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SHORT COMMUNICATION

A sorption balance-based method to study the initial drying of dispersion droplets

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Abstract The initial drying of dispersion samples with varying geometries and surface areas was continuously recorded in a sorption balance at different temperatures and relative humidities. The samples were applied as small (5–20 mg) droplets on glass. We were able to show a linear dependence of the evaporation rate on the exposed surface area of the samples if the evaporative cooling was taken into account. The method outlined in the present paper facilitates scaling and comparison of results obtained from drying experiments with different-sized dispersion samples.

Keywords Sorption balance · Drying · Dispersions · Film formation

Introduction

Drying of water is a common unit operation in many industrial processes as well as in nature. Often, the drying process involves dispersion droplets of different forms, e.g., in spray drying of pharmaceutical applications or in ink-jet printers. It is also a common practice to study drying phenomena for coatings that are applied on flat surfaces—like paints and coated paper products—using small-scale convex samples. However, it is known that one cannot uncritically compare results of experiments made with droplets of different sizes [1]. In response to this, the present paper presents a sorption balance-based method to record controlled drying rates and a method to scale the results from the drying of convex samples of varying sizes.

When a droplet is placed on a surface, its shape is determined by the liquid–solid contact angle and the volume of the droplet. Small liquid droplets form perfectly spherical segments, whereas larger droplets have flattened upper surfaces (still maintaining the correct contact angle). Increasing the volume even further will result in flat films in which the edge effects will decrease with increasing sample sizes [2]. There is also a difference in drying behavior when droplets of either pure liquids or dispersions (containing small particles) are dried on a surface. Pure liquids on ideal surfaces dry with a constant contact angle and a decreasing radius, while the initial radius is preserved during the drying of dispersions by a phenomenon known as *pinning* caused by the particles being transported to the edge of the droplet [2]. However, because of surface defects and other nonidealities, pinning may also occur for non-dispersions. The most commonly used dispersion types are polymer latices, which, for example, are used as binders in water-borne coatings, adhesives, and many types of paper coatings. The important process that gives latex many of its application characteristics occurs during drying; that is, the dispersion forms a film provided that the drying temperature is higher than the latex polymer glass transition temperature. Traditionally, film formation of (latex) dispersions has been divided into three stages: (1) Water evaporates bringing the

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polymer latex particles into close contact, (2) the particles deform, and (3) the particles coalesce by diffusion of polymer chains across particle interfaces [3]. However, this study focus only on stage 1, which has been found to be very important for the applicability of theoretic predictions on latex film formation [4–6]. During the initial part of the film formation, the particles move with their characteristic Brownian motion, and the water concentration in the dispersion is uniform, i.e., *homogeneous drying*. When no organic solvents are present, the water evaporates from the latex at the same rate as for pure water. The mass transport of water vapor from a droplet surface to air occurs by diffusion and convection, and the flow rate is proportional to the difference in vapor pressure between the droplet and the surrounding air, which can be expressed as:

$$W = k_{\mathrm{G}}A(p_{\mathrm{w}} - p_{\mathrm{a}}) \tag{1}$$

In this equation, W (kg s^{-1}) is the mass flow rate (the mass loss rate), k_G (kg m^{-2} s^{-1} Pa^{-1}) is a mass transfer coefficient, A (m^2) is the exposed surface area, and p_{w} and p_{a} (Pa) are the vapor pressures of the droplet surface and the air, respectively [7]. Equation 1 is rearranged to obtain an expression for an overall mass transfer coefficient (K; kg s^{-1} Pa^{-1}):

$$K = k_{\mathrm{G}}A = \frac{W}{(p_{\mathrm{w}} - p_{\mathrm{a}})} \tag{2}$$

The mass transfer coefficient K contains information on the droplet geometry and the air flow pattern. Normally, the vapor pressure of the droplet is close to that of pure water, but with high concentrations of dispersed substances, it will be reduced.

In coating science, one often discusses drying as the speed by which the film decreases in thickness, h' (m/s):

$$h' = \frac{W}{A\rho} \tag{3}$$

In this equation, A (m^2) is the exposed surface area and ρ (kg/m^3) is the density of the liquid phase. The parameter h' will generally be constant when flat films are dried [7] (when temperature, vapor pressure difference, and convection are kept constant), but for other geometries, it will be a function of the size of the sample [8]. For example, h' will increase with a decreasing water droplet size [1, 7]. Deegan et al. [2] have, by studying the flux rate of particles in dispersion droplets, shown that h' is higher at the edges for convex samples. The increased evaporation rates at the sample edges were found to depend on the contact angle (θ_{c}) between the substrate and the drop surface, and the variation in evaporation rate across a sample was proportional to the distance from the edge to where the sample became flat.

In the present work, the change in the initial drying rate for latex dispersions with varying geometries and surface areas was studied at several temperatures and vapor pressures using a sorption balance, which is a highly sensitive gravimetric instrument. A general approach to scale the evaporation rate from small convex samples to large area samples was developed from the experimental data, and a model of how to predict the evaporation rate for large surfaces from small convex samples is presented.

Experimental section

Material

A methyl methacrylate-*co*-methyl acrylate latex dispersion with a particle size of 120 nm, a glass transition temperature (T_{g}) of 18 °C, and a minimum film formation temperature of 8 °C was used for the drying studies. Preparation details are presented elsewhere [9]. The dispersion was completely cleaned from the surfactant and low-molecular-weight species by dialysis for 7 days in continuously exchanged deionized water using a preconditioned dialysis tube (Spectra/Por Membrane, MWCO: 100 000).

Sorption balance measurements

A DVS 1000 sorption balance (Surface Measurement Systems, UK) was used to study the drying of dispersion droplets [10]. This type of instrument is normally used to measure sorption isotherms on small samples of, e.g., pharmaceutical compounds. The samples are then placed in pans and exposed to a flow of nitrogen with a programmed relative humidity. In the present study, we have instead used the instrument to study droplet drying at constant relative humidity in the gas stream. It is well suited for this as the temperature, relative humidity, and the gas flow rate are very well controlled, and the mass is measured with a 0.1-μg balance (Kahn D-200).

Dispersion specimens of 5–20 mg were applied with a micropipette onto thin circular (diameter 12 mm) microscope coverslips placed on a holder as shown in Fig. 1. The holder was hanging centrally in a vertical tube in the sorption balance with a nitrogen gas flow rate from below of 100 ml/min. The mean air speed was about 5 mm/s at the coverslip. The initial surface areas of the samples were 15–45 mm^2, and the drying of the dispersions was followed by the continuously recorded mass change of the samples. The measurements were performed at 10 to 50 °C (±0.5 °C) and 0 to 90% (±1.5%) relative humidity. The radii of the dispersion droplets were determined after the experiments from the footprint left by the dispersion particles.

To check the applicability of the vapor pressure relationships (originally derived for pure water) in Eq. 1, the initial

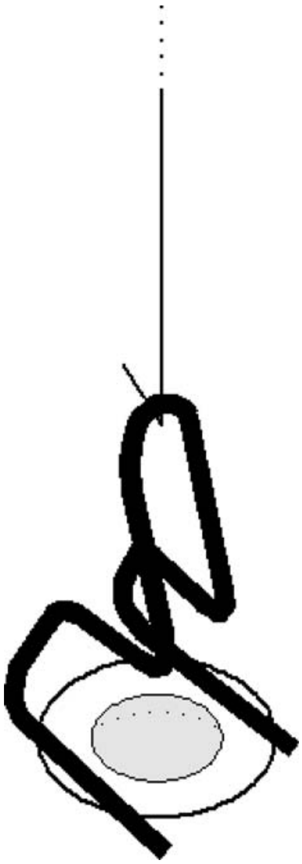

Fig. 1 The droplets were placed on circular cover slips that were placed on a fork-shaped holder. In the sorption balance, the holder was hanging on the balance hang-down with a flow of nitrogen from below

mass loss rate for similarly sized circular samples of either pure water (masses 8.9±0.3 mg) or latex dispersions (masses 11.0±0.6 mg and solids contents of 16–20%) was measured at 30 °C. The results were identical for water and the different latex dispersions. Thus, the initial evaporation rate was not influenced by the presence of the dispersion particles.

Cooling of droplets by evaporation

The evaporation of water cooled the sample like in a psychrometer, and separate measurements of this cooling effect were carried out with a thin thermocouple fastened to the upper side of a glass coverslip. The thermocouple was insulated from the glass and placed inside an applied water droplet. The whole arrangement was hanging in the thermocouple wires. The evaporative temperature drop was used in a psychrometric equation to calculate a psychrometric constant γ (Pa/K):

$$p_{\mathrm{a}} = p_{\mathrm{w}} - \gamma(T_{\mathrm{a}} - T_{\mathrm{w}}) \tag{4}$$

Calculation of surface area of droplets

We measure evaporation rates of droplets in the sorption balance to be able to compare different experiments with different droplet sizes. In Eq. 2, the mass transfer coefficient K is a function of the droplet geometry and the gas flow pattern. As we keep all factors constant between experiments except the droplet size, it is natural to see if we can find a relation between the mass transfer coefficient and the exposed surface area of the droplets. Therefore, we here derive equations for the surface area of droplets that we later test with data from drying of dispersion droplets.

All samples measured in the sorption balance were circular and initially spherical segments as illustrated in Fig. 2a. The sample volume V (m^3) and the radius a (m) of the circular area on the glass surface were used to derive the convex exposed surface area, A_c (m^2), from Eqs. 5 to 7.

$$h(2r - h) = c^2 \tag{5}$$

$$V = \frac{\pi}{3}h^2(3r - h) \tag{6}$$

$$A_c = 2\pi rh \tag{7}$$

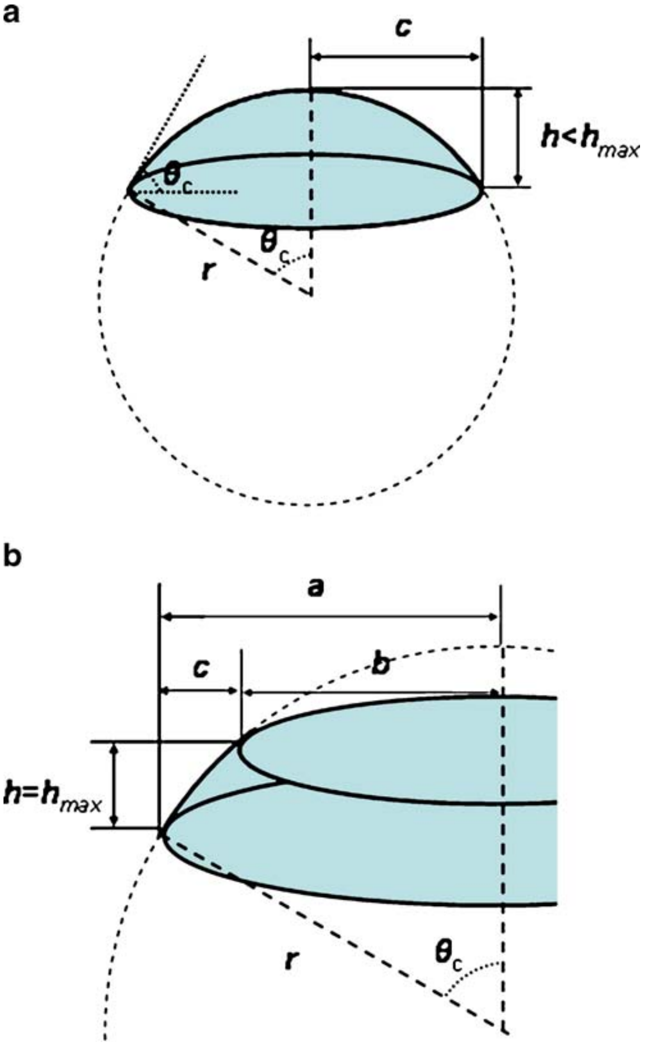

Fig. 2 Cross-section view for the **a** small convex sample and **b** large sample with a flat top surface. The nomenclatures used in the calculations are given for both cases

The notations used in the above equations are given in Fig. 2. At this stage, it is also possible to calculate the contact angle θ_c from the following equation:

$$c = r\sin(\theta_c) \tag{8}$$

For liquids and dispersions that are applied on flat surfaces and that have contact angles θ_c less than 90°, there is a maximum height h_{max} (m) of the droplet. When the maximum height is reached and the volume increases, the droplet will expand, and the exposed area will approach the footprint area as shown in Fig. 2b. The maximum height for the studied dispersion was found to be 1.5 mm by contact angle measurements. The exposed area, A_a, for a large circular sample can be calculated from Eqs. 9 to 14.

$$c = a - b \tag{9}$$

$$a = r\sin(\theta_c) \tag{10}$$

$$h = r(1 - \cos\theta_c) \tag{11}$$

$$V_{flat} = \frac{\pi}{6}h\left(3a^2 + 3b^2 + h^2\right) \tag{12}$$

$$A_b = \pi b^2 \tag{13}$$

$$A_a = A_c + A_b \tag{14}$$

We have started with spherical droplet caps (Fig. 2a) and calculated the surface area by Eqs. 5 to 7. When the decreasing droplet height h reaches h_{max}, we instead use Eqs. 9 to 14 (Fig. 2b).

Results and discussion

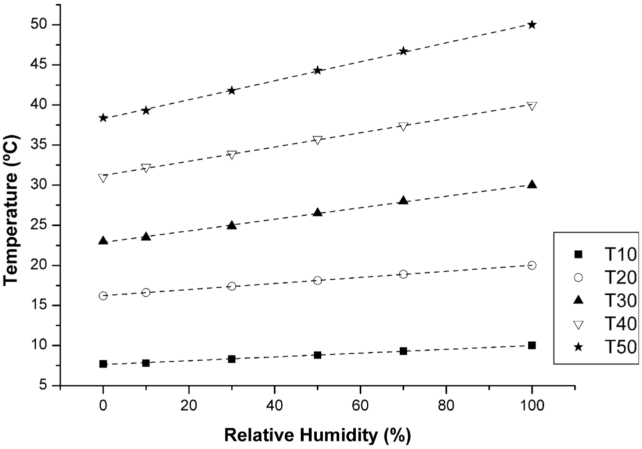

Fig. 3 The measured temperature of the dispersion droplets

The measured bulk temperatures of the dispersion droplets are shown in Fig. 3, and it can be seen that the temperature lowering is significant at low relative humidities and high temperatures. The calculated mean psychrometric constant γ of Eq. 4 was 480±55 Pa/K (values with very low temperature depressions were omitted from the calculation as one from these could not make accurate determinations of γ). It is natural that γ for this application is significantly higher than the generally accepted value of about 67 Pa/K for psychrometers [11] because in our arrangement, evaporation (cooling) only takes place from the droplet air interface, but heat conduction (heating) is occurring from the whole exposed surface including the bottom of the coverslip. In normal psychrometers, one will arrange so that vaporization and heat conduction takes place over the same surface. It should be noted that γ will be different for different experimental setups so the value 480 Pa/K is specific to the present experimental situation.

The decrease of droplet temperature in the present experiments was as high as 10 K, and the results show that such decrease of the droplet temperature would not be unusual under normal experimental conditions. This can give unwanted consequences if the actual temperature of a droplet in a drying experiment or a wet coating applied (e.g., water-borne paint) is lowered by 10 K. Even at low convection, erroneous results because of the effects of cooling might arise. When coating larger surfaces, there will also be evaporative cooling, and the coating performance can be affected because the glass transition temperatures (T_g) for many commercial latex dispersion polymers are designed to be close to the anticipated application temperature. However, as substrates usually have a much higher heat capacity than the film, the temperature drop will in most real situations be significantly lower than in the present experiments.

The value of γ and Eq. 4 makes it possible to calculate the actual temperature of the dispersion droplets in the sorption balance as a function of gas stream temperature and relative humidity. This value was then used to calculate the overall surface mass transfer coefficient K. We have in all cases assumed that the droplet had the vapor pressure of pure water.

Figure 4 shows the mass transfer coefficient K determined at the initial drying of more than 60 dispersion droplets of

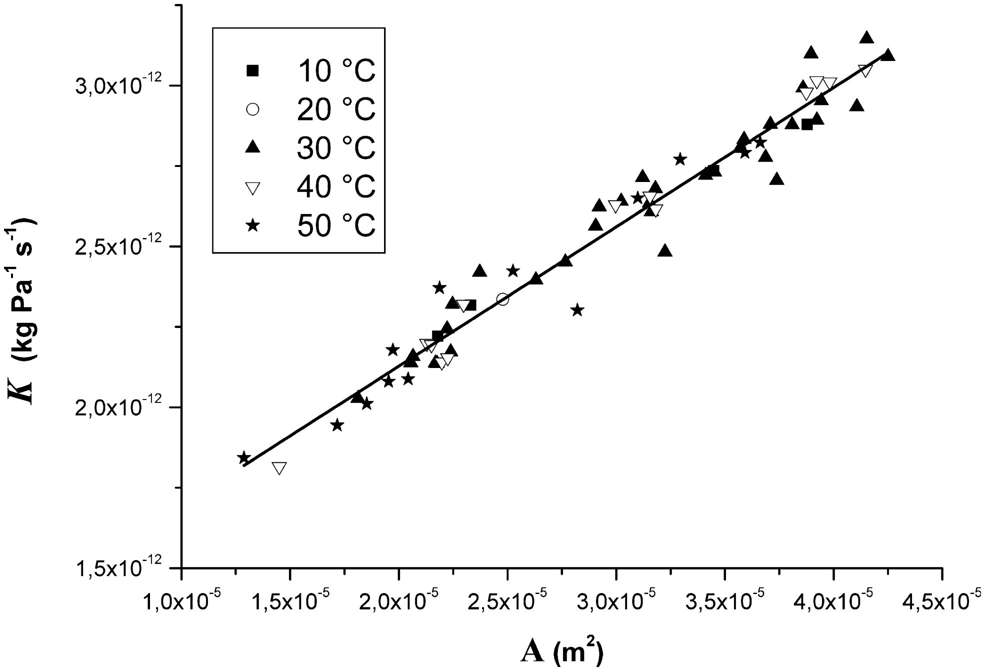

Fig. 4 The mass transfer coefficient (K) plotted as a function of the exposed sample area for temperatures ranging from 10 to 50 °C and relative humidities ranging from 0 to 90%

different sizes, plotted as a function of the exposed area. It is seen that the results show a linear trend:

$$K = C_1 A_a + C_2 \tag{15}$$

In this equation, C_1 and C_2 are constants whose values in the present experiments were about 43×10^{-9} kg Pa^{-1} s^{-1} m^{-2} and 1.26×10^{-12} kg Pa^{-1} s^{-1}, respectively. This may have useful practical implications; for example, if a process with invariable conditions is being studied, the determination of C_1 and C_2 will provide good opportunities for further optimization of the drying process.

As discussed earlier, in many drying applications, it is convenient to express the drying rate as a speed of decrease in the film or average droplet thickness $\overline{h'}$. By combining Eqs. 2, 3 and 15 we get the following expression for $\overline{h'}$:

$$\overline{h'} = \left(\frac{C_1}{\rho} + \frac{C_2}{A_a \rho}\right)(p_{\mathrm{w}} - p_{\mathrm{a}}) \tag{16}$$

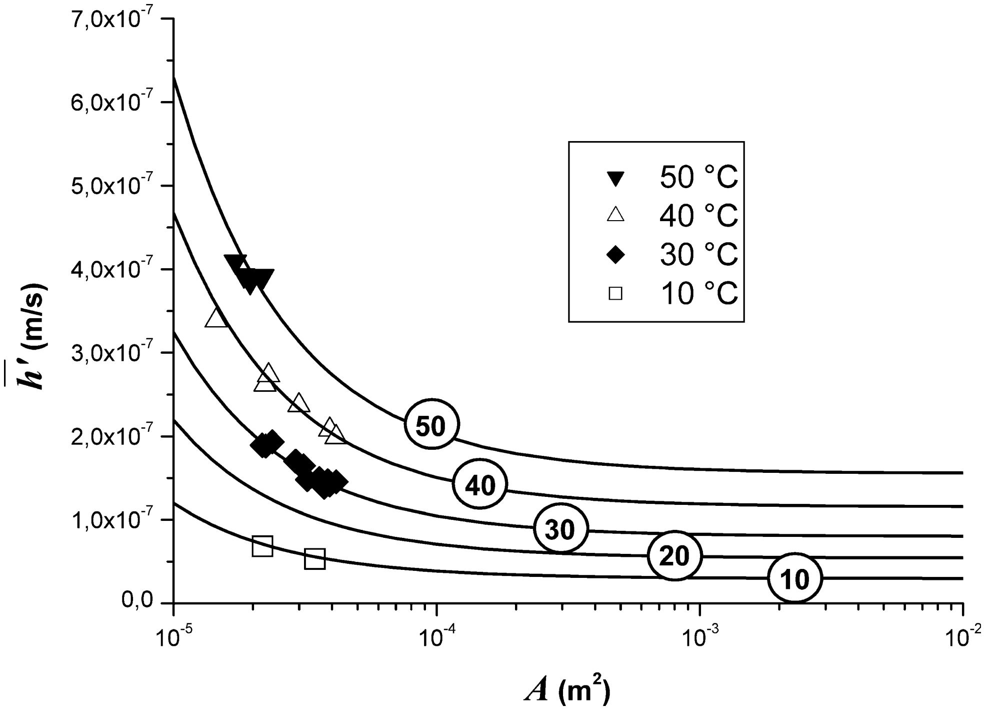

Fig. 5 The rate of the decrease in film thickness (h') plotted as a function of the exposed drying sample area. The *symbols* show the experimental results, and the *lines* are extrapolations using Eq. 18

In Fig. 5 the $\overline{h'}$ results are shown for various temperatures (using the calculated cooled surface temperature) together with extrapolations using Eq.16.

For small areas, the second term in Eq. 16 will dominate and we may write:

$$h' \approx \frac{C_2}{A_a \rho}(p_\mathrm{w} - p_\mathrm{a}) \tag{17}$$

For large areas we may similarly write:

$$h' \approx \frac{C_1}{\rho}(p_\mathrm{w} - p_\mathrm{a}) \tag{18}$$

The described method makes it possible to perform small-scale drying measurements and then extrapolate these results to larger drying surfaces. With the equations given above, it was possible to account for different surface areas used in the sorption balance, but the accuracy of an extrapolation to much larger surfaces has not been fully tested yet. We have, however, found that C_1 values from film-drying experiments were similar to those reported here. In our large film-drying experiments, C_2 values could not be determined accurately, and it is generally a problem to perform experiments with film drying as it is difficult to arrange for the exact same conditions in many experiments performed at different scales. However, in experiments using the sorption balance, all parameters (temperature, relative humidity, flow rate, geometry) are well controlled, and the small size of the samples facilitates accurate measurements as well as a fast handling of the specimens, and we have therefore found the present method to be a useful way of quantifying drying kinetics.

Another question is whether one can extrapolate the results in time, i.e., as a dispersion droplet dries and shrinks. The problem then is mainly that of knowing the vapor pressure on the droplet surface. As we have shown in the present study, one can assume that the vapor pressure on the surface is close to that of water before a film is formed (or some other process that hinders surface diffusion to take place). However, once a film is formed, the surface vapor pressures will drop, and the extrapolation will not be valid anymore unless one knows how p_w changes and can adjust for that, and the use of a sorption balance for latex film formation studies during the later stages is discussed elsewhere [9].

Conclusions

In a sorption balance under well-controlled conditions, it was possible to perform measurements by weighing a droplet on a glass substrate that resulted in an accurate method to quantify drying kinetics of droplets. Evaporative cooling of the drying samples even at low convection should be considered when results from drying of droplets studies are interpreted.

We also showed that the mass flow rate (W) for samples of dialyzed and pure water shaped like spherical segments analyzed as a function of time was initially independent of the solids content within the given interval (SC 0–20 wt%) and that during the initial stage (<5 min) W was constant. The overall mass transfer coefficient was a linear function of the surface area of the specimens, and this provides a method to predict drying kinetics of thin films applied to a larger surface from measurements on droplets.

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