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Dielectric method for the determination of a_w

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Abstract

The measurement of a specific surface area with water vapour by the classical methods of sorption always proceeds by the conditioning of the material under constant P/P_0 of the given vapour. This makes the method very slow, typically lasting a few days. Dielectric spectroscopy in the microwave domain, in which the relaxation of free water is strongly discriminated from that of bound water, allows the quantification of the adsorption and desorption of water vapour on the surface of solid materials. In this paper we present a new dielectric methodology, using a special resonant cavity, for simultaneously obtaining the dielectric parameters and the weight losses of hydrated material under test. A theoretical approach was developed to calculate (during desorption or adsorption), the value of water activity a_w. For that, a resonant cavity was projected and tested to allow calculation of the specific surface area with water vapour of a paper sheet, using the BET model.

Keywords: Ad/desorption curves; Resonant cavity; Microwaves; Water activity

1. Introduction

Broad band dielectric spectrometry shows that water possesses three domains of relaxation, reported by Hasted (1973): solid water (ice), which relaxes in the kHz region, bound water, b_w, relaxing around MHz and free water, f_w, about 20 GHz.

In the microwave domain (without conductivity) the ratio $\varepsilon'_{fw}/\varepsilon'_{bw}$, usually takes values between 1 and 10000 in hydrated materials, which shows that the dielectric measurement allows a good discrimination between free and bound water.

The work of Le Bot (1957) at a fixed frequency, 9.4 GHz, on montmorillonites, as dehydration proceeds, shows that the dielectric loss reaches a maximum, and its amplitude decreases and is displaced towards high temperatures. The P_0/P versus $\log(T_{max})$ shows a break point corresponding to a transition from free to bound water. The work of Abadie, Charbonnière, Gidel, Girard, and Guilbot (1957), at fixed temperatures, on starches from MHz to GHz shows that the maximum of dielectric losses is displaced toward low frequencies as dehydration proceeds. The ε' versus $\%H_2O$ curve shows a break, corresponding to the transition free water/bound water.

The studies of Rosen (1963) on packed serum albumin powders, that of Kent (1972) on different materials in the biological and food domains, Henry, Moré, and Berteaud (1979) on polymers and Henry and Noé (1989) on hydrated cellulose fibres, confirm the preceding results. At a constant temperature, the variation of dielectric losses ε'' versus the quantity of water shows a break, during the water desorption, corresponding to the free/bound water transition.

The slope before and after the critical volume fraction of water is proportional to dielectric losses of bound and free water, respectively.

2. Materials and methods

In Fig. 1, a schematic representation of the experimental set up is shown.

The cavity, operating in $TE_{3,5,7}$ resonant mode, is thermally stabilised by the circulation of a fluid in a jacket, and separated from the environmental atmosphere by a glove box. A Cahn microbalance maintains the sample holder in a stable position inside the resonant cavity. A tube passing throughout the resonant cavity prevents water condensation on the walls of the

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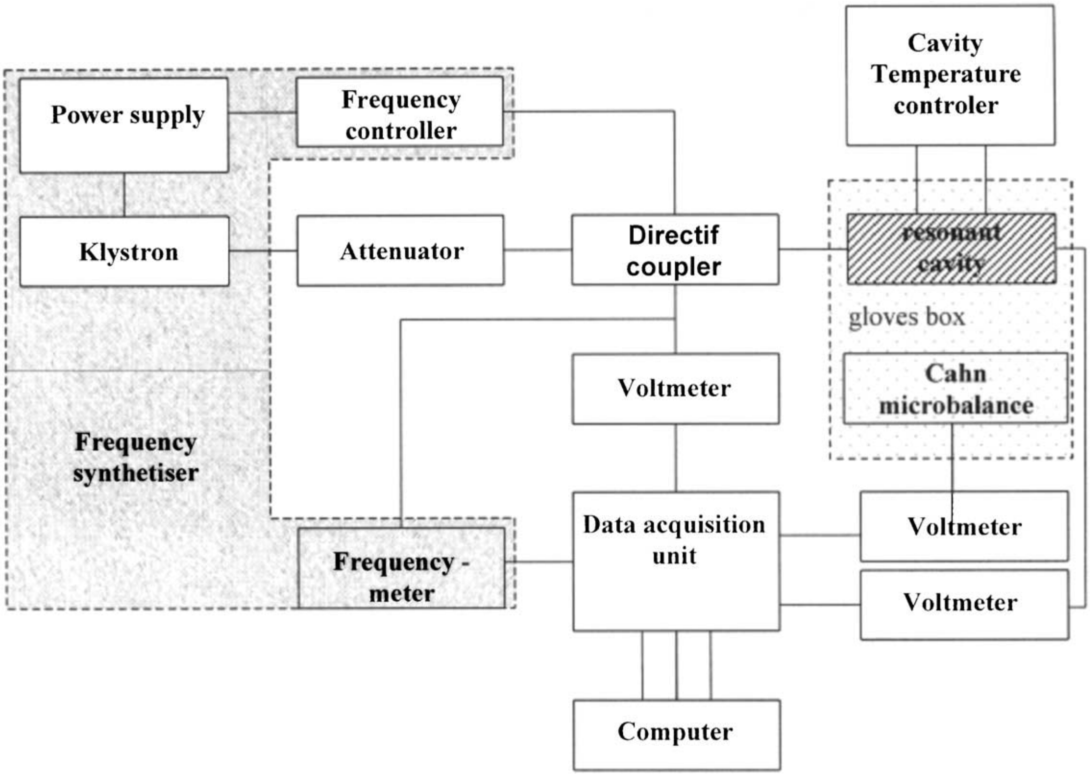

Fig. 1. Experimental set-up.

cavity. The system can operate in desorption in the presence of a strong desiccant (P_2O_5 powder) or in adsorption of water vapour.

The microwave signal is generated by a Wiltron 6769B synthesiser. A crystal detector is used to obtain a signal proportional to the transmission of the cavity, measured by a Yokogawa 7551 multimeter.

The small perturbation theory of resonant cavities allows the link of the decrease of resonance of the cavity, $\Delta f/f_e$, and the lowering of the reciprocal of the surtension factor $\Delta(1/Q)$ of the cavity, to the ratio between the absorbed energy in the dielectric sample to the total energy transported in the cavity. The proportionality factor (ε^*_m) corresponds to the complex dielectric constant. For a small perturbation and elementary geometric form of the sample, these relations are simple, considering only the first order perturbation in the electric field (Henry & Berteaud, 1980),

$$\frac{\Delta f}{f_e} + j\frac{1}{2}\Delta\left(\frac{1}{Q}\right) = \varepsilon_0\left(\varepsilon^*_m - 1\right)\frac{\int\int\int_{V_m} E_i^* E_0 \mathrm{d}v}{\int\int\int_{V_c} \varepsilon_0 E_0^2 \mathrm{d}v}$$
$$= \varepsilon_0\left(\varepsilon^*_m - 1\right)\frac{\text{energy stored in material}}{\text{energy stored in cavity}} \qquad (1)$$

In this expression, f_e is the resonance frequency of the empty cavity, ε^*_m the complex permitivitty of the material, E_i and E_0 the electric fields inside and outside the material. The index m corresponds to the dielectric material in the cavity, and ε_0 is the dielectric permittivity of the free space.

The integration is made in the volume of the sample V_m, and in the volume of the cavity V_c. Separating the real and imaginary parts,

$$\frac{\Delta f}{fe} = k\left(\varepsilon'_m - 1\right)\frac{V_m}{V_c} \quad \text{with} \quad \frac{\Delta f}{f_e} = \frac{f_{\text{empty}} - f_{\text{load}}}{f_{\text{empty}}} \qquad (2)$$

$$\Delta\left(\frac{1}{Q}\right) = \frac{k}{2}\varepsilon''_m\frac{V_m}{V_c} \quad \text{with} \quad \Delta\left(\frac{1}{Q}\right) = \frac{1}{Q_{\text{load}}} - \frac{1}{Q_{\text{empty}}} \qquad (3)$$

where K is a constant related to the depolarisation factor, which depends upon the geometric parameters.

The measured perturbation is then proportional to the products $\varepsilon'_m V_m$ and $\varepsilon''_m V_m$ and inversely proportional to the volume, V_c, of the resonant cavity.

To calculate the dynamic dielectric specific surface area of materials, exposed to water vapour (Henry, Houitte, Costa, & Serpelloni, 2000), we postulate that the variation of dielectric loss of a material under test ($\Delta(1/Q)$) is proportional to the variation of the partial pressure of the water vapour which is found in the material and in the immediate environment. This is expressed by

$$\Delta\left(\frac{1}{Q}\right)_{\text{distributed water}} = \left[\Delta\left(\frac{1}{Q}\right)_{\text{wet material}} - \Delta\left(\frac{1}{Q}\right)_{\text{dry material}}\right] = \frac{K}{2V_{\text{c}}}\left[(\varepsilon''V)_{\text{free water}}+(\varepsilon''V)_{\text{bound water}}\right] \tag{4}$$

The total pressure of a mixture of gases, representing the different states of water, is, according to Dalton's law, equal to the sum of the pressures of its constituents. As a consequence, the division of each of the following expressions by the total volume of water present at the same instant (water calculated using the Cahn microbalance) shows:

(1) at the instant $t=0$, $\Delta(1/Q)$ is proportional to the water content, in the material and its surrounding atmosphere, due to initial conditioning, and given by

$$\left(\frac{A}{V_{\text{total water}}}\sum_{j\text{ states of water}}\varepsilon''_j V_j\right)_{t=0} \approx \left(\frac{1}{V_{\text{total water}}}\sum_{j\text{ states of water}}P''_j V_j\right)_{t=0} = (P_{\text{total}})_{t=0} \tag{5}$$

with $A=K/(2V_{\text{c}})$

(2) at any instant t during dehydration, this same proportionality is maintained when the material under test has sufficient time to reach an equilibrium,

$$\left(\frac{A}{V_{\text{total water}}}\sum_{j\text{ states of water}}\varepsilon''_j V_j\right)_{t} \approx \left(\frac{1}{V_{\text{total water}}}\sum_{j\text{ states of water}}P''_j V_j\right)_{t} = (P_{\text{total}})_{t} \tag{6}$$

The normalisation of $\Delta(1/Q)$, is obtained on dividing (6) by (5), and again dividing the resultant equation by P_0,

$$\frac{\left(\sum\limits_{j\text{ states of water}}\varepsilon''_j V_j\right)_t}{\left(\sum\limits_{j\text{ states of water}}\varepsilon''_j V_j\right)_{t=0}} = \frac{P_t/P_0}{P_{t=0}/P_0} \tag{7}$$

giving the proportionality between a_{w} or P_{t}/P_0 with the quality factor (Q) of the cavity,

$$P_t/P_0 = (P_{t=0}/P_0)_{\substack{\text{conditioned}\\ \text{atmosphere}}}\frac{(\Delta(1/Q)/V_{\text{total water}})_t}{(\Delta(1/Q)/V_{\text{total water}})_{t=0}} \tag{8}$$

3. Results and discussion

Mathematical analysis of the transmission curve (T_{r}) allows us to obtain the frequency ($f_{\max}$) and quality factor (Q_{load}), proportional to permittivity and dielectric losses of the material under test, respectively.

$$T_{\text{r}}(f) = \frac{T_{\text{r}}(f_{\max})}{1+Q^2_{\text{load}}\left(\dfrac{f}{f_{\max}}-\dfrac{f_{\max}}{f}\right)^2} \tag{9}$$

with

$$f=f_{\max}+\Delta f/2,$$

and

$$T_{\text{r}}(f) = \frac{T_{\text{r}}(f_{\max})}{2}.$$

Then we obtain,

$$Q=\frac{f_{\max}}{\Delta f} \tag{10}$$

In Fig. 2, we can observe the variations of the resonant frequency (F), the inverse of surtension factor ($1/Q$) and weight of the material (m), as a function of time, during desorption. On these curves, the asymptotes correspond to the dielectric and weight parameters of the dry material.

Using (4), the division by the total volume of water ($V_{\text{total water}}$), as in expression (5), leads to Figs. 3 and 4. Hence, we can observe the break point of free/bound water transition, in the case of a coated paper sheet.

Using (8), establishing a relationship between water activity a_{w}, after normalisation, and the dielectric losses of the hydrated material in the cavity of a microwave resonator, under a controlled atmosphere (T and P/P_0), we can plot the variation of water content in environmental

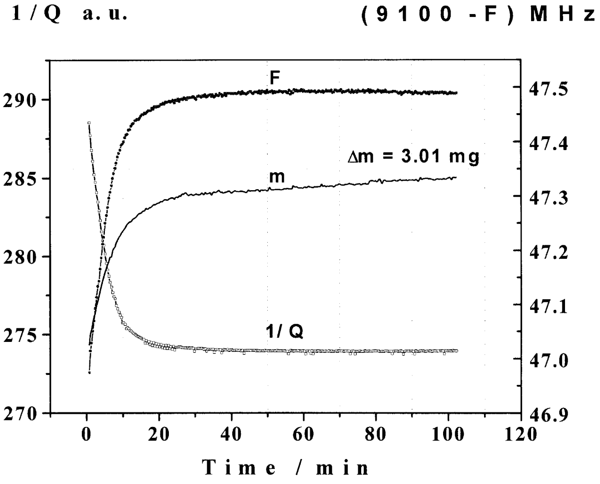

Fig. 2. Dielectric parameters and weight versus time, during desorption of water of coated paper ($P/P_0=95\%$, $T=25$ °C), $1/Q=$quality factor ≈dielectric losses, $F=$resonance frequency, m = cumulative losses in weight of water.

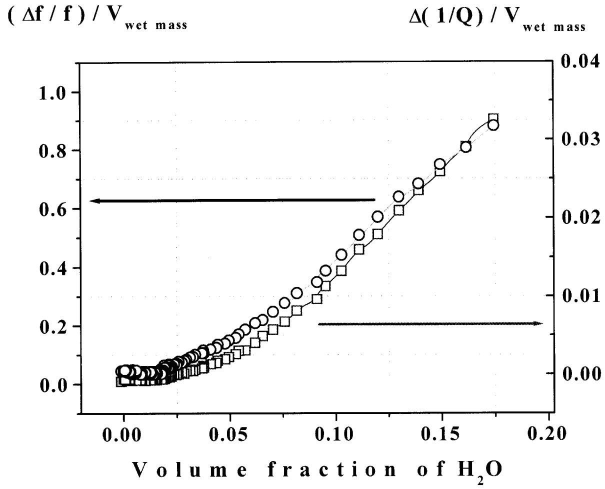

Fig. 3. Variation of dielectric parameters, $(\Delta f/f_{\mathrm{e}})/V_{\mathrm{total\ water}}$, $(\Delta(1/Q))/V_{\mathrm{total\ water}}$ during desorption versus volume fraction of water obtained from Fig. 2.

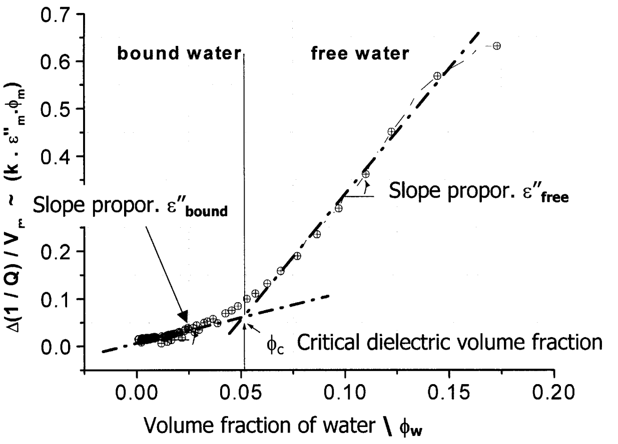

Fig. 4. Desorption curve, before ε″ normalisation, for a coated paper.

atmosphere of the material versus normalised dielectric losses (a_{w}), as is shown in Fig. 5. The form of this curve looks like the desorption curve.

The linearized expression of the desorption curve, using BET theory, in the P/P_0 domain between 0.05 and 0.40, can be written as

$$\frac{P/P_0}{\mathrm{m}(1-P/P_0)}=\frac{1}{Cm_0}\left[1+(C-1)\frac{P}{P_0}\right] \tag{11}$$

where m_0 is the mass of the first shell of adsorbed water and C a constant.

To calculate m_0,

$$m_0=\frac{1}{\mathrm{slope}+\mathrm{intercep}} \tag{12}$$

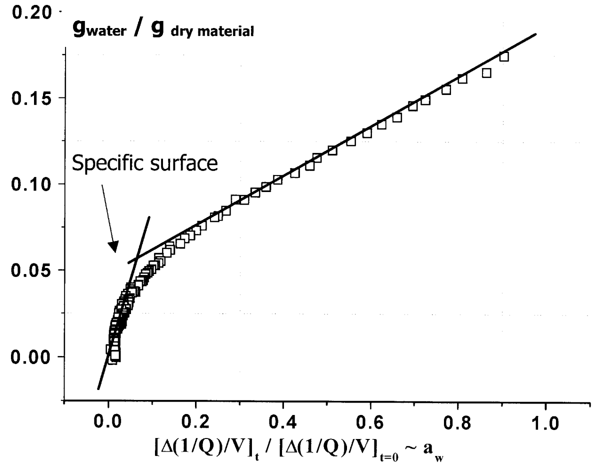

Fig. 5. Desorption curve, after ε″ normalisation, for a coated paper.

Knowing the atomic mass A, and the specific surface area of the water molecule σ, the dynamic dielectric specific surface area with water vapour, DDSS, is then defined by

$$\mathrm{DDSS}=m_0\frac{N_A}{A}\sigma \tag{13}$$

where N_{A} is the Avogadro number.

It is important to note that the BET approach needs to proceed in a stationary state of partial pressure of water vapour. This condition is not always realistic in the material and in the near environment of it. Our dielectric approach is closest to the Polanyi potential theory (Polanyi, 1921) in which the adsorbed layer resembles the atmosphere of a planet—it is most compressed at the surface of the solid and decreases in density outwards.

Nevertheless, it is easier for good comparisons, to calculate the specific surface area of water vapour by the BET approach.

For different paper sheets, we obtained DDSS values between 320 and 400 $\mathrm{m}^2\mathrm{g}^{-1}$. These results are higher than those calculated by the classical methods, which can be explained by the fact that the shrinkage of the material during the experiments is less rapid than the physical departure of the water.

4. Conclusions

The time used to construct the adsorption/desorption curves of materials is clearly reduced with this new method, when compared with classical methods. In this last case, the measurements of a_{w} are made at low frequencies, using a condenser and assuming a stationary equilibrium, which is not always true. In our new method, we can quantify the water activity in the material and environment, working in a dynamic process of adsorption or desorption. In our technique, we can always obtain a static equilibrium, which makes this method rather powerful and accurate.

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