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Citation for published version:

Wang, Z, Orejon, D, Sefiane, K & Takata, Y 2019, 'Coupled thermal transport and mass diffusion during vapor absorption into hygroscopic liquid desiccant droplets', International journal of heat and mass transfer, pp. 1014-1023. https://doi.org/10.1016/j.ijheatmasstransfer.2019.01.084

Digital Object Identifier (DOI):

10.1016/j.ijheatmasstransfer.2019.01.084

Link:

Link to publication record in Edinburgh Research Explorer

Document Version: Peer reviewed version

Published In: International journal of heat and mass transfer

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1 Coupled thermal transport and mass diffusion during vapor absorption

2 into hygroscopic liquid desiccant droplets

3 Zhenying Wang^{a,b,†}, Daniel Orejon^{a,b}, Khellil Sefiane^{c,a}, Yasuyuki Takata^{a,b,‡}

4 a International Institute for Carbon-Neutral Energy Research (WPI-I²CNER), Kyushu University, Fukuoka 819-0395, JP

5 b Thermofluid Physics Laboratory, Department of Mechanical Engineering, Kyushu University, Fukuoka 819-0395, JP

6 c Institute of Multiscale Thermofluid, School of Engineering, University of Edinburgh, King's Buildings, Edinburgh EH9 3JL, UK

7 Corresponding author: † z.wang@heat.mech.kyushu-u.ac.jp; ‡ takata@mech.kyushu-u.ac.jp.

8 Tel: (+81) 092-802-3133; (+81)092-802-3100.

9 ABSTRACT

Phase change phenomena at a droplet scale have gained extensive attention in recent years due to 10 the unique aspects that can be exploited in a wide range of domestic and industrial applications. 11 Different from existing studies on droplet evaporation and/or dropwise condensation, this work focuses 12 13 on the mechanisms of vapor absorption into hygroscopic liquid desiccant droplets, which are of interest to many dehumidification and absorption processes. In particular we investigate the coupled heat and 14 mass transport during vapor absorption into single droplets using optical imaging and infrared 15 thermography. Driven by the vapor pressure difference between the ambient and the droplet surface, 16 desiccant droplets grow due to water uptake. The droplet growth rate and final expansion ratio depend 17 on the ambient temperature and relative humidity. After liquid desiccant droplet deposition onto the 18 19 substrate, and as a consequence of the initial fast vapor absorption, droplets experience an increase in temperature. They then gradually cool down as a result of heat dissipation into the substrate and into 20 the ambient combined with the decrease in the vapor absorption rate, *i.e.*, heat of absorption. The 21 22 temperature rise measured by infrared thermography is confirmed by the calculation of the heat of absorption for six representative environmental conditions. Furthermore the vapor pressure at the 23

droplet surface is estimated by combining the changes of interfacial temperature and salt concentration 24 within the droplet bulk. As water absorbs into the droplets, the salt concentration decreases and so does 25 26 the driving force for vapor diffusion and hence the heat of absorption. As a contrast, experiments with evaporating water droplets show different evolution of droplet profile, different dynamics of the triple 27 28 contact line, as well as the occurrence of evaporative cooling. We conclude on the importance of taking account of the coupling mechanisms of absorptive heating and volume growth during vapor absorption 29 into liquid desiccant droplets. Findings presented here provide a valuable extension to existing 30 literature of phase change at the droplet scale, which contributes to a more complete understanding of 31 32 the role of liquid desiccant droplets in dehumidification processes.

33 Keywords: vapor absorption, liquid desiccant, droplet evaporation, heat transport, mass diffusion

34 1. INTRODUCTION

Liquid desiccant is a type of aqueous salt solution characterized by its excellent 35 hygroscopic properties [1] widely used in dehumidification [2] and absorption systems [3-5]. By taking 36 advantage of the vapor absorption capability of liquid desiccants, further optimization of indoor 37 environment control, energy conservation, and emission reduction, has been pursued. In the 38 abovementioned practical systems, the heat and mass transfer between liquid desiccant and humid air 39 (or water vapor) is paramount. This has gained increasing attention from researchers in the field of 40 energy system design and optimization. Nevertheless, despite the numerous existing studies on 41 dehumidification devices mainly carried out at the macroscale [6-9], the behavior of single liquid 42 desiccant droplets in contact with humid air has been scarcely reported. 43

44 Up to now, existing studies on the phase change phenomena at the droplet scale mainly focus on

droplet evaporation [10-14] and on dropwise condensation [15-17]. Different from single-component
droplets, liquid desiccant is a mixture of water and desiccant salt. The different composition of liquid
desiccant droplets provides unique hygroscopic properties that differ from those of pure liquid droplets.
Along with vapor absorption or desorption, the solute concentration within the droplet changes, which
in turn influences the solute diffusion and the phase transition at the droplet surface.

Regarding aqueous salt solution droplets, research mainly focuses on the evaporation behavior 50 and on the crystalline deposits from drying droplets due to water loss. Soulie et, al. [18] investigated 51 the behavior of aqueous saline-water (NaCl-H₂O) solution droplets with various salt concentrations. 52 53 They concluded on the strong effects of salt concentration on both contact line pinning and evaporation rate. Brenn [19] simulated the concentration distribution within aqueous salt solution droplets during 54 evaporation. Larger concentration gradient, function of the radial coordinate, is reported at high 55 56 evaporation rate. Misyura [20-22] carried out experiments with aqueous salt solution droplets on smooth and structured heated surfaces, and provided detailed analyses of the heat transfer within the 57 liquid layer and on the effect of crystallization on the evaporation rate. Zhong et, al. [23] studied the 58 effect of surface wettability on the evaporation of sessile saline droplets. Results demonstrate the 59 dependence of contact line dynamics and crystalline morphology on salt concentration and surface 60 wettability. Other influencing factors on the evaporation behavior and on the crystal patterns formed 61 from the dry-out of saline droplets have been presented by McBride [24], Shahidzadeh-Bonn [25], 62 Kaya [26], Harrington et al. [27]. The reader is also referred to the review papers of Sefiane and Parsa 63 et al. [28, 29]. 64

65 The studies reported above confirmed the strong effects of non-evaporative salt ions present in the

droplet on the evaporation process. For aqueous solution droplets, the vapor pressure at the droplet 66 surface is lower due to the existence of non-evaporating salt ions, and therefore a heated surface is 67 68 usually required to assist droplet evaporation. Moreover, the evaporation rate depends on the type of dissolved salt. As revealed by Misyura's experiments [30], the evaporation rates of NaCl, CsCl, and 69 BaCl₂ salt solutions are virtually constant throughout the complete evaporation process, whereas the 70 evaporation rates of LiBr, LiCl, CaCl₂, MgCl₂ liquid desiccant salt solutions decrease as a consequence 71 of the increase in salt concentration as water evaporates. Compared to ordinary salts such as NaCl, 72 desiccant salts (LiBr, LiCl, CaCl₂, MgCl₂) have much higher adhesion force to water molecules, 73 74 therefore, the vapor pressure at the droplet surface is strongly function of the salt concentration. Recently, Wang et al. reported on the mechanisms of growth and spreading of hygroscopic lithium-75 bromide droplets during water vapor absorption, initiating a new avenue for the study of the 76 77 fundamentals of vapor absorption into liquid desiccant droplets [31]. The mentioned work mainly focuses on the effects of substrate wettability on the vapor absorption rate and on the droplet dynamics. 78 An unexpected droplet spreading on hydrophilic glass substrates is observed and explained by 79 theoretical analyses. This work, on the other hand, focuses on the thermal transport and mass diffusion 80 process during vapor absorption. At ordinary ambient conditions and without additional substrate 81 heating, the vapor pressure at the surface of a liquid desiccant droplet becomes lower than the partial 82 vapor pressure of the ambient. Driven by the vapor pressure difference between the ambient and the 83 droplet surface, water vapor diffuses from the ambient towards the droplet interface. Then water gets 84 absorbed into the droplet bulk, and the droplet volume increases. Along with the vapor-liquid phase 85 change at the droplet surface, heat of absorption is released causing a temperature increase at the 86

droplet surface. Then, because of the induced temperature gradient, heat transfer between the droplet 87 and its surroundings takes place. The temperature change also influences the vapor pressure at the 88 89 droplet surface, which subsequently affects the vapor diffusion on the air side. The strong coupling of heat and mass transfer mechanisms in single liquid desiccant droplets shows the interesting and 90 91 complex phenomena taking place during vapor absorption at the droplet scale. A better understanding 92 of the coupling mechanisms of heat and mass transfer during vapor absorption is of significance to basic science and can be utilized for a better design of the initial stage in dehumidification processes. 93 Consequently, in this study, we investigate the heat and mass transport coupling mechanisms 94 during vapor absorption into lithium bromide desiccant (LiBr-H₂O) droplets in controlled 95 environmental conditions. The evolution of droplet profile and the temperature distribution at the 96 droplet surface are investigated using optical imaging and infrared (IR) thermography. In addition, 97 98 experimental observations of droplet growth during absorption into liquid desiccant droplets are compared to those of water droplet evaporation. In the case of water droplets, the effect of evaporative 99 cooling causes a temperature decrease at the droplet interface, and subsequently affects the evaporation 100 rate. Whereas in the case of liquid desiccant droplets, both the salt concentration and temperature at 101 the droplet interface will change due to water uptake and due to the heat released during phase 102 103 transition. The local change of the salt concentration and temperature at the droplet interface in turn 104 affects the driving force for vapor diffusion on the air side. Further analyses are carried out to quantitatively explain the heat and mass transfer mechanisms underlying the reported phenomena. We 105 conclude on the need for an accurate account of the coupled heat and mass transfer mechanisms in 106 order to provide a complete description of the vapor absorption process into liquid desiccant droplets, 107

108 which is of great importance for the accurate design of the initial stage for dehumidification processes.

109 2. EXPERIMENTAL METHODS

110 **Experimental setup:** Experiments are conducted within an environmental chamber with accurately controlled conditions (800L, -20 °C ~ 100 °C, 20% ~ 98% RH, PR-3KT from ESPEC Corp.). The 111 accuracy of environmental temperature is ± 0.5 °C, while that of relative humidity is $\pm 5\%$ RH. Figure 112 1(a) shows the experimental setup used in this study. Six representative experimental conditions are 113 chosen with ambient temperature of 25 °C, 45 °C, and relative humidity of 30% RH, 60% RH, 90% 114 *RH* (presented in Figure 2(a)). During experiments, the evolution of the droplet profile is recorded with 115 116 a high-definition CCD camera (Sentech STC-MC152USB with a RICOH lens and 25-mm spacing ring) at 4.8 frames per second, and an LED backlight is applied to enhance the image contrast. The recorded 117 video of the droplet profile is then processed with MATLAB[®] and ImageJ[®] to extract the evolution of 118 119 contact radius, R (mm), and contact angle, θ (deg), of the droplet with time, t (seconds). Figure 1(b) includes a typical snapshot of the droplet profile used to extract the droplet contact radius, contact 120 angle, and height. Further details regarding the experimental setup and procedure abovementioned can 121 122 be found in Ref. 31 [31]. Additionally, to be able to address the heat transport problem, an IR camera, FLIR SC-4000 with a spectral range between 3.0 and 5.0 µm and a resolution of 18 mK, is setup 123 vertically looking at the substrate from the top. Thermal evolution at the droplet liquid-gas interface is 124 125 recorded at 2 frames per second. The influence of ambient condition on the transmissivity of the air (different ambient temperature and different RH) between the droplet surface and the IR camera lens 126 is corrected depending on the experimental conditions using the ThermCam Researcher PRO 2.10 127 128 software from FLIR.



Figure 1 Overview of the experimental setup. (a) Experimental setup: environmental chamber, CCD camera, IR camera, back light, stainless steel vertical platform, x-y platform, droplet dosing system;
 (b) Data acquisition system with ImageJ[®] and Matlab[®].



Figure 2 Environmental conditions and surface characterization: (a) Experimental temperature and relative humidity shown on the psychrometric chart; (b) Cross profile of PTFE surface characterized by Olympus LEXT OLS4000.



systems, is investigated as the testing substrate. The representative cross profile of the PTFE surface 142 is shown in Figure 2(b), which is characterized with a confocal laser scanning microscope (Olympus 143 144 LEXT OLS4000, Japan). The thermophysical properties of PTFE are listed in Table 2. Before experiments, substrates are cleaned by immersing each sample in an ultrasonic bath with ethanol for 145 15 minutes. After that, the sample is taken out and flushed with large amount of deionized water. Then, 146 substrates are further dried with filtered compressed air to remove any possible remaining dust or 147 contaminants. After cleaning, the substrate is placed inside the chamber for sufficiently long time for 148 the substrate and the environment to reach equilibrium. Then, a droplet with a controlled volume of 149 150 3.2 ± 0.3 microliters is deposited on the PTFE substrate. We note here that the contact radius of both pure water and LiBr-H₂O droplets lies below the capillary length scale ($\lambda = \sqrt{\gamma_{lg}/\rho g}$ [32]), which is 151 ca. 2.7 mm for water and ca. 2.42 mm for 54 wt.% LiBr- H₂O in air at 20 °C. Thus, the gravity effect 152 153 on the droplet shape can be neglected and the droplet shape can be reasonably assumed as a spherical cap. Before droplet deposition, both CCD and IR thermography acquisitions are started, and the 154 evolution of droplet profile is recorded in time. Since the dosing system is also located inside the 155 environmental chamber, the temperature of both liquid desiccant and water before deposition can be 156 157 considered to be in equilibrium with that of the ambient.

Properties of 54% wt. LiBr solution and distilled water as specific heat capacity c_p (kJ/kg/K); 158 Table 1 density ρ (kg/m³); liquid-gas surface tension γ_{lg} (mN/m); dynamic viscosity v (mPa·s); thermal 159 160 conductivity k (W/m/K); and saturation temperature T_{sat} (°C). Properties shown were obtained at 161 20 °C and at 1 atm. Liquid type c_p (kJ/kg/K) ρ (kg/m³) γ_{lg} (mN/m) v (mPa·s) k (W/m/K) T_{sat} (°C) 54% wt. LiBr solution 1.98 1600 91.54 4.751 0.429 140 998 Distilled water 4.18 72.75 1.005 0.598 100

162

Table 2 Properties of PTFE substrate as density ρ (kg/m³); specific heat capacity c_p (kJ/kg/K); thermal

conductivity k (W/m/K); thermal diffusivity α (m²/s), $\alpha = k/\rho c_p$; substrate thickness δ (mm); surface 163 roughness $S_{a}(\mu m)$; and equilibrium contact angle for a 3 μ L water droplet, θ_{0W} (°), and LiBr-H₂O 164 165 droplet, $\theta_{0,S}$ (°), at 20 °C and 1 atm. k α ρ c_p δ S_{q} Equilibrium Equilibrium Material (mm) (μm) $\theta_{0,\mathrm{W}}(\circ)$ $\theta_{0,\mathrm{S}}(\circ)$ (kg/m^3) (kJ/kg/K) (W/m/K) (m^2/s)

0.52

10.0

0.357

0.25

 $95^\circ \pm 3^\circ$

 $101 \pm 3^{\circ}$

166 **3. EXPERIMENTAL RESULTS**

1.05

167 **3.1. Evolution of droplet profile**

2200

PTFE

168 Figure 3 shows typical profile evolution of LiBr-H₂O droplets at 45°C and humidity of 30%*RH*, 60%RH, 90%RH. Figure 4 represents the variation of the contact angle, θ (deg), and the non-169 dimensional contact radius, R/R_0 , of LiBr-H₂O droplets versus non-dimensional time (normalized by 170 the experimental duration), τ . On a smooth PTFE substrate, the initial contact angle of LiBr-H₂O 171 droplet is ca. $101^{\circ} \pm 3^{\circ}$. As vapor absorbs into the droplet, an expansion in volume is recorded 172 especially when the ambient humidity is high. The droplet expansion is demonstrated by the 173 174 simultaneous increase in droplet height and contact radius, while the droplet contact angle remains almost constant throughout the entire experimental duration. At high humidity conditions of 90% RH, 175 the contact angle decreases by ca. 5°, which is attributed to the decreasing liquid-air surface tension as 176 177 the desiccant solution gets diluted due to water uptake. On the other hand, the contact radius increases depending on the ambient humidity. When the ambient humidity is low, e.g. 30% RH, the contact 178 radius increases slightly to about 1.03~1.05 times of its initial value after 10 minutes. At ambient 179 180 humidity of 60% RH, the contact radius increases more significantly to 1.14~1.20 times of its initial value after 30 minutes. At higher ambient humidity of 90% RH, the contact radius of LiBr-H₂O droplet 181 keeps increasing to about 1.6 times of its initial value. 182





Figure 3 Profile evolution of LiBr-H₂O droplets during vapor absorption for ambient condition of 45°C and 30% *RH*, 60% *RH*, 90% *RH*, for $\tau = 0, \tau = 0.25, \tau = 0.5, \tau = 0.75$ and $\tau = 1$.







almost constant and θ decreases along with time to account for the loss of volume for the first 20% of 194 the droplet lifetime. Thereafter, as the contact angle decreases to approximately $86^{\circ} \pm 3^{\circ}$, the contact 195 196 line starts receding and droplets evaporate in the constant contact angle (CCA) mode, where θ remains almost constant, and R/R_0 monotonically decreases. The CCA mode lasts for approximately 60% of 197 198 the overall droplet lifetime. Lastly, as the droplet becomes smaller, towards the end of the evaporation process, droplet evaporation turns into a mixed mode where both θ and R/R_0 decrease, which takes 199 approximately the remaining 20% droplet lifetime. The three distinctive regimes reported here, *i.e.*, 200 CCR, then CCA and lastly the mixed mode, are in agreement with previous studies [11,33-35] on water 201 202 droplets evaporating on smooth PTFE substrates.



Figure 5 Profile evolution of pure water droplets during evaporation for ambient condition of 45°C and 30% *RH*, 60% *RH*, 90% *RH*, for $\tau = 0$, $\tau = 0.25$, $\tau = 0.5$, $\tau = 0.75$ and $\tau = 1$.

203



Figure 6 Evolution of (a) contact angle θ (deg), and (b) non-dimensional contact radius R/R_0 of pure water droplets, versus non-dimensional time, τ , for (closed symbols) $T_{amb} = 25$ °C and (open symbols) $T_{amb} = 45$ °C at (square) 30% RH, (up-triangles) 60% RH, and (diamonds) 90% RH on smooth PTFE.

3.2. Evolution of droplet volume

Figure 7 presents the volume evolution of LiBr-H₂O droplets during vapor absorption and that of

212 pure water droplets during evaporation. Moreover, initial vapor absorption and evaporation rates for

the six experimental conditions are included in Table 3.



Figure 7 Evolution of non-dimensional droplet volume with respect to the original volume, V/V_0 , along with time, t (s), during vapor absorption and evaporation for the six environmental conditions.

217Table 3Initial evaporation rate, -dV/dt, and initial vapor absorption rate, dV/dt, for the six experimental218conditions. (We note here that at 30% *RH*, the vapor absorption is very small, thus calculations are219only carried out for 60% *RH* and 90% *RH* conditions)

			-			,	
-	Condition	25°C30%RH	25°C60%RH	25°C90%RH	45°C30%RH	45°C60%RH	45°C90%RH
-	Absorption rate <i>dV/dt</i> (nL/s)	-	4.20	4.59	-	5.96	6.97
	Evaporation rate - <i>dV/dt</i> (nL/s)	4.25	3.02	0.83	9.42	5.40	1.27

From both Figure 7 and Table 3, it is clear that both evaporation and vapor absorption rates are 220 strongly function of the ambient condition. In the case of LiBr-H₂O droplets, both ambient temperature 221 and relative humidity have an impact on the initial instantaneous vapor absorption rate, whereas the 222 final droplet volume is only function of the relative humidity. From Table 3 the vapor absorption rate 223 increases with ambient temperature and with relative humidity. For the presented cases, the initial 224 vapor absorption rate follows the order of $dV/dt|_{45^{\circ}C90\% RH} > dV/dt|_{45^{\circ}C60\% RH} > dV/dt|_{25^{\circ}C90\% RH} > d$ 225 $dV/dt|_{25^{\circ}C60\% RH}$. Regardless of ambient temperature, the final normalized volume is almost the same 226 for the same relative humidity: V/V_0 (30% RH) ≈ 1.1 , V/V_0 (60% RH) ≈ 1.6 and V/V_0 (90% RH) ≈ 3.0 227 228 \sim 3.5. In the case of pure water droplets, the evaporation rate increases with ambient temperature, while it decreases with increasing relative humidity. For the six experimental conditions, the evaporation rate 229 follows an order of $-dV/dt|_{45^{\circ}C30^{\circ}RH} > -dV/dt|_{45^{\circ}C60^{\circ}RH} > -dV/dt|_{25^{\circ}C30^{\circ}RH} > -dV/dt|_{25^{\circ}C60^{\circ}RH} > -dV/dt|_$ 230 $dV/dt|_{45^{\circ}C90\% RH} > -dV/dt|_{25^{\circ}C90\% RH}$ as presented in Table 3. 231

232 4. ANALYSIS AND DISCUSSION

233 4.1. Heat transfer analysis

234 Within the droplet, both heat convection and heat conduction may occur, which can be evaluated

by the Péclet number expressed as Eq. (1).

$$Pe=\rho c_p UR/k,\tag{1}$$

where R is the droplet contact radius, ρ is the density, c_p is the heat capacity, U is the radial flow 236 velocity within the droplet, and k is the thermal conductivity of the liquid studied. For evaporation of 237 water droplets with contact angles ca. 90°, the evaporative mass flux can be regarded as uniform across 238 the droplet interface [11, 36, 37]. In this case, the radial flow velocity, U, is rather low in the order of 239 240 10⁻⁷ m/s. In the case of liquid-desiccant droplets where the water vapor diffuses towards the droplet interface, homogeneous absorption flux is also expected for contact angles ca. 90°. Hence, the 241 242 concentration gradient along the droplet surface is rather small, and the concentration-induced Marangoni effect can therefore be neglected. Moreover, the IR images measured at the liquid-gas 243 interface also show the homogeneity of the temperature profile and the absence of thermal gradients 244 (Fig. 8(a) & Fig. 8(b)). In view of the above, we can then safely state that the radial flow velocity, U, 245 246 remains small and is not further enhanced by the presence of Marangoni flows. Then, the Pe number is estimated as << 1 [38], confirming that the convective heat transfer within the droplet is negligible 247 [39-41]. 248

The heat conduction process within the droplet can be further evaluated by the characteristic time, τ^* , given by Eq. (2).

$$\tau^* = \rho c_p h^2 / k,\tag{2}$$

where *h* is the droplet height. Taking into account the thermal properties of the LiBr-H₂O droplets and water droplets reported in Table 1, τ^*_{LiBr} is calculated as 10.51 s, and τ^*_{Water} is *ca*. 9.91s. Right after the deposition of a liquid desiccant droplet, a temperature profile within the droplet may develop during the first instants of the vapor absorption process. However, compared to the overall droplet lifetime $(\sim 10^3 \text{ seconds})$, the characteristic time for heat conduction is quite short, $\sim 1\%$ of the total lifetime. The timescale analysis indicates that the heat flux induced by evaporation or absorption can timely diffuse throughout the droplet volume so as to even out the temperature gradient within the droplet bulk, and we can consider the temperature distribution within the droplet as homogenous ($\nabla^2 T_{drop} = 0$) during most of the droplet lifetime.

Even though the spatial temperature distribution across the droplet is homogenous, the average 260 surface temperature of LiBr-H₂O droplets varies slowly along with time as a result of the balance 261 between heat absorption and dissipation. To provide further evidences on the temperature evolution, 262 263 Figure 8 shows the average temperature at the droplet surface in time along with characteristic IR thermography snapshots. It shows that the temperature distribution along the droplet surface is nearly 264 uniform throughout the vapor absorption process, which demonstrates experimentally the above 265 266 timescale analysis of heat transfer within the droplet. The droplet surface experiences the highest temperature right after being deposited on the substrate. This indicates that vapor absorption starts as 267 the droplet is generated from the needle and gets in contact with humid air. The released heat due to 268 269 vapor-to-water phase change and absorption causes the observed temperature increase when respect to ambient conditions. After being deposited on the substrate, the absorbed heat is at the same time 270 271 dissipated both through heat conduction towards the substrate, and through convective heat transfer 272 into the ambient air. As a combined result of heat dissipation and decreasing absorption rate, the droplet surface gradually cools down towards equilibrium with the ambient as indicated by Figure 8. In the 273 case of pure water, droplets experience the lowest surface temperature right after being deposited as 274 they cool down due to evaporative cooling, then gradually warm up as they reach equilibrium with the 275



Figure 8 Evolution of average temperature at droplet surface and corresponding IR images during vapor absorption for ambient conditions of 30% *RH*, 60% *RH*, 90% *RH*, and (a) 25 °C, (b) 45 °C.

Figure 9 summarizes the surface temperature increase of LiBr-H₂O droplets and decrease of pure 279 water droplets right after droplet deposition for the six experimental conditions. The initial temperature 280 change depends strongly on the ambient temperature and relative humidity. In general, the initial 281 temperature variation is more noticeable at high ambient temperature (45 °C) than at low temperature 282 (25 °C) independently of the liquid or the relative humidity studied. For the same ambient temperature, 283 the initial temperature rise of LiBr-H₂O droplets is more apparent at high relative humidity conditions, 284 while the initial temperature decrease for pure water droplets becomes smaller at high relative humidity 285 conditions. Typically, the increase in the surface temperature of a liquid desiccant droplet is function 286 of the absorption rate, while the decrease in the surface temperature of a water droplet is proportional 287 to the evaporation rate. Then, quantitative calculations of the average heat flux into the droplet surface 288 can be carried out based on the surface area and on the vapor absorption rate, or the evaporation rate 289 in the case of water droplets, by making use of eq. (3). Vapor absorption and evaporation rates are 290

291 calculated for the first instants right after droplet deposition.

$$\Phi_{q} = \frac{\dot{Q}}{S} = \frac{L_{vl}\rho \frac{dV}{dt}}{\pi \left(h^{2} + R^{2}\right)},$$
(3)

Where Φ_q represents the average heat flux across the droplet surface, kW/m², \dot{Q} is the rate of heat flow, kW, *S* repsrents the area of droplet surface, m², and L_{vl} is the latent heat released during vaporliquid phase change, kJ/kg. The calculation results are summarized in Table 4.



The heat flux induced by absorption heating or evaporative cooling differs depending on the ambient condition. In the case of LiBr-H₂O droplets, the absorption heat flux follows the order of $\Phi_{q,45^{\circ}C90^{\circ}RH} > \Phi_{q,45^{\circ}C60^{\circ}RH} > \Phi_{q,25^{\circ}C60^{\circ}RH} > \Phi_{q,25^{\circ}C60^{\circ}RH} > \Phi_{q,25^{\circ}C30^{\circ}RH} \approx \Phi_{q,4530^{\circ}RH}$, which corresponds

with the order of initial temperature rise in the six experimental conditions. Since vapor absorption is 305 driven by the partial pressure difference between the ambient and the droplet surface, at low relative 306 307 humidity conditions, *i.e.*, small gradient of concentration, the vapor absorption rate is rather low, hence similar values of average heat flux are reported for 30% RH conditions in Table 4. In the case of pure 308 water droplets, the heat flux caused by evaporative cooling follows the order of $\Phi_{q,45^{\circ}C30\%RH}$ > 309 $\Phi_{q,45^{\circ}C60\%RH} > \Phi_{q,25^{\circ}C30\%RH} > \Phi_{q,25^{\circ}C60\%RH} > \Phi_{q,45^{\circ}C90\%RH} > \Phi_{q,25^{\circ}C90\%RH}$, which also corresponds with 310 the order of initial temperature decrease at the surface of water droplets. For water droplets, 311 evaporation is driven by the partial pressure difference from the droplet surface to the ambient; hence 312 313 the high relative humidity conditions hinder droplet evaporation and the evaporative cooling effect. The quantitative calculations included above stress that the heat flux induced by absorption heating 314 and evaporative cooling is the dominating factor for the initial temperature variation at the droplet 315 316 surface during and right after droplet deposition. To accurately estimate the water vapor pressure at the droplet surface, the following mass transfer analysis takes into account the concentration variation 317 within the droplet bulk and the temperature variation at the droplet surface captured by IR thermograph. 318

319 4.2. Mass transfer analysis

The mass transfer process includes the vapor diffusion on the air side, the vapor-water transition at the droplet interface, and the solute diffusion on the droplet side. Typically, the mass diffusion rate in the gas phase is $10^3 \sim 10^4$ times of that in the liquid phase $({}^{D_{water/air}}/D_{LiBr/LiBr - H_20} \sim 10^{-5}/10^{-9} \sim$ $10^4)$ [42]. Therefore, the vapor absorption rate is limited by the mass diffusion process on the liquid side [31]. The solute diffusion rate, D_1 , on the liquid phase is related to the liquid temperature, *T*, and dynamic viscosity, μ , according to the Stokes-Einstein equation [43]. For the cases of 45 °C and 25 °C, 326 the ratio of solute diffusion rate within the droplet can be calculated as Eq. (4).

$$D_{1} = \frac{k_{B}T}{6\pi\mu r}, \quad \frac{D_{T_{1}}}{D_{T_{2}}} = \frac{T_{1}}{T_{2}}\frac{\mu_{T_{2}}}{\mu_{T_{1}}}, \quad \frac{D_{1,45^{\circ}C}}{D_{1,25^{\circ}C}} = \frac{318.15}{298.15}\frac{0.004286}{0.002963} \approx 1.54, \quad (4)$$

where $k_{\rm B}$ represents the Boltzmann's constant, and *r* is the radius of the spherical particle, *i.e.*, the Li⁺ and Br⁻ ions.

The above calculation presented in Eq. (4) shows that the solute diffusion rate at 45 °C is 50% 329 greater than that at 25 °C. Hence, at higher temperature, the solute diffuses more effectively from the 330 high concentration at the droplet bulk towards the interface. Then, droplets at higher temperature can 331 maintain a relatively higher solute concentration at the droplet interface. In response to the higher salt 332 concentration at the droplet interface, the vapor pressure is lower, and therefore the vapor absorption 333 rate at 45 °C is higher when compared to 25 °C especially at the initial stage of vapor absorption. The 334 greater absorption rates at high temperatures presented (in Table 3) in turn induce greater average heat 335 336 flux and a further increase of the surface temperature (see Table 4 and Figure 9, respectively).

The vapor pressure at the droplet interface, $P_{vapor,surface}$, can be evaluated according to the fitting correlations derived by Patek and Klomfar (Eqs. (5) and (6)) [44].

$$P_{vapor,surface} = P_{sat}\left(\Theta\right) \tag{5}$$

where P_{sat} is the saturation vapor pressure of pure water at "shifted temperature", Θ , due to the presence of dissolved salts. Θ is function of the mole fraction, x_{mole} , and temperature, T, of LiBr-H₂O solution, and can be calculated as Eq. (6).

$$\Theta = T - \sum_{i=1}^{8} a_i \left(x_{mole} \right)^{m_i} \left| 0.4 - x_{mole} \right|^{n_i} \left(\frac{T}{T_c} \right)^{t_i}$$
(6)

342 where T_c is the critical temperature of pure water, 647.096 K, $a = \{-2.41303 \times 10^2, 1.91750 \times 10^7, -1.91750 \times 10^7, -1.917500 \times 10^$

343 1.75521×10^8 , 3.25432×10^7 , 3.92571×10^2 , -2.12626×10^3 , 1.85127×10^8 , 1.91216×10^3 }, $m = \{3, 4, 4, 8, 1, 1, 4, 6\}$, $n = \{0, 5, 6, 3, 0, 2, 6, 0\}$, $t = \{0, 0, 0, 0, 1, 1, 1, 1\}$, and the mole fraction, x_{mole} , is calculated 345 by Eq. (7).

$$x_{mole} = \frac{x/M_{\rm LiBr}}{x/M_{\rm LiBr} + (1-x)/M_{\rm H_2O}},$$
(7)

where *x* is the mass fraction of LiBr solute in LiBr-H₂O solution, and *M* represents the molar mass. Since the initial concentration of the LiBr-H₂O solution is known, any increase in the droplet volume is due to water absorbed, from experimental observations of droplet profile evolution in time, the mass fraction of LiBr can be estimated.

Then, combining Eq. (5), (6) and (7), the vapor pressure difference can be calculated. Because the 350 vapor absorption rate is low and no apparent volume increase is observed at low relative humidity of 351 30% RH, in the following calculations we only consider 60% and 90% relative humidity conditions. 352 353 Figure 10(a) shows the evolution of vapor pressure difference between the droplet interface and the 354 ambient air during vapor absorption. From experimental observations of droplet profile, the vapor absorption rate is estimated in time, which is presented in Figure 10(b). Both Figure 10(a) and 10(b) 355 356 clearly indicate that vapor pressure differences and absorption rates are greater right after droplet deposition, independently of the condition studied. As vapor absorption proceeds and the droplet gets 357 diluted, the vapor pressure difference between the ambient and the droplet surface diminishes and so 358 does the vapor absorption rate. Moreover, the order of initial vapor pressure difference, $\Delta P|_{45^{\circ}C90\% RH}$ > 359 $\Delta P|_{45^{\circ}C60\% RH} > \Delta P|_{25^{\circ}C90\% RH} > \Delta P|_{25^{\circ}C60\% RH}$, corresponds with the order of initial vapor absorption rate 360 for the four experimental conditions, $dV/dt|_{45^{\circ}C90\% RH} > dV/dt|_{45^{\circ}C60\% RH} > dV/dt|_{25^{\circ}C90\% RH} > dV/dt|$ 361 362 $dV/dt|_{25^{\circ}C60\% RH}$.



363Figure 10Evolution of (a) calculated vapor pressure difference, ΔP (kPa), between the droplet364interface and ambient air, and (b) rate of droplet volume increase, dV/dt (µL/s) during vapor365absorption on PTFE substrates for ambient conditions of 25 °C, 45 °C, and 60% RH, 90% RH.

366 According to Eqs. (5) and (6), the influence of T_{surface} and x_{LiBr} on the vapor pressure at the droplet 367 surface, $P_{\text{vapor,surface}}$, are opposite. On one hand, the increase in T_{surface} induces the increase of $P_{\text{vapor,surface}}$, while on the other hand, the increase in x_{LiBr} causes the decrease of $P_{\text{vapor,surface}}$. Therefore, for constant 368 ambient conditions, *i.e.*, constant P_{amb} , the driving force for vapor absorption, $\Delta P = P_{amb} - P_{vapor,surface}$, 369 depends strongly on both T_{surface} and x_{LiBr} . As the vapor absorption process proceeds, both T_{surface} and 370 x_{LiBr} decrease with time. The decreasing T_{surface} tends to increase ΔP , whereas the decreasing x_{LiBr} tends 371 372 to decrease ΔP . Results on the evolution of the vapor absorption driving force ΔP included in Figure 10(a) show a clear decreasing trend of ΔP along with vapor absorption time. The decreasing ΔP 373 374 indicates that the influence of x_{LiBr} on ΔP greatly outweighs the influence of T_{surface} . As the droplet gets further diluted, the driving force decreases along with time due to the decrease in x_{LiBr} , and the vapor 375 absorption rate decreases accordingly as demonstrated in Figure 10(b). 376

4.3. Comparison with droplet evaporation

Based on the experimental results and analyses presented above, the main features during droplet

evaporation and vapor absorption are summarized in Table 5.

380	Table 5	Summary of features during droplet evaporation and vapor absorption on smooth hydrophobic PTFE
381		substrates (TCL: triple contact line, RH: relative humidity, CCR: constant contact radius).

Comparison	Vapor absorption	Water evaporation	
Droplet profile	Expands with advancing TCL	Shrinks with receding TCL	
Rate of evaporation/ vapor absorption	Increases with temperature and increases with <i>RH</i>	Increases with temperature and decreases with <i>RH</i>	
Heat transfer	Absorptive heating effect T_{surface} increases initially, then decreases along with time	Evaporative cooling effect T_{surface} decreases initially, then increases along with time	
Mass transfer	Solute diffusion dominates	Vapor diffusion dominates	
Driving force Decreases along with time Volume increases in a saturation trend		Constant if neglecting evaporative cooling Volume decreases linearly for droplets in the CCR mode	

382 In the psychrometric chart in Figure 11, solid black lines present the iso-relative humidity curves of humid air at 20% RH, 40% RH, 60% RH, 80% RH, 100% RH, while the dashed black lines present 383 the iso-concentration curves of LiBr-H₂O solution at 20 wt.%, 30 wt.%, 40 wt.%, 50 wt.%, 60 wt.%. 384 For pure water droplets, the droplet liquid-air interface is always saturated. During evaporation, the 385 physical state of the droplet liquid-air interface as humidity ratio (y-axis) versus temperature (x-axis) 386 transits from W₀ to W₁ along the saturation line (100% RH or 0 wt. % solute concentration), as marked 387 388 with blue arrows in Figure 11. After droplet deposition, the droplet experiences a decrease in interfacial temperature due to evaporative cooling, and as the droplet attains equilibrium with the ambient, the 389 interfacial temperature increases. For the high humidity case 90% RH (Figure 11 (a)), the temperature 390 at the droplet surface increases from 45 °C to T_{amb} , ca. 46 °C, while for the low humidity case 30% 391 *RH* (Figure 11 (b)) the temperature increases from 40 °C to T_{amb} , ca. 45 °C. It is noteworthy to mention 392 that at low ambient humidity conditions such as 30% RH, the effect of evaporative cooling is stronger 393

due to the greater driving force, ΔP , hence the initial surface temperature is lower, and the variation of droplet interfacial temperature is more apparent as presented in Figure 11(a).

396 On the psychrometric chart, the state point of LiBr-H₂O droplet indicates the solute concentration (dotted curve) within the droplet bulk, as well as the relative humidity (solid curve), temperature (x-397 398 axis), and humidity ratio (y-axis) of the equilibrium humid air layer near the droplet interface. In Figure 11, the state variations of LiBr-H₂O droplets during vapor absorption are marked with red arrows from 399 S₀ to S₁. Different from pure water droplets, the vapor pressure at the surface of LiBr-H₂O droplets is 400 much lower. For 54 wt.% LiBr-H₂O droplets, the vapor pressure is theoretically in equilibrium with 401 402 low humidity air of ca. 20% RH. As vapor absorption proceeds, LiBr-H₂O droplets get diluted with 403 decreasing salt concentration due to water uptake. As a result, the state of LiBr-H₂O droplet moves 404 across the iso-concentration curves shown in the psychrometric chart and toward equilibrium with the 405 humid atmosphere. Moreover, the heat released due to vapor-water phase change also causes the temperature increase in the droplet surface at early stages shown as the initial state points of LiBr-H₂O 406 droplets in Figure 11. At high ambient humidity such as 90% RH, the salt concentration of LiBr-H₂O 407 droplet decreases more markedly due to the large amount of water uptake, which induces a stronger 408 absorptive heating effect. Therefore, in high humidity cases, the state point moves across the iso-409 concentration curves with greater temperature decrease as marked with red arrow, $S_0 \rightarrow S_1$, in Figure 410 411 11(b).



Figure 11 Psychrometric chart of humid air at different relative humidity (solid lines), and equivalent humid air layer at the surface of LiBr-H₂O solution with different concentrations (dashed lines). Marks inside the graph presents the state of ambient air bulk (Green points, Air), the state variations of droplet during evaporation (blue arrows, $W_0 \rightarrow W_1$) and during vapor absorption (red arrows, $S_0 \rightarrow S_1$) for ambient conditions of 45 °C, and (a) 30% *RH*, (b) 90% *RH*.

417 **5. CONCLUSION**

418 The coupled heat and mass transfer process during vapor absorption into LiBr-H₂O droplet has been experimentally investigated under controlled environmental conditions. Due to the strong 419 adhesion force of LiBr salt ions to water molecules, the vapor pressure at the droplet surface is greatly 420 421 reduced, and water vapor diffuses from the air side to the liquid side, causing the growth of the droplet volume. Along with water vapor absorption, heat of absorption is released inducing a temperature 422 increase at the droplet surface. IR thermography shows that desiccant droplets experience the highest 423 surface temperature right after being deposited on the substrate, and then gradually cool down as a 424 combined result of the decreasing vapor absorption rate and the heat dissipation into the substrate and 425 into the ambient. Moreover, the initial temperature rise at the droplet surface is quantitatively in 426 427 agreement with the absorption heat flux depending on the ambient conditions studied.

428 The variation of surface temperature, in turn influences the vapor pressure at the droplet surface

and hence the vapor diffusion on the air side. The vapor pressure difference between the ambient air 429 and the droplet surface is evaluated taking into account the evolution of the surface temperature as well 430 431 as the evolution of the salt concentration in the droplet bulk. Along with water uptake, the desiccant solution gets gradually diluted, and the vapor pressure difference between the ambient air and the 432 433 droplet surface decreases along with time. We conclude on the need to couple the heat and mass transfer mechanisms taking place during vapor absorption into liquid desiccant droplets for accurately 434 predicting this phenomenon. Furthermore, similarities and differences in the mechanisms governing 435 vapor absorption into liquid desiccant droplets and those of water droplet evaporation have been 436 437 summarized.

438 Acknowledgements

The authors gratefully acknowledge the support received by the International Institute for Carbon-Neutral Energy Research (WPI-I²CNER). ZW acknowledges the support received by the Japanese Society for the Promotion of Science (JSPS). DO gratefully acknowledges the support received from JSPS KAKENHI (Grant no. JP16K18029 and JP18K13703). KS acknowledges the support received from EPSRC through the grant number EP/N011341/1. All the authors thank Dr. Prashant Valluri for sharing his ideas and providing valuable suggestions on the theoretical analysis.

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