The mass of the cork sample is around 40 mg. Prior to each experiment, the cork sample is outgassed under vacuum (10^{-5} hPa) at 298 K for 24 h.

Adsorption of gaseous sulphur dioxide was studied for pressures ranging from 10^{-5} to 40 hPa and at 298 K. This corresponds to the relative pressure range: $0 \leq p/p_s \leq 0.01$, the saturated vapour pressure of SO_2 (p_s) being equal to 4000 hPa at 298 K. So, studied pressure range covers the partial pressures of SO_2 found in the headspace of a bottle of wine.

Pre-hydration of the cork sample before SO_2 adsorption has also been performed by submitting the sample at 298 K to a saturated vapour pressure of water equal to 23 hPa. Under this pressure, the water content in cork at equilibrium was of 5 wt %. Then, the adsorption of the gaseous sulphur compound was carried out by successive increments of the partial pressure of SO_2 in the balance. For each partial pressure, the amount of SO_2 adsorbed was measured considering that the preadsorbed water amount is constant (no desorption of water).

2.4. Differential calorimetry coupled with manometry

Adsorption heats of SO_2 on dry cork or hydrated cork were measured with a differential calorimeter (Thian-Calvet, Setaram C80) coupled with manometry. This device has been previously described in detail in other studies (Moise and Bellat, 2005, Simonot-Grange et al., 1997, Weber et al., 2008). It allows measuring the molar adsorption enthalpy $\Delta H^a(m^a)$ of water, so called the adsorption heat Q^a as a function of the adsorbed amount m^a . Adsorption was realised at 298 K for cork powder samples of about 640 mg, previously outgassed under vacuum at 10^{-5} hPa for 72 h. The SO_2 pressures ranged from 10^{-5} hPa to 40 hPa. For hydrated cork, the same protocol of hydration as previously described for thermogravimetry was followed. After outgassing under vacuum at 298 K, cork was submitted to a saturated water vapour pressure of 23 hPa. The water vapour adsorption equilibrium was reached after 12 h. Then, SO_2 adsorption is performed on this hydrated cork sample in order to measure the adsorption heats.

3. Results and Discussion

3.1. Physico-chemical characterization of cork material

The physical structure of cork material displays an orientation defined along three main directions: axial (vertical, parallel to the centre of the tree), radial (horizontal) and tangential (perpendicular to the axial-radial plane). Cork stoppers are punched out along the axial dimension (Figure 1). Cork pieces used in this study mostly correspond to the plane A (axial), which is in contact with the wine (horizontal storage) or the headspace of the wine bottle (vertical storage). SEM observations show that the radial structure of cork is a homogeneous tissue composed of thin-walled alveoli of hexagonal sections arranged in a honeycomb type pattern with no intercellular spaces (Figure 1). In axial and tangential planes, the cells appear as rectangular prisms, stacked base to base, parallel to the radial axis. It is interesting to note that the mechanical characteristics of cork are roughly isotropic in the plane perpendicular to the radial axis, as dictated by its special shape and cell structure (Gibson et al., 1981). It is, however, anisotropic in the two other planes, as also revealed by compression studies (Rosa and Fortes, 1988). Average cork cells are 45 μm tall with an hexagonal face of 20 μm and with a thickness of 1 μm (Gibson et al., 1981). Cork always contains varying numbers of lenticular channels running radially (defining the quality grading), which are hollow and approximately cylindrical, and constitute the macroscopic porosity (diameters higher than 50 nm, accordingly to IUPAC (Sing et al., 1985)). The existence of a small microporosity in cork (diameters lower than 2 nm, accordingly to IUPAC (Sing et al., 1985)), with a volume of micropores of $0,026 \text{ cm}^3 \cdot \text{g}^{-1}$, has been pointed out by Hanzlik *et al.* (2004) by adsorption of carbon dioxide in the pressure range 100-1500 hPa at a temperature of 298 K. However, for our sample, neither nitrogen adsorption (1-1000 hPa at 77 K) nor krypton adsorption (1-3 hPa at 77 K) is detectable. This could indicate that there is probably no microporosity in the material, or that pores could not be accessible for nitrogen and krypton molecules if cell contraction occurs under

vacuum outgassing and low temperature. From nitrogen adsorption manometry the density of cork can be estimated around $125 \text{ kg}\cdot\text{m}^{-3}$, therefore a very low density material.

3.2. Adsorption isotherm of sulphur dioxide by dry cork

The adsorption-desorption isotherm of sulphur dioxide by dry cork (plate geometry) at 298 K is displayed in Figure 2. The adsorbed amount is given in g per 100 g (wt %) of cork activated under vacuum. The first adsorption branch has been obtained from the outgassed sample and the second desorption branch from the sample in equilibrium under 40 hPa of SO_2 .

For this pressure range, which corresponds only to very low relative pressures of SO_2 ($0 < p/p_s < 0.01$), the adsorption capacity of cork is low: 1.2 wt % under 40 hPa. This is extremely low compared to that one of zeolite which can reach 20 wt % for example (Marcu and Sandulescu, 2004). The amount of SO_2 adsorbed under the pressure of 5 hPa is around 0.5 % (Figure 2). This pressure corresponds to the partial pressure of SO_2 in the headspace of a bottle of wine, calculated with Henry's law by taking, for the concentration of SO_2 in wine, the maximal value of $400 \text{ mg}\cdot\text{L}^{-1}$. When extrapolated to the weight of a standard natural cork closure, the mass of SO_2 adsorbed on cork stopper is equal to 15 mg. This represents less than 5 % of the total SO_2 content in a bottle of wine. Therefore the amount of sulphur dioxide trapped by a cork stopper is negligible.

The Henry constant of adsorption, determined from the slope of the adsorption branch at low pressure is equal to $1.6 \times 10^{-3} \text{ g}\cdot\text{g}^{-1}\cdot\text{hPa}^{-1}$. This value is largely lower than that one observed on zeolite ($0.03 \text{ g}\cdot\text{g}^{-1}\cdot\text{hPa}^{-1}$), microporous adsorbent which is known to exhibit a rather strong adsorption affinity of SO_2 owing to the specific interactions between the polar sulphur molecules and the Lewis and Brønsted acidic sites present at the surface of this material (Marcu and Sandulescu, 2004). But this value is of the same order of magnitude as that one found on activated carbon ($4 \times 10^{-3} \text{ g}\cdot\text{g}^{-1}\cdot\text{hPa}^{-1}$) (Arunov et al., 1977). This weaker affinity of cork for sulphur dioxide is related to the chemical properties of its surface. Cork is composed of organic matter with little strong adsorption sites as localized positive charges (cationic

sites) or acidic sites (hydroxyl groups) present in zeolites. So, one can expect that sulphur dioxide is essentially adsorbed on cork under the effect of dispersion forces. However, as outlined above, the adsorption isotherm of SO₂ on outgassed cork exhibits a hysteresis loop between adsorption and desorption. Desorption levels for a given SO₂ pressure are systematically slightly higher than adsorption levels. Such hysteresis phenomena have already been observed for other adsorbate / adsorbent systems, like n-butane / activated carbons or NH₃, CH₃OH, pyridine / montmorillonite (Gregg and Sing, 1982). This has been attributed to a swelling of the material. For cork, this could similarly be due to the deformation of the structure of this non-rigid material during the adsorption process of the first SO₂ molecules, which consequently renders accessible other adsorption sites for other SO₂ molecules. Then, during desorption process, these last SO₂ molecules could be entrapped in the cork structure, when the first adsorbed molecules are released. Nevertheless, it may be noticed that the desorption process of SO₂ is not complete (Figure 2). It remains sulphur dioxide adsorbed on cork (about 0.35 %) even after pumping under vacuum for several days. A reactive adsorption of a small amount of SO₂ with the cork surface is therefore suspected. It is well known that chemisorption also creates hysteresis on adsorption isotherm. The adsorbed amount of SO₂ being extremely low, the effect of swelling is probably negligible. So, the hysteresis phenomenon observed on the isotherm is rather due to chemisorption than swelling.

The adsorption-desorption isotherm of sulphur dioxide by dry cork has also been performed on a powder sample (~25 mg). Results are displayed in Figure 3. Compared to the previous adsorption isotherm on the same material in plate geometry, the amounts of SO₂ adsorbed at equilibrium are systematically higher in the whole pressure range. Nevertheless, the adsorption capacity still remains at a very low level (the maximum being around 1.7 wt % for 40 hPa). The isotherm displays similar adsorption and desorption branches, with the same hysteresis phenomenon and a constant non-desorbed fraction of SO₂ molecules. Cork powder has a granulometry lower than 500 µm and therefore exhibits a larger developed surface area for SO₂ adsorption. This could be in favour of a surface adsorption

mechanism rather than in volume. The adsorption mechanism of SO₂ on cork is similar to that one on non porous or macroporous solid.

3.3. Adsorption heat of sulphur dioxide by dry cork

The dependence of the loading on the adsorption heats of SO₂ (given in absolute value) on dry cork is shown in Figure 4. For the first adsorption, the heat of adsorption at low filling is high, around 100 kJ·mol⁻¹. This value is unusually high for an adsorption process which is supposed to occur on a hydrophobic plane surface (Gomes et al., 1993). Then, the adsorption heat sharply decreased as the filling increases. Above 1 wt % of adsorbed SO₂, it finally tends to the enthalpy of liquefaction of SO₂ which is equal to 22.9 kJ·mol⁻¹ (2005), as expected for a physisorption process. Such high adsorption heats at low filling has already been reported for SO₂: ~63 kJ·mol⁻¹ for adsorption on graphitised carbon blacks near 0 K (Beebe and Dell, 1955), ~100 kJ·mol⁻¹ for adsorption on carbon blacks at 323 K (Murphy et al., 1977) and up to ~500 kJ·mol⁻¹ for adsorption on Chrysotile at 323 K (Murphy and Ross, 1977). These high energies are typical of chemical bonds. A second adsorption has also been performed after outgassing the sample under vacuum at 298 K during 72 hours in order to evacuate all the molecules physisorbed at the surface. In this case, the adsorption heat at low filling becomes half-reduced, around 50 kJ·mol⁻¹, a value which is usually observed in physical adsorption. These results clearly show that the first SO₂ molecules in contact with cork strongly react with the surface. It brings additional arguments in favour of a chemisorption mechanism for the first adsorbed molecules. Thus it appears that a small fraction of SO₂ molecules involves high energy binding with a few specific adsorption sites on the cork surface. At this stage of our study, it is not possible to identify what are the adsorption sites at the cork surface. From the data of the literature, the physisorption sites could be carboxylic groups or OH terminals^{4, 31}. Regarding the reactive sites, a small fraction of SO₂ could also react with the hydroxyls to form HSO₃⁻ as chemisorbed specie. Unless, SO₂ could be bound to the

organic surface through C-O and/or C-S bonds, as it has been observed by Pliego *et al.* (2005) on graphite surface.

3.4. Molar entropy of the adsorbed phase

The molar entropy of the adsorbate is an interesting value which gives information about the physical state of the matter adsorbed at the surface. Let us consider the physisorption equilibrium gas \leftrightarrow adsorbate, the molar entropy of the adsorbed phase is given by the following relation:

$$S^a(m^a) = \Delta S^a(m^a) + S^0_{(g)} \quad \text{Equation 1}$$

with: $S^a(m^a)$ = molar entropy of the adsorbed phase at a given loading m^a ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

$\Delta S^a(m^a)$ = molar entropy of adsorption ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

$S^0_{(g)}$ = gas standard molar entropy = $248 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for sulphur dioxide at 298 K (2005).

$\Delta S^a(m^a)$ is determined, from the calorimetric adsorption heat (equivalent to the isosteric heat in our experimental conditions) and the adsorption isotherm with the following equation (Bellat and Simonot-Grange, 1995) at constant m^a :

$$\Delta S^a(m^a) = (\Delta H^a(m^a)/T) - (R \cdot \ln(p/p^0)_{m^a}) \quad \text{Equation 2}$$

with: $\Delta H^a(m^a)$ = molar enthalpy of adsorption ($\text{J}\cdot\text{mol}^{-1}$)

T = adsorption temperature (K)

R = ideal gas constant ($8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

p = equilibrium pressure at the loading m^a (Pa)

p^0 = standard pressure (10^5 Pa)

The evolution of the molar entropy (S^a) of SO_2 adsorbed on cork as a function of the loading at 298 K is displayed in Figure 5. Standard molar entropy values for gas, liquid and solid SO_2 at 298 K are also reported. These data have been obtained from the software PhysProps[®] (G&P Engineering Software). The results obtained from the first adsorption show very low molar entropy of SO_2 at low filling, close to zero. Such values are too much low for a physisorption phenomenon alone. For physisorption, molar

entropy usually tends at minimum to the solid entropy when the adsorbate is highly confined, as for example in the case of the adsorption of mercaptan or saturated and aromatic hydrocarbons in zeolites (Bellat and Simonot-Grange, 1995, Weber et al., 2008). This could be explained by chemisorption of the first SO₂ adsorbed molecules on cork. In that case, the molar entropy calculated by equation 2, has no physical meaning, because a chemisorption phenomenon adds to SO₂ physisorption. On the other hand, the molar entropy of SO₂ calculated for the second adsorption ranges between those of solid and gas. This really corresponds to a physisorption process. At low filling, the molar entropy is close to that one of the solid. The SO₂ molecules are “frozen” on their adsorption sites. On the contrary, at higher filling, their molar entropy lies between that ones of liquid and gas, indicating that the sulphur molecules have much more degrees of freedom at the surface. If at low covering the adsorption process seems rather localized, it is replaced by a mobile adsorption process at higher covering.

3.5. Effect of cork hydration on sulphur dioxide adsorption

Cork, in its common use of closure, is not only in contact with sulphur dioxide but with a lot of volatile organic molecules. The headspace of a wine bottle contains mainly water vapour, but also many other organic vapours, such as ethanol or aroma compounds in equilibrium with the liquid phase. Therefore, the adsorption process of gaseous SO₂ can also be dependent on the adsorption of other chemical species. We focus in this part to the effect of the presence of water previously adsorbed on cork.

The adsorption isotherm of SO₂ on cork containing 5 wt % of water is displayed in Figure 6. Adsorption isotherm on dry cork is also reported for comparison. The isotherm is significantly modified when SO₂ is adsorbed on hydrated cork, the adsorption capacity being divided by a factor 3. At first glance this seems surprising because sulphur dioxide is highly soluble in water (Sander, 1999). Indeed, it was expected that because of its high solubility sulphur dioxide could be adsorbed in higher quantities when cork is hydrated or that adsorbed water molecules could be active sites for SO₂ adsorption by

formation of hydrogen bonds with SO₂ molecules. Being in absence of oxygen, any reaction of oxidation of SO₂ as SO₃ and hydration of SO₃ as H₂SO₄, as observed on activated carbons, can be excluded (Arunov et al., 1977, Bagreev et al., 2002, Furmaniak et al., 2006, Kisamori et al., 1994, Zhang et al., 2007). Therefore, we suspect that the decrease of the adsorption capacity of SO₂ in the presence of water is the result of a competitive adsorption between water and sulphur dioxide. After preadsorption of water, a lot of sites could not directly interact with SO₂ because already occupied by water molecules. Our calorimetric measurements seem to support this hypothesis. Figure 7 shows the adsorption heat of SO₂ on hydrated cork powder, measured in a larger pressure range than for dry cork (up to 60 hPa). It may be noted that the shape of the calorimetric curve is very different in the presence of preadsorbed water. At zero loading, the adsorption heat is largely lower than that one observed on dry cork (60 against 100 kJ·mol⁻¹). Then the adsorption heat increases with the loading to reach a maximal value around 110 kJ·mol⁻¹, before to decrease sharply to about 50 kJ·mol⁻¹. It is worthy to point out that the maximal value of the adsorption heat is observed at the filling of 0.35 wt %, which is exactly the value of the amount of SO₂ chemisorbed on the surface, as observed by thermogravimetry (Figure 2). So, it is tempting to attribute the ascending part of the calorimetric curve to the chemisorption of SO₂ on sites previously occupied by water molecules. The heat involved would correspond on the one side to the exothermic chemisorption of SO₂ and on the other side to the endothermic desorption of water. This would explain why the resulted adsorption heats are lower than on dry cork. It is difficult to elucidate the reason why the adsorption heat increases in this range of loading. This could be due to adsorbate-adsorbate interactions especially between water and sulphur dioxide which are certainly engaged in hydrogen bonds. The descending part of the calorimetric curve would correspond to the physisorption of SO₂ on sites probably free of water once the chemisorption sites are completely saturated. However, this remains a hypothesis. No solid experimental evidence allows us to confirm it and this interpretation must be considered with precaution.

4. Conclusion

For the first time the adsorption of sulphur dioxide on cork has been studied in the gas phase by thermogravimetry and calorimetry. The adsorption capacity of SO_2 has been determined with accuracy at 298 K and for pressures up to 40 hPa. The adsorption capacity of sulphur dioxide on cork is rather low. Thus, it has been possible to show that the amount of SO_2 that can be trapped by a standard cork stopper from the headspace of the bottle wine is negligible. Therefore, thermodynamics of adsorption on cork cannot account for the decrease of SO_2 content in wine during aging. We clearly indicate on the adsorption isotherm a hysteresis loop in desorption which has been attributed to a reactive adsorption of SO_2 on cork. A hysteresis in desorption due to a swelling of the material is not excluded but unlikely considering the low adsorbed amount. Nevertheless, the amount of sulphur dioxide chemisorbed on the surface is low and one can consider that the interaction of SO_2 with cork is mainly governed by a physisorption process. Surprisingly, in the presence of water preadsorbed on cork, the adsorption capacity of SO_2 is divided by a factor 3. This decrease in the adsorption capacity would result from the occupancy of the adsorption sites by water molecules. The only sites accessible to SO_2 would be the ones where SO_2 is chemisorbed. It is only on these strong specific sites that SO_2 could find the energy required for displacing the water previously adsorbed on them. Thus, competitive adsorption mechanisms between water and SO_2 could occur on cork. From a practical point of view, that could also mean that many other polar molecules are susceptible to adsorb selectively with SO_2 on cork. In that case, the real adsorption capacities could be very different than that ones determined from the adsorption of single components on cork. So, thermodynamics of coadsorption of SO_2 with other molecules, in particular with water, must be more developed on this system. Moreover, the adsorption of SO_2 has been studied only on crude cork. It will be of a great interest to study the effects of various chemical treatments of cork, such as washing and paraffining, on its adsorption properties. Study of adsorption and coadsorption of various compounds on crude and pre-treated cork is in progress.

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