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Original Citation

Beverley, Katharine J., Clint, John H., Fletcher, Paul D. I. and Thubron, Sarah (1999) Evaporation rates of water contained within porous silica particles. *Physical Chemistry Chemical Physics*, 1. pp. 909-911. ISSN 1463-9076

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Evaporation rates of water contained within porous silica particles

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Received 26th November 1998, Accepted 18th January 1999

We have used a gravimetric technique to measure the rate of evaporation of water contained within the pores of powdered silica particles. The experimental conditions are such that the rate is directly proportional to the water vapour pressure. For silica powders of different mean pore sizes, the reduced water evaporation rates are in agreement with the reduction of vapour pressure predicted according to the Kelvin equation. For a particular silica powder, evaporation rates determined from samples with different water contents show the variation in effective pore radius as a function of pore filling volume. Experiments in which a partially water filled powder is overlaid with a dry powder show that the achievement of a homogeneous distribution of water throughout the powder sample takes several hours.

Evaporation rates are of interest from a number of viewpoints including assessment of hazards arising from the spillage of volatile liquids, drying processes, release of volatile active components from commercial products and the retardation and control of evaporation by adsorbed monolayers or entrapment of the liquid within colloidal microstructures such as porous ceramic materials. In this study we have used a simple gravimetric technique, described recently,¹ to investigate evaporation rates of water contained within porous silica particles under conditions of controlled gas flow. Although investigations of evaporation from porous materials have been described previously, (see, for example, refs. 2–5), the experimental arrangement used here enables us, for the first time, to quantitatively compare evaporation rates measured for different pore size particles with theoretical predictions.

Experimental

Water was purified by reverse osmosis and passed through a Milli-Q reagent water system. Davisil silica particles were obtained from Supelco. The manufacturer's figures for mean pore diameter, pore volume and surface area for the three types studied are given in Table 1.

The apparatus for measurement of the evaporation rates is described fully in ref. 1. Briefly, the sample is contained in a cylindrical glass sample tube (inner diameter 17.8 mm) suspended from a Precisa 125A balance. Dry nitrogen gas is passed through a column of activated charcoal (Puritube supplied by Phase Sep.) to remove any impurities and a flow meter to record the gas volume flow rate. The purified nitro-

gen stream flows through a thermostating coil and enters the measurement vessel through an annular opening of approximately 1 mm gap. The gas then flows vertically upwards around the sample tube and emerges from the top of the vessel. The vessel containing the suspended sample tube is contained within a stirred, thermostatted outer vessel. The evaporation rate is determined from the sample mass loss (± 0.0001 g) recorded on the Precisa balance and logged into an EXCEL spreadsheet using a PC equipped with TAL Technologies WinWedge software which allows data transfer from the RS232 interface of the balance. Initial evaporation rates reported here are the mean of several runs and the reproducibility was approximately $\pm 3\%$. We have demonstrated previously¹ that, for relatively low vapour pressure liquids such as water (used in this study), there is no significant cooling of the sample during the evaporation, *i.e.* the sample remains at the thermostatted temperature.

Samples were prepared by mixing accurate weights of dried silica powder (previously dried by storage in a vacuum desiccator) and water in sealed flasks. The mixed samples were allowed to equilibrate for a minimum of several hours before transfer to the measurement vessel in order to ensure homogeneous distribution of the water throughout the powder. All mixtures with less than approximately 80% of the total pore volume filled with water felt dry to the touch.

All measurements were made at 25.0 °C.

Results and discussion

We consider the rate of loss of vapour from a sample containing a mass m of liquid with a thickness h of stagnant gas phase above it. As described fully in ref. 1, in the presence of a reasonably high gas flow rate, the evaporation rate E reaches a gas flow rate independent limit given by:

$$E = -\frac{dm}{dt} \approx \frac{MADP}{hRT} \quad (1)$$

where M is the molecular weight of the evaporating species, A is the surface area of the sample, D is the diffusion coefficient of the evaporating species in the stagnant gas space, P is the equilibrium vapour pressure, R is the gas constant and T is the absolute temperature. Eqn. (1) is valid for evaporating species with P much less than atmospheric pressure, a condition which is fulfilled for water at 25 °C. For this study, the

Table 1 Manufacturer's values of mean pore diameter, pore volume and surface area for the three silica samples investigated

Powder No.	Pore diameter /nm	Pore volume /ml g ⁻¹	Surface area /m ² g ⁻¹
1	3.0	0.43	550
2	6.0	0.75	500
3 ^a	14.2	1.10	309

^a This data refers to the specific sample lot used for this work and was determined by N₂ adsorption. Data for the other samples is taken from the product catalogue entry. It should be noted that the data for sample 3 agrees with the general catalogue values for this product within 5%.

flow rate of dry nitrogen was kept constant at 1920 ml min^{-1} , sufficiently high that eqn. (1) is valid. The stagnant layer thickness was kept constant at 21 mm. The same sized sample tube was used for all measurements and thus the value of A is also constant.

Fig. 1 shows typical initial mass loss plots. It can be seen that the initial evaporation rate of water contained within the 6.0 nm pore diameter silica particles is reduced relative to that of pure water. From eqn. (1), it can be seen that the rate reduction must arise from a reduction in the vapour pressure of the water since all other parameters are held constant in the experiments. For a liquid contained within the narrow pores of a solid, the vapour pressure is changed according to the appropriate form of the Kelvin equation.⁶

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2\gamma V_m}{RT(r_{\text{pore}}/\cos\theta)} \quad (2)$$

where P is the vapour pressure of the liquid in the pores, P_0 is the vapour pressure of bulk liquid, γ is the liquid–air surface tension, V_m is the molar volume of the liquid, r_{pore} is the pore radius and θ is the contact angle made by the liquid on the porous solid material. Because all parameters in eqn. (1) except P are held constant, we can equate P/P_0 with E/E_0 where E is the evaporation rate for a silica/water sample and E_0 is the rate for bulk water. Values of γ and V_m for water were taken from ref. 7. We assume that the contact angle θ for water within the pores is zero, as for pure water on clean glass.⁸ Fig. 2 compares the measured initial water evaporation rates for silica particles of different mean pore radii with those calculated according to eqns. (1) and (2). For each sample, the water content corresponds to 50% of the total pore volume as specified by the particle manufacturer. The agreement between theory and experiment is good. It is worth remarking that, for these powders containing water (which all feel dry to the touch), a rather small pore radius is required in order to significantly reduce the evaporation rate. Of course, from eqn. (2), it can be seen that the vapour pressure reduction is expected to be greater for liquids of higher molar volume. This point is relevant to the use of porous materials used to ‘soak up’ spillages of hazardous liquids.

We next examined the variation of evaporation rates from samples containing different fractions of the total pore volume filled with water. Fig. 3 shows the initial evaporation rate with fraction of the pore volume filled for particles with 6.0 and 14.2 nm diameter pores. For cylindrically shaped pores (*i.e.* with constant radius for all pore depths) one expects a constant evaporation rate until the pores are totally filled when,

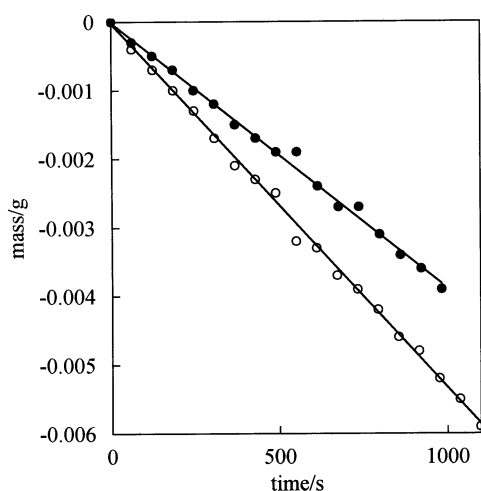


Fig. 1 Plots of sample mass *vs.* time for pure water (○) and 6.0 nm pore diameter silica particles with 50% of the pore volume filled with water (●). The solid lines are the best fit straight lines used to obtain the initial evaporation rates.

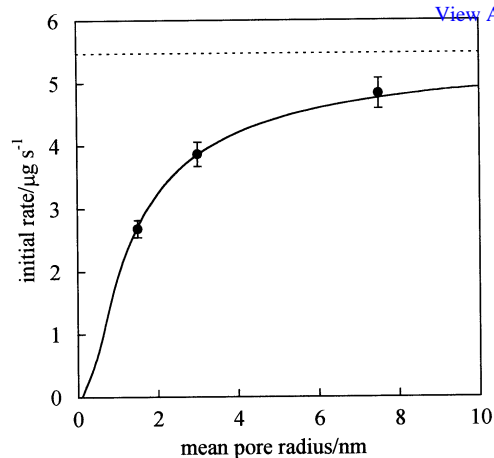


Fig. 2 Variation of initial evaporation rate with mean pore radius for particles with 50% filled pore volumes. The solid line is calculated according to eqns. (1) and (2). The dashed line shows the rate for pure, bulk water under these experimental conditions.

at total filling, the rate for bulk water should be obtained. From Fig. 3, it can be seen that the rates increase steadily with the fraction of pore volume filled which implies the effective radius of the pores changes as a function of the extent of filling. Using eqn. (2), the data of Fig. 3 has been converted to show the variation of effective pore radius with the fraction of pore volume filled (Fig. 4). Although the experimental uncertainties become large for big pore radii, this plot shows that

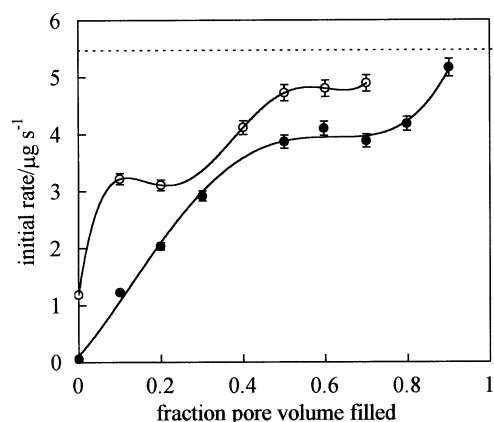


Fig. 3 Variation of initial evaporation rate with fraction of pore volume filled for 3.0 nm (●) and 7.1 nm (○) pore radius powders. The dashed line shows the evaporation rate for pure water.

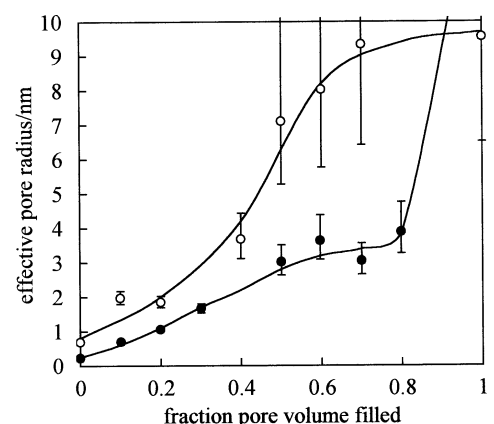


Fig. 4 Effective pore radius *vs.* fraction of pore volume filled for 3.0 nm (●) and 7.1 nm (○) mean pore radius powders.

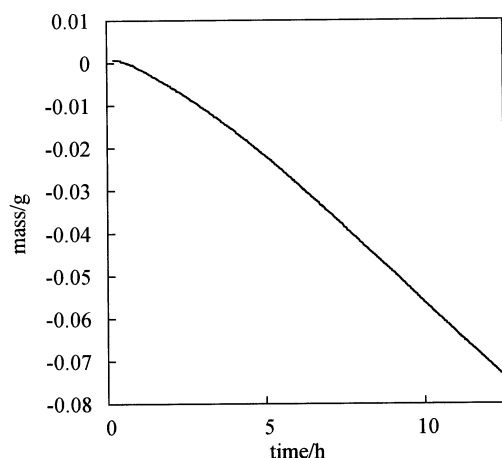


Fig. 5 Mass *vs.* time for a sample containing 1.04 g of 3.0 nm pore radius silica to which a volume of water corresponding to 50% pore volume filled has been added and overlaid with 1.04 g of dry silica of 3.0 nm pore radius.

the pores have a wide distribution of radii with, as expected, small radius pores being filled at low water contents.

We also investigated water evaporation rates in a more complex situation in which the sample tube was partially filled with a water containing powder and overlaid with dry powder. Fig. 5 shows the mass *vs.* time curve recorded for a sample with 1.04 g of 6.0 nm pore diameter silica containing water corresponding to 50% filling of the pore volume. This

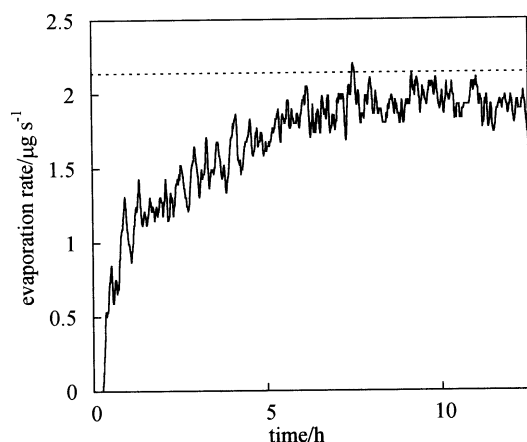


Fig. 6 Evaporation rate *vs.* time for the sample of Fig. 5. The dashed line shows the rate for 2.08 g of 3.0 nm silica with 25% of pore volume filled with water.

was overlaid with 1.04 g of dry 6.0 nm pore diameter silica. The final value of the stagnant gas layer thickness was 21 mm and the depth of the dry powder overlay was 10.5 mm. Initially, water evaporates from the 50% filled layer and equilibrates with the dry powder layer to give a sample corresponding to 25% pore volume filling. The data of Fig. 5 was differentiated to show the evaporation rate *vs.* time and is compared with the rate expected for a sample of (homogeneous) 25% pore volume filling in Fig. 6. It can be seen that the rate asymptotically approaches the rate expected for a powder with 25% filled pore volume at long times. The time taken to achieve homogeneous distribution of the water throughout the total powder volume is approximately 5 h.

Conclusions

We have shown that the evaporation rate of water contained within porous silica particles of different mean pore diameters is correctly predicted by the Kelvin equation. The evaporation rate varies with the extent of filling of the total pore volume showing that the pores have a non-cylindrical shape. The evaporation rate from a water-containing powder overlaid with a dry powder shows an initially slow rate but reaches the rate expected for a homogeneously filled powder sample after several hours.

Acknowledgements

We thank Dr M. T. McKechnie of Reckitt & Colman Products for helpful discussions. We are grateful to Reckitt & Colman Products and the University of Hull for funding.

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