Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Studies of Competing Evaporation Rates of Multiple Volatile Components from a Single Binary-Component Aerosol Droplet

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Supplementary Information

Evaporation rates of mixed ethanol:water droplets at varying temperatures

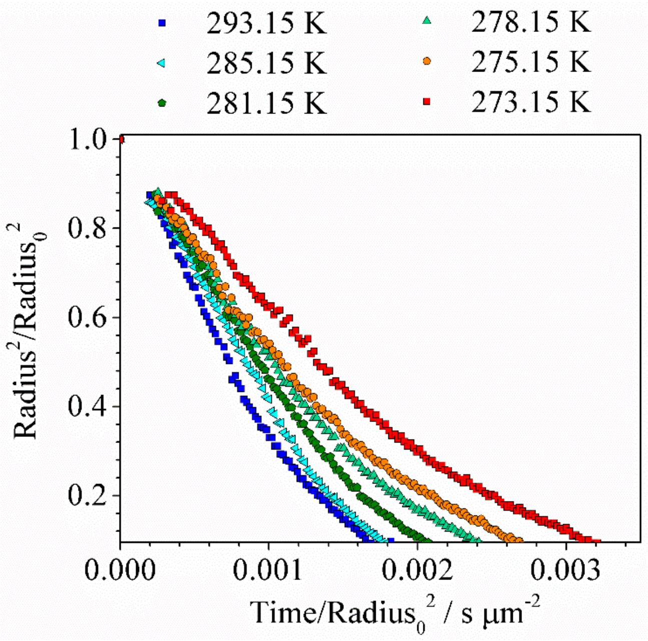

Figure S1: The evaporation profiles of droplets containing 70% ethanol : 30% water (wt/wt) in dry nitrogen over a range of gas phase temperatures. The data is the same as that presented in Fig. 2 in the manuscript but here normalised with respect to the initial radius^2.

Temperature-dependent vapour pressure of ethanol and water

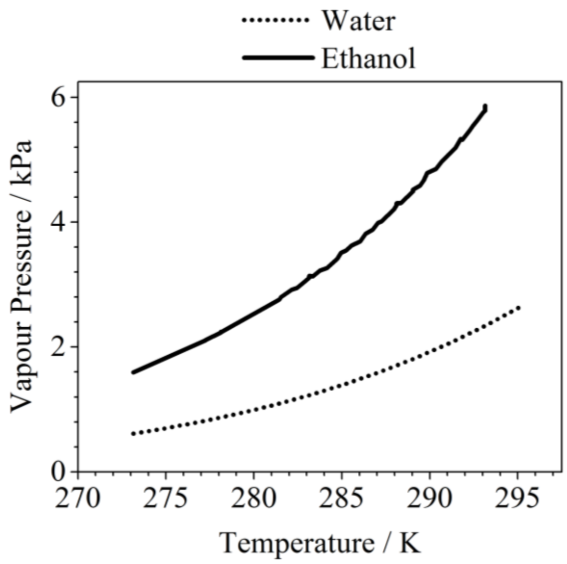

Figure S2: The pure-component vapour pressure of water and of ethanol, as a function of gas-phase temperature. [1,2]

Uncertainties in Evaporation Measurements and Sensitivities of Model Predictions

Compositional uncertainty in the experiment

Compositional changes in the initial solution prior to the experiment could occur from evaporation either from the bulk solution or at the tip of the droplet-on-demand generator. The droplet dispensers produce a droplet when an electric pulse actuates a piezoelectric crystal, forming a liquid jet of solution which breaks down into the single droplet that enters the CK-EDB chamber. To keep the concentration of solution at the dispenser tip to be assumed constant, it is continuously flushed through the dispenser with a pulse voltage of 10 Hz. The pulses in the continuous purge pulse-sequence have a lower voltage amplitude than that required for a droplet to travel far enough to reach the trapping region of the CK-EDB chamber, so that the droplets produced in the continuously purging pulses do not interfere with the droplet that is trapped. [3] This technique has been validated for the accurate study of the evaporation of aqueous droplets [4] however in this work when ethanol is present, its high volatility makes the 0.1 s time between each 10 Hz pulse critical. Given the relative volatilities of ethanol and water in the solutions, it is possible that the droplets actually appearing in the measurements could contain a higher fraction of water and lower fraction of ethanol than initially intended. This would explain the higher radius at the point of a change in evaporation rate in the experimental data compared to the model. Fig. 1 demonstrates the high evaporation rate of ethanol into dry conditions at 293 K, and Fig. 5a predicts the extent of compositional change that can occur in such a short timescale.

Fig. S3 present the results of the numerical model being run at different starting compositions of the droplets, with an increasing water content, and the fit between the model and experiment is seen to improve as the concentration of ethanol in the initial starting solution is lowered. The stated composition of the droplets was 50% ethanol : 50% water (wt/wt). For the data taken at 58% RH, a droplet composition of 40% ethanol : 60% water accurately reproduces the experimental data, whilst for the measurements at 87% RH and 91% RH a composition of 35% ethanol : 65% water is necessary for a match between model and experiment. Such losses of ethanol from the solution are larger than can be realistically expected, but may be a contributary factor in the mismatch between the experimental data and the model.

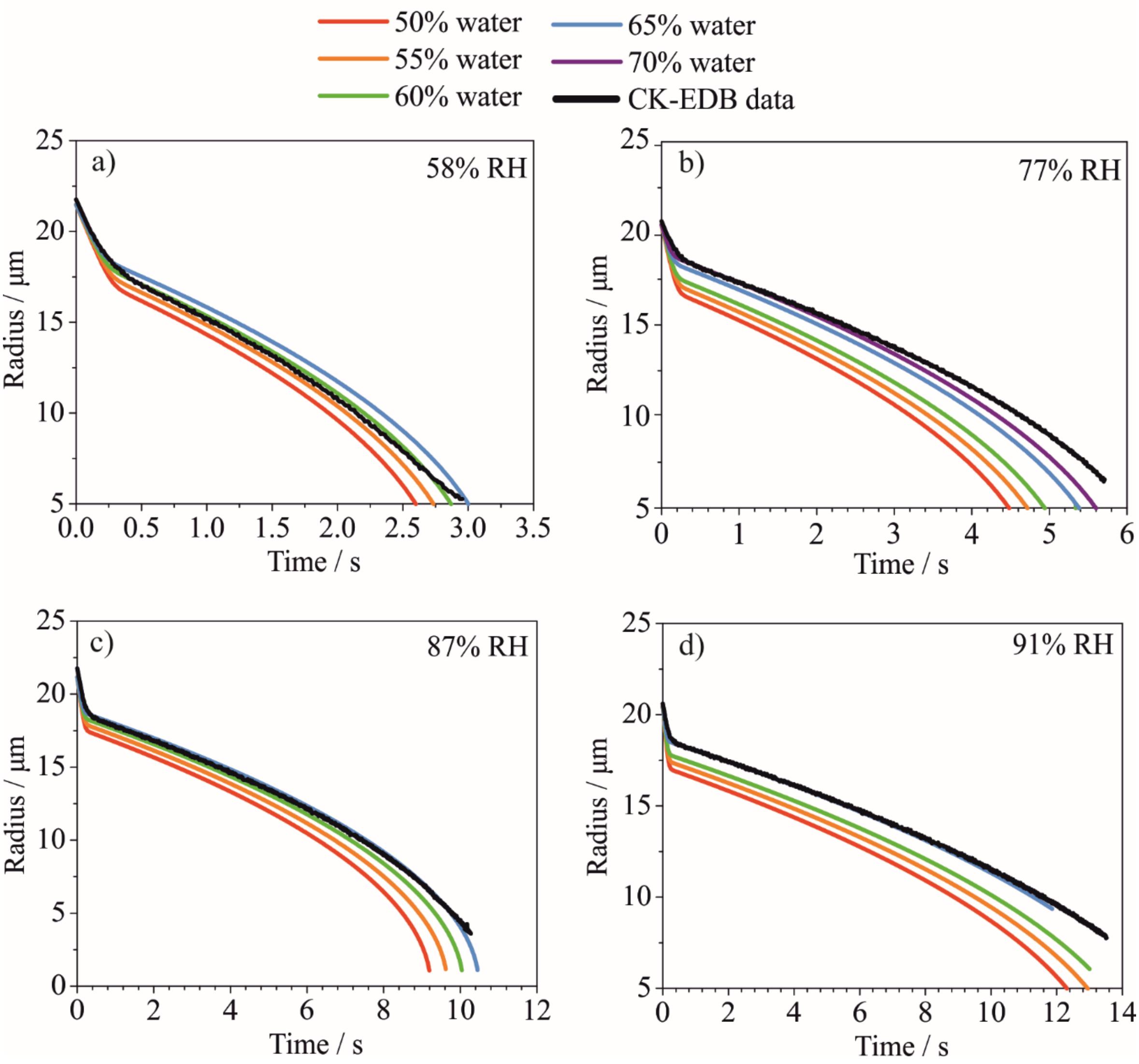

Figure S3: Simulations of droplets with varying starting composition from 50% ethanol : 50% water to 30% ethanol : 70% water, compared to the experimental data from the CK-EDB presented in Fig. 3a in the manuscript. The simulations were run at 293 K and gas phase RH of a) 58%, b) 77%, c) 87% and d) 91%.

Extrapolation of initial points to determine the radius at t=0

In previous work of measuring evaporation of aerosol droplets in a CK-EDB, the initial droplet size was estimated by a linear back extrapolation of the temporal dependence of the radius-squared (r^2) recorded immediately following droplet capture. [5] However, in this work, the initial evaporation rate of an ethanol-water droplet is likely to be non-linear in r^2 with time, as the droplet temperature is varying rapidly. The time-dependent evaporation rate of a pure ethanol droplet evaporating into 91% RH (i.e. the droplet in Figure 6a) is shown in Figure S4, along with the droplet temperature to demonstrate the correlation between droplet temperature and evaporation rate. The evaporation of the droplet during the water regime of the drying process (i.e. after 0.5 s into the droplet lifetime) has a constant rate and can be considered as isothermal. However, the evaporation of the ethanol from the droplet, in the first 0.4 s, is not following a constant rate, as shown in Fig. S4.

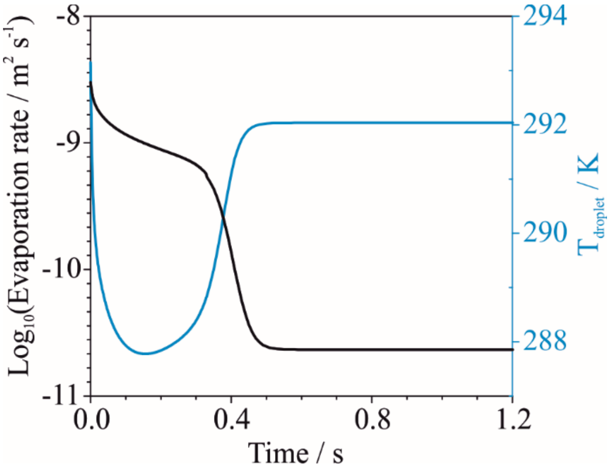

Figure S4: The model results of the evaporation rate of a pure ethanol droplet drying into an 91% RH environment, with the droplet temperature shown in blue.

The size of the droplet at *t*=0 to use in the model was extrapolated from the first 10 experimental datapoints using a linear fit in the r^2 and using a 2nd order polynomial fit in the r^2. The difference in initial radius values from these fits, and the resulting effect on the model is shown in Figure S5. Changing from a linear fit to a polynomial fit made the model lie closer to the experimental data, however the model still underpredicts the radius of the droplet at the inflexion point. The droplet starts at room temperature, but the initial evaporation is so fast that the droplet undergoes rapid evaporative cooling. Thus, in the first few milliseconds the droplet vapour pressure drops rapidly. [6] Thus, in the model results presented in this work a polynomial fit of r^2 versus time was performed to back extrapolate an initial droplet radius, as this is more likely to represent the initial non-isothermal part of the evaporation process. The use of the polynomial fit improved the mismatch between the experimental data and model prediction, but did not fully correct it.

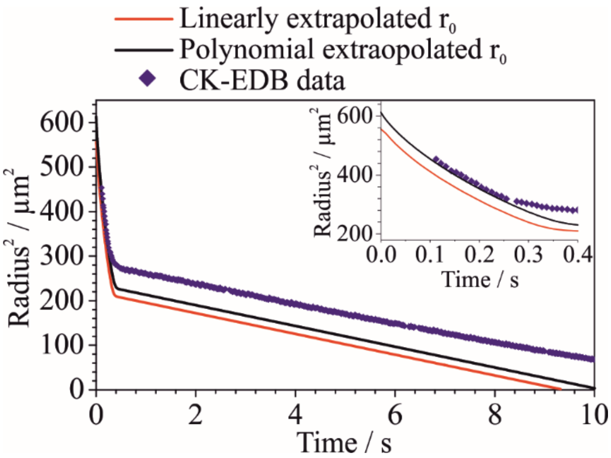

Figure S5: The effect on the model simulations of a pure EtOH droplet in 91% RH of changing the extrapolation method to retrieve the initial droplet radius. Inset: the first 0.4 s of the evaporation curve in greater detail.

Error in the initial t=0 point

The starting size of the droplet can strongly affect the model fit to the data, as it relates directly to the point of inflexion. A larger droplet will contain more water, and hence the inflexion point (at which water is assumed to be the only component remaining in the droplet) will occur at a larger radius and better match the data. Allowing a time shift of ± 0.1 s, although we do not believe this to be conceivable, does indeed make the model fit the data.

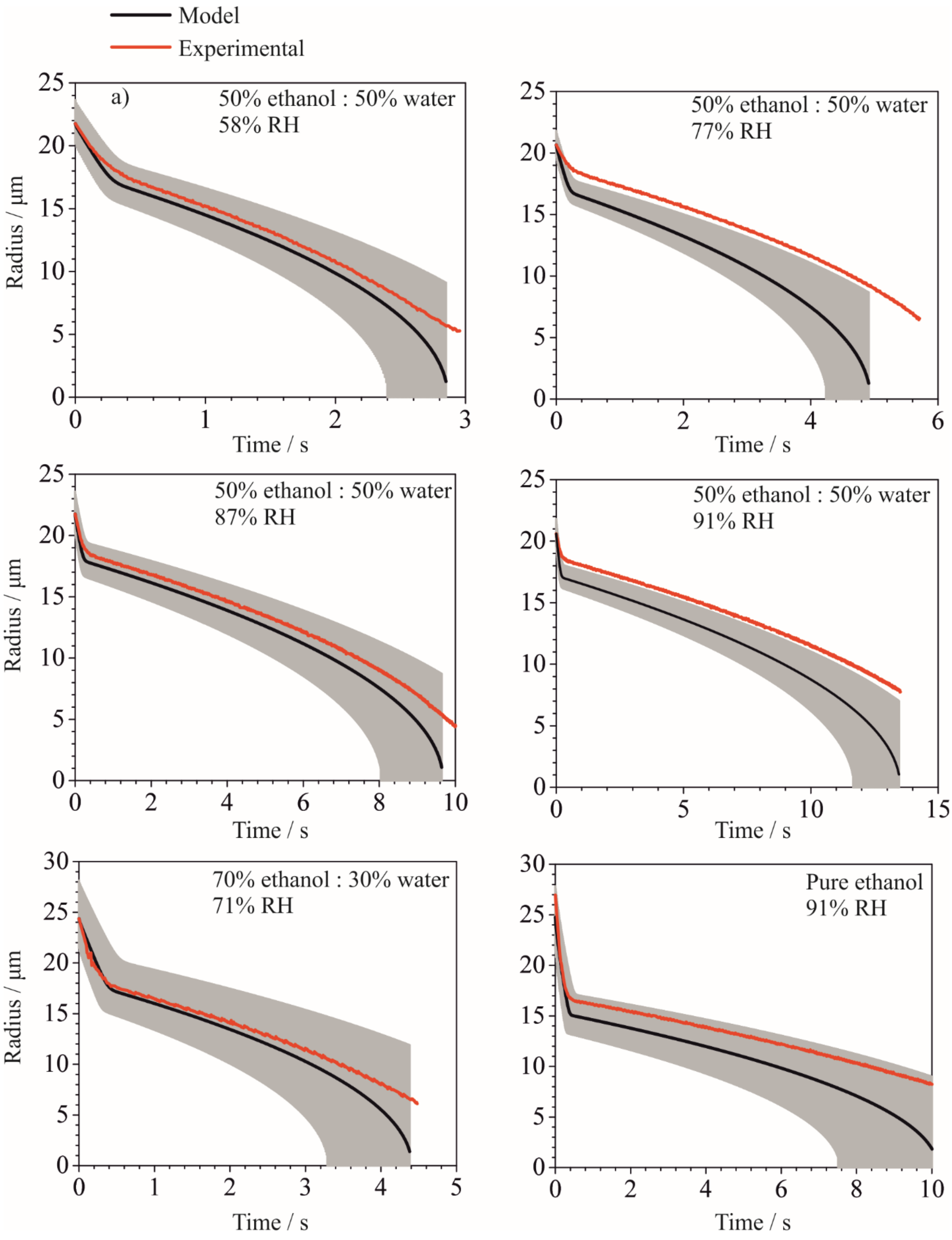

Figure S6: The effect that an error of ±0.1 s on the generation time of a droplet would have on the initial radius, and hence on the simulation of the evaporation of a mixed ethanol : water droplet into varying RHs at 293 K.

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