BRIEF ORIGINAL

Determination of the water diffusivity dependence with the flow rate using a DVS equipment

Antoni Sánchez-Ferrer[1] · Max Engelhardt[1]

Abstract

The effects on the measurement of water sorption and apparent diffusivity when using different flow rate values and different experimental setups, i.e., closed pan, open pan and hanging setup, have been studied in a series of Dynamic Vapor Sorption (DVS) experiments on a spruce sample. The results confirm a concave exponential growth dependency between apparent diffusivity and flow rate and an effect from the setup used, with the hanging setup being optimal for conducting such experiments due to the exposure of both areas of the disk to the airflow.

1 Introduction

Water diffusivity of wood samples can be evaluated using Dynamic Vapor Sorption (DVS) equipment. DVS has advantages over saturated salt slurry (SSS) setups because of the constant monitoring of the sample mass, no need for removal of the sample for weighing, setting of a defined temperature and precise initial and final relative humidity (RH) values that the sample is exposed to (Majka et al. 2019). Moreover, for a DVS with electronic beam balance, the mass of the samples might be as low as 1–100 mg, requiring a small amount for an exact measurement.

One key parameter in a DVS equipment that not too much attention has been paid to in the past is the flow rate (Q) of the conditioned gas. A DVS equipment continuously monitors the sample's mass until reaching the desired equilibrium moisture content (EMC) faster than the simple SSS setup—in a steady-state situation where water molecules in the air are mainly controlled by Brownian diffusion (Newman 1932), or chambers with circulating air assisted by a fan. At high Q values, a vapor concentration nearly identical to the environmental gas phase is available to the surface, and thus, higher apparent diffusivity (D_{app}) values are achieved. Contrarily, in a low Q situation, the number of water molecules available at the surface of the sample is a bottleneck, since the sample reduces the near-surface vapor concentration by adsorption and, therefore, leading to lower D_{app} values (Söderström and Salin 1993).

The DVS method is the perfect way ideal for observing the influence of Q at different RH values during the adsorption processes. The EMC of a spruce disk sample cut in the longitudinal direction was measured as a function of time in steps of 5% RH using three different setups and at different Q values for predicting the maximum D_{app} for each setup and at each RH value.

2 Materials and methods

Dynamic Vapor Sorption (DVS) experiments were conducted using a gravimetric vapor sorption device (DVS Advantage ET, Surface Measurement Systems). The device is equipped with a microbalance and a chamber that is purged with a nitrogen flow of 10–200 cm³/min (0.6–12 L/h) at a selected RH value obtained by mixing different flows of dry and water-saturated nitrogen.

Three different setups were used, i.e., two aluminum pans (closed), two aluminum-perforated pans (open), and two paper clips (hanging), for conducting these experiments and placing the sample in one of them while using the other as a reference to eliminate sorption effects from the holders.

After conditioning the sample at 25 °C and at 0% RH until complete dryness—ca. 2 days by controlling the mass by stability criterion—the measurement started by increasing the RH of the nitrogen flow in steps of 5% until 100%

✉ Antoni Sánchez-Ferrer
   sanchez@hfm.tum.de

   Max Engelhardt
   engelhardt@hfm.tum.de

1 School of Life Sciences, Chair of Wood Science, Technical University of Munich, 80797 Munich, Germany

RH (actually, ca. 96% RH). The criterion for increasing the set RH value is a threshold in the variation in mass per unit time with respect to the initial dry mass to a value of $d(m/m_0)/dt < 0.001\%/min$ over 10 min, where at this point, the sample is measured for one extra hour prior to changing the RH for the next measuring step.

The sample was a 44.8 mg spruce disk (12.0 mm in diameter and 1.06 mm in thickness) cut in the longitudinal direction.

Each dynamic moisture adsorption step was analyzed using a double-stretched exponential (DSE) model to obtain an equivalent lifetime value τ (Sanchez-Ferrer et al. 2023). With this, the corresponding apparent diffusivity D_{app} was calculated following the expression $D_{app} = F/\tau$, with the shape factor $F = \pi l^2/16$, where l is the thickness of the sample. Moreover, the DSE model allowed for the estimation of the EMC values at each adsorption step, which were used for constructing the corresponding adsorption moisture sorption isotherm (MSI) after fitting the data to a modified GAB model (Sanchez-Ferrer et al. 2023). The corresponding fitting to the MSI was used to precisely interpolate the EMC values for each curve at any RH value for each Q and for each setup (Fig. 1A).
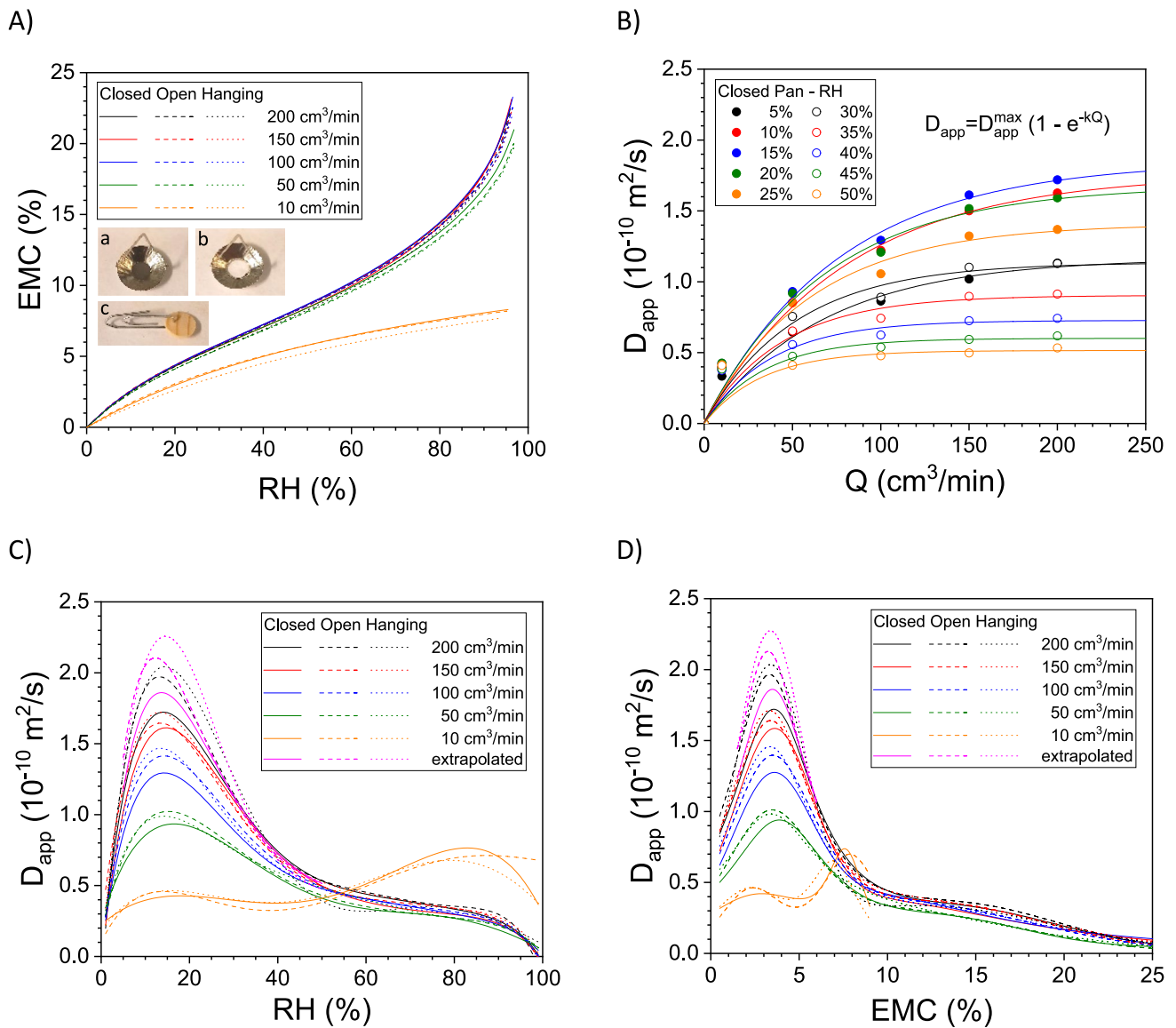

Fig. 1 **A** Moisture sorption isotherm (MSI) curves at different flow rates and with the three different setups, i.e., a) closed, b) open and c) hanging. **B** Diffusion coefficient (D_{app}) values as a function of the flow rate (Q) together for the different relative humidity (RH) values with the corresponding fitting curves using a closed pan. Diffusion coefficient profiles as a function of **C** relative humidity (RH), and **D** equilibrium moisture content (EMC), at different flow rates and with the different setups

Table 1 Diffusion coefficient (D_{app}) values at RH ≈ 15% or EMC ≈ 3.5%, at different flow rates (Q) and for the different setups

	Q (cm³/min)	10	50	100	150	200	500	D_{app}^{max}
D_{app} (10^{-10} m²/s)	Closed pan	0.23	0.89	1.35	1.59	1.72	1.85	1.85
	Open pan	0.25	0.95	1.45	1.73	1.88	2.05	2.05
	Hanging setup	0.24	0.93	1.47	1.79	1.98	2.24	2.25

3 Results and discussion

In order to observe the effect of Q for the three different setups—i.e., closed, open, hanging—on the adsorption MSI curve, the EMC values were fitted using a modified GAB model. These EMC values were determined by fitting the moisture content evolution at each RH step with a DSE function (Sanchez-Ferrer et al. 2023). The corresponding MSI curves (Fig. 1A) at Q = 100, 150 and 200 cm³/min showed the characteristic S-shape for wood and lignocellulosic materials and an almost perfect overlapping between them. Deviations started to be visible at high RH values at Q = 50 cm³/min, indicating that there was not enough water to be adsorbed for the imposed dm/dt threshold and the mass chosen. These deviations became significantly more accentuated at Q = 10 cm³/min, where the EMC values obtained at higher Q values were never reached, and the curves showed a parabolic shape. Nevertheless, the actual MSI at 10 cm³/min could still be obtained if the dm/dt threshold was adjusted down (Thybring et al. 2019), resulting in extremely long measurements while preserving the high errors in D_{app} for low Q values.

From the DSE fitting protocol of the moisture content evolution at each RH step, the D_{app} values obtained—at each Q and for each setup—were plotted and fitted following a concave exponential function $D_{app} = D_{app}^{max}\left(1 - e^{-kQ}\right)$—similar to a CDF for an exponential distribution—as shown in Fig. 1B. Since the model fails at low Q values, the D_{app} values at Q = 10 cm³/min were excluded due to the dominant mass transport from Brownian motion. The constant k ranges from 1.1 10^{-2} min/cm³ at the maximum diffusivity, i.e., at 15% RH—to 3.8 10^{-2} min/cm³ at the lowest one, i.e., at 50% RH. Moreover, with this approach, the maximum apparent diffusivity was estimated D_{app}^{max} at each RH value.

Finally, with all obtained D_{app} values from the DSE fitting protocol, the diffusivity profile as a function of RH or EMC was obtained at different Q values and for the different setups (Fig. 1C and D). At low RH values, all samples showed a high diffusivity with values between 5 10^{-11} and 2 10^{-10} m²/s, while from 50% RH onwards, the diffusivity converged to values of $D_{app} \lesssim 5$ 10^{-11} m²/s. Moreover, it seems that hanging the samples and exposing both areas of the disk to the airflow help water molecules to be adsorbed and diffuse faster through the wood sample with up to 5% and 15% increase in the D_{app} at RH = 15% respect the use of an open and closed pan, respectively. The same tendency was observed when plotting the extrapolated D_{app} values at Q = 500 cm³/min (pink curves in Fig. 1C and D)—which match the D_{app}^{max} from the exponential growth function -, indicating that the setup has some effect on the diffusivity. All D_{app} values at RH ≈ 15% or EMC ≈ 3.5% are reported in Table 1 for a better comparison between setups and airflows, together with the extrapolated value at 500 cm³/min and the D_{app}^{max} fitting parameter.

The values at 500 cm³/min were obtained by extrapolation and the D_{app}^{max} is obtained by fitting the D_{app} values with an exponential growth function (Fig. 1B).

4 Conclusion and outlook

This study highlights how important it is to choose the DVS setup parameters, i.e., sample setup—closed pan, open pan and hanging setup—and flow rate Q for the determination of the apparent diffusivity D_{app}. Flow rates of Q ≤ 50 cm³/min reduce the adsorption rate due to the lowered concentration of vapor molecules near the surface boundaries, while higher Q values, e.g., 200 cm³/min, cause the concentration gradient toward the surface to diminish, reducing its effect, which was quantified using a concave exponential growth. The open pan or the hanging setup shows higher D_{app} values than the closed pan provided by the manufacturer due to the exposure of both circular surfaces to the airflow.

Declarations

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