Interaction of Evaporating Multicomponent Microdroplets with Humid Environments

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INTRODUCTION

Evaporation and condensation of liquid aerosols or microdroplets are of importance in a broad area of environmental studies, engineering, pharmaceutics, and medicine [1,2,3]. These phenomena are especially crucial in the investigation of hygroscopicity of inhalable particles, as well as their manufacturing processes such as spray-drying. For instance, some quantity of water vapor might condense onto propellant droplets ejected from the mouthpiece of a pMDI in a humid environment, due to their low wet-bulb temperature [2,4], potentially affecting deposition and efficacy of the aerosol. Also, the calculation of evaporation rates and composition of co-solvent droplets are of great importance in the rational design of spray-dried particles [5].

In this work, a semi-analytical/numerical model and a single-particle levitation method have been combined to study the drying kinetics of multi-solvent droplets. Water and ethanol were chosen, because this co-solvent system is gaining popularity for the manufacturing of drugs with low aqeous solubility. Single water/ethanol droplets and

pure ethanol droplets were evaporated in a controlled humid environment, and the size history of the droplets was compared to numerical predictions.

EXPERIMENTAL METHOD

Droplets of pure ethanol or mixtures of ethanol and water were injected into the center of an Electrodynamic Balance (CK-EDB) using droplet-on-demand microdispensers (MJ-ABP-01, MicroFab Technologies, Plano, Texas, USA) [6]. An electrode induces a charge-separation on the droplets such that they become stabilized in the electric field at the center of the instrument, produced by applying an AC voltage to two concentric cylindrical electrodes. Illuminating the droplet with a 532 nm green CW laser causes interference between reflected and refracted rays, leading to an angular phase function pattern, which is collected by a camera centered at a 45° scattering angle. The angular separation between the fringes in the scattering pattern can be used to calculate the droplet diameter using the geometric optics approximation to Mie theory [7].

The droplet was confined within a gas flow, which is a mixture of dry and humidified nitrogen flows. Adjusting the mixing ratio with mass-flow controllers allows relative humidity (RH) control. A comparative kinetics approach is used to determine the RH in the chamber, whereby a probe water droplet was initially trapped in the instrument, and the comparison between the droplet evaporation kinetics and the well-established Kulmala model allows the accurate determination of the RH [8].

MODEL

For co-solvent systems the evaporation rate is expected to change as a function of time. This behaviour was modeled using Maxwell's equation to find the evaporation or

condensation rate of each component ($\dot{m}_i$), at each time-step during the evaporation according to the following equation [4]:

$$\dot{m}_i = -2\pi d D_{v,i}(C_{s,i} - C_{\infty,i}). \tag{1}$$

Here, d is the instantaneous droplet diameter, $D_{v,i}$ is the diffusion coefficient of each component in air and $C_{s,i}$, $C_{\infty,i}$ are the vapor concentrations at the droplet surface and far away, respectively. These values are then added together to give the total mass transfer rate of the multi-component droplet:

Next, the vaporization or condensation energies needed for each component are summed and used in an energy balance of the droplet, to find the instantaneous droplet temperature (T_d) as follows:

$$-\beta - K_{air}(T - T_\infty) = \frac{\rho_d c_p d^2}{12}\frac{dT_d}{dt}, \tag{2}$$

where,

$$\beta = \sum_i L_i D_{v,i}(C_{v,i} - C_{\infty,i}). \tag{3}$$

In these equations, K_{air}, ρ_d, c_p and L_i are thermal conductivity of the air, average droplet density, average droplet specific heat and latent heat of vaporization of each component, respectively. All material properties are then recalculated for the next time step according to this new droplet temperature.

Results and Discussions

Drying kinetics of micro-droplets of pure ethanol and water-ethanol mixtures at high humidity were studied for three cases. The initial droplet diameters are in the range of

48 µm to 53 µm, and the ambient temperature is 20.0 ± 0.5 °C in all the cases. The history of droplet size, water content and temperature for these cases are presented in Figure 1.

The size history and the change in evaporation rates predicted by the model match the experimental results. There is preferential evaporation of ethanol, due to its higher volatility. Also, it is observed that water condenses rapidly onto a pure ethanol droplet in humid air, due to the significant decrease in the temperature. The condensed water then evaporates after the ethanol is completely gone. This behaviour can also be infered from the evaporation rates (κ) and droplet temperatures (T_d) shown in these figures. Initially, the total evaporation rate is higher as ethanol is evaporating; this leads to a decrease in the droplet's temperature below the wet-bulb temperature at the respective ambient relative humidity. It is also evident that at higher humidity values, more water condenses on the droplet as expected. Also, the initial evaporation rates are lower at lower ethanol mass fractions, due to the depression of ethanol vapour pressure (due to lower temperatures) near the droplet's surface.

a)   0% water:100% ethanol by mass, 90.9% RH
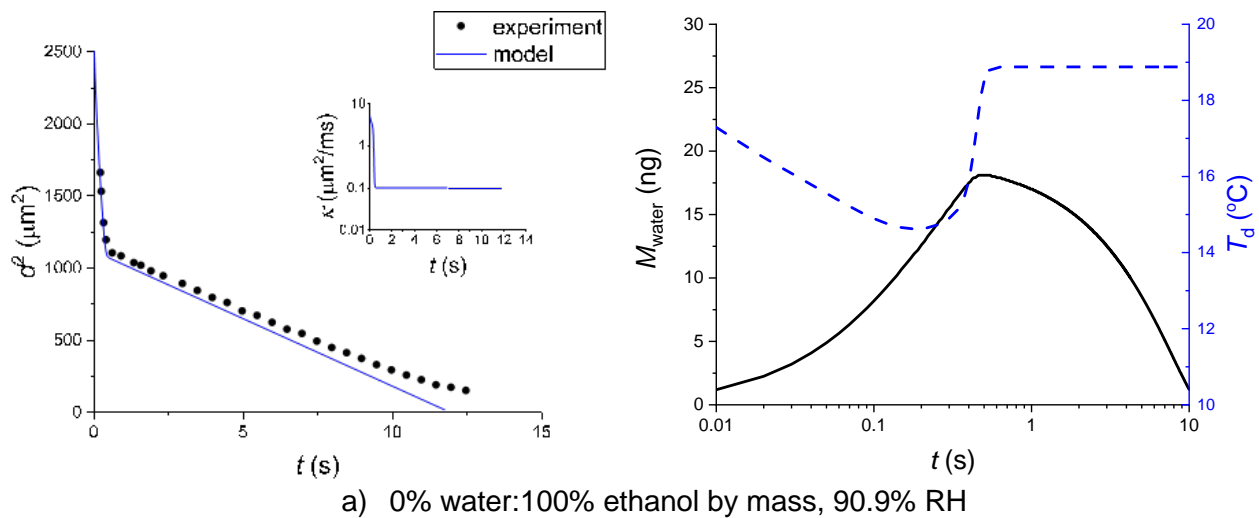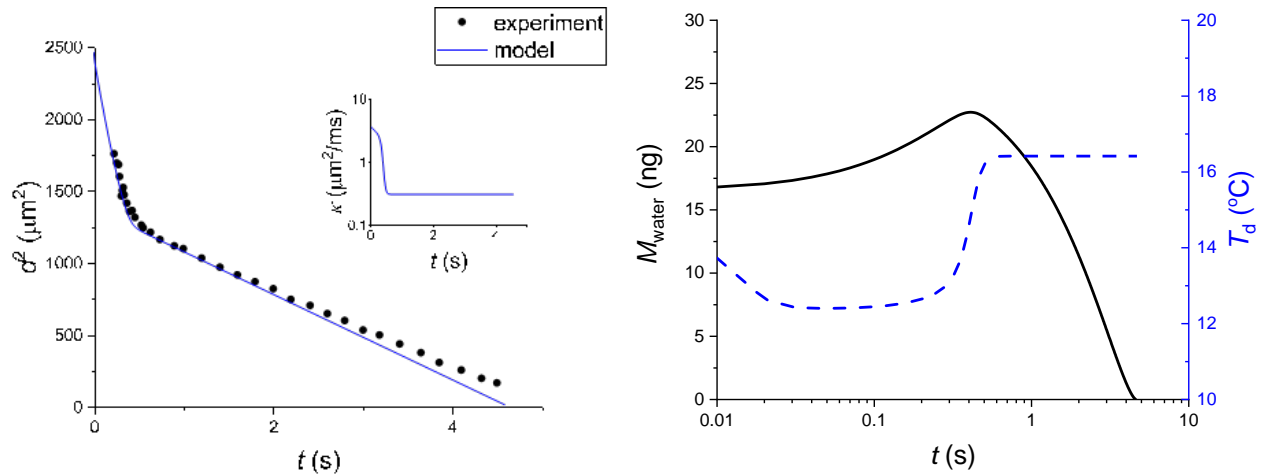
b) 30% water:70% ethanol by mass, 71.8% RH
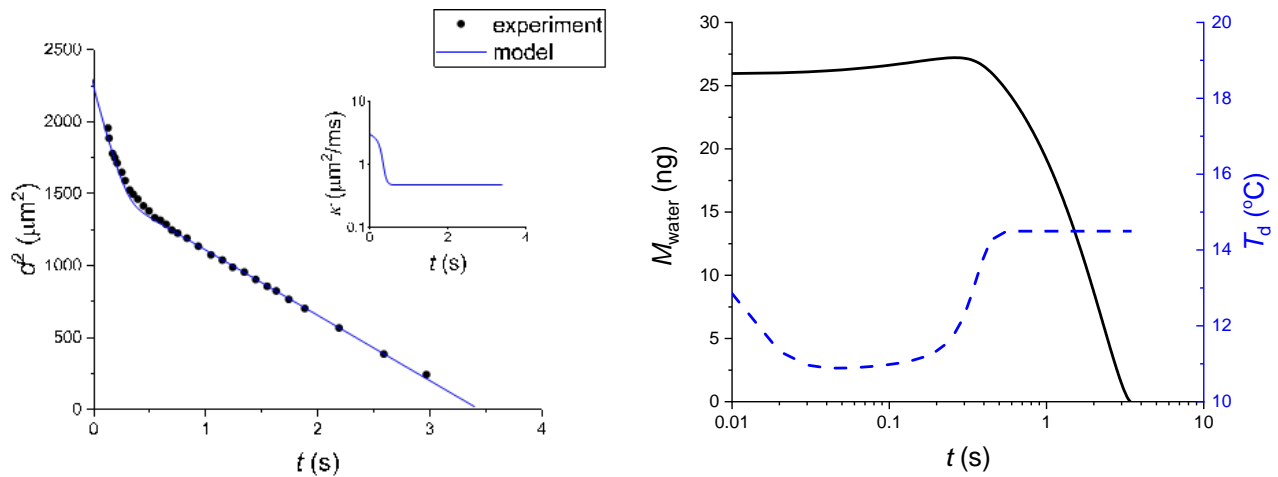
c) 50% water, 50% ethanol by mass, 58.0% RH

Figure 1 Size and composition history of the droplets. Plots on the left show the diameter squared vs time and inset plots show the evaporation rates. Plots on the right show water content (closed lines) and droplet temperatures (dashed lines) vs time. In all the cases the gas temperature was 20 °C.

Conclusion

It was shown that humidity of the drying environment has a significant effect on the evaporation rate and composition of multicomponent aerosol particles. This change of solvent composition might have a substantial impact on the properties of the inhaled therapeutic particles, because the actives or excipients may precipitate or dissolve as these changes occur. The methods discussed here can be used to study these phenomena in more detail.

ACKNOWLEDGEMENTS

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