

Factors Controlling the Drop Evaporation Constant

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In this paper, we discuss the factors affecting drop evaporation. We found that the droplet morphology at a specific temperature was controlled by the physical properties of the liquid itself, such as the molecular weight, density, diffusion coefficient in air, and heat of vaporization. Two processes are included in drop evaporation: diffusion of liquid molecules into the air (diffusion part) and flow of the liquid molecules from inside the drop to the free outer shell liquid layer within the liquid–vapor interface (evaporation part). The diffusion part remained steady during drying and was not sensitive to the variation of temperature. The evaporation part, however, was an active factor and determined the differences in drop evaporation behaviors.

Introduction

Drop evaporation is a common phenomenon in everyday life. A great deal of research has been conducted to understand this phenomenon. Over 100 years ago, Maxwell derived the classic relationship to explain the evaporation of a drop. He stated that the variation rate of the square of the contact base diameter was a constant which was proportional to the diffusion coefficient of the vapor, the molecular weight of the vapor, the vapor pressure, the liquid density, and the temperature.¹ Picknett first suggested that there existed two basic modes for evaporation, i.e., the constant contact angle mode, where the base shrank with time while the contact angle remained a constant, and the constant contact base mode, where the base diameter remained pinned while the contact angle decreased with time. Evaporation occurred either with these two distinct modes or with some combination of the two.² Bridi found that the evaporation rate scaled with the radius of the drop.³ Kuz, however, claimed that the evaporation rate was a parabolic function of the drop radius. He suggested that the evaporation proceeded until the drop radius reached the Tolman length, when the liquid and vapor are indistinguishable.⁴ Shanahan noticed that the drop evaporation process normally included three to four stages and described the shape features of each stage.⁵

In 1995, Rowan et al.⁶ revealed a very basic equation relating the changing rate of the drop volume, dV/dt , to its height, h : $dV/dt = -\lambda h$. This equation has been widely adopted for various purposes since its publication.^{7–10} The drop evaporation constant, λ , in the equation was defined to be $2\pi D(C_\infty - C_0)/\rho$ by Rowan et al., where D is the diffusion coefficient of the vapor molecules in air, ρ is the density of the drop liquid, and C_0 and C_∞ are the vapor concentrations of the liquid at the drop surface and at an infinite distance away from the drop, respectively. Physically, λ should be uniquely determined by the intrinsic properties of the liquid. However, this point was not reflected in the definition given by Rowan et al. In this paper, we focus on obtaining a better understanding of physical parameters governing the drop evaporation constant.

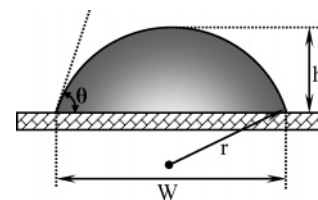


Figure 1. A schematic drawing of a sessile drop, with the definitions of the contact angle, θ , contact base diameter, W , drop spherical radius, r , and drop height, h .

Theoretical Background

A typical drop is illustrated schematically in Figure 1. According to previous studies,^{1–10} the evaporation exhibits the following relationship containing the shape and intrinsic properties of the drop:

$$\frac{dV}{dt} = -\frac{\pi DM}{\rho RT} W \frac{(1 - \cos \theta)}{\sin \theta} (P_s - P_\infty) \quad (1)$$

where M is the molecular weight of the liquid, R is the universal gas constant, T is temperature, W is the contact base diameter, θ is the contact angle, and $W(1 - \cos \theta)/(\sin \theta) = 2h$. P_s and P_∞ are the vapor pressures of the liquid on the drop surface and at infinite distance away from the drop, respectively.

Since the vapor pressure at the liquid–gas boundary (outer shell) is close to that of the saturated state, we may take P_s to be the saturated vapor pressure of the liquid. The saturated vapor pressure of a liquid is the partial pressure exerted by vapor molecules that are in equilibrium with the condensed state and is determined by the intermolecular cohesive energy in the liquid, which is linked to the heat of vaporization, ΔH_{vap} . The relationship between the saturated vapor pressure, P_s , and the heat of vaporization is given by the Clausius–Clapeyron equation:¹¹

$$\ln P_s = \frac{-\Delta H_{\text{vap}}}{RT} + K_1 \quad (2)$$

where K_1 is the value of $\ln P_s$ when $\Delta H_{\text{vap}} = 0$. At this ideal condition, there are no attractive forces between the vapor

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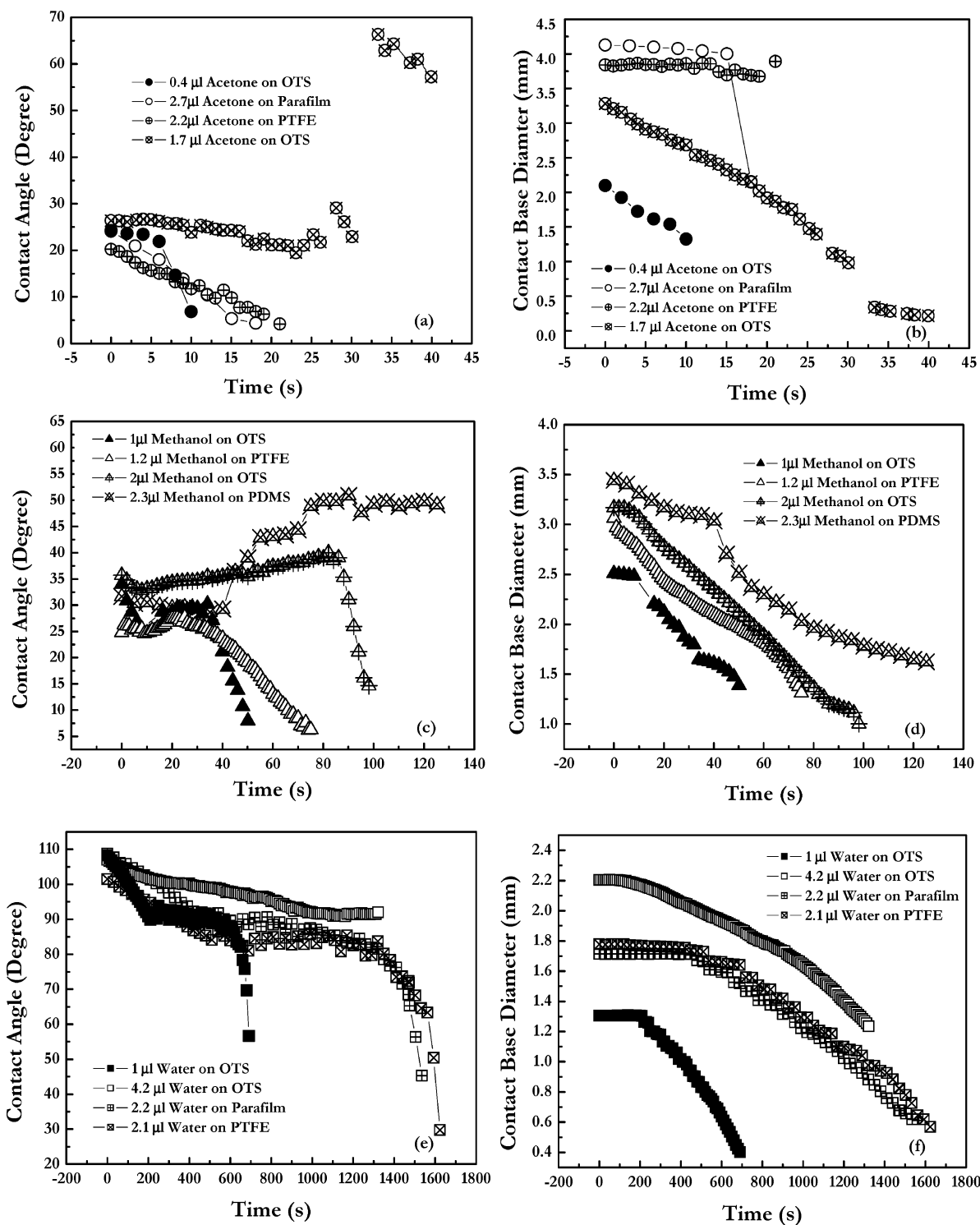


Figure 2. Contact angle, θ , and contact base diameter, W , versus time for multiple size drops of (a, b) acetone, (c, d) methanol, and (e, f) deionized (DI) water evaporating on different surfaces at 25 $^{\circ}\text{C}$ and 1 atm.

molecules, making the two coexisting phases indistinguishable. Thus, K_1 is a universal constant that is independent of the particular liquid.

For convenience, we assume P_{∞} to be zero. After combining eq 1 with the Clausius–Clapeyron equation, we obtain the following relationship for the behavior of a drying drop:

$$\frac{dV}{dt} = - \left[\frac{2\pi DM}{\rho RT} \exp \left(\frac{-\Delta H_{\text{vap}}}{RT} + K_1 \right) \right] h \quad (3)$$

Therefore

$$\lambda = \frac{2\pi DM}{\rho RT} \exp \left(\frac{-\Delta H_{\text{vap}}}{RT} + K_1 \right) \quad (4)$$

Since the molar volume of the liquid $V_m = M/\rho$, we further obtained

$$\ln[-(dV/dt)/2h] = \ln \frac{\pi DV_m}{RT} + \left(\frac{-\Delta H_{\text{vap}}}{RT} + K_1 \right) \quad (5)$$

To simplify the discussion, we define the left side and right side of eq 5 as C_{left} and C_{right} , respectively. Thus

$$C_{\text{left}} = \ln[-(dV/dt)/2h] \quad (6)$$

$$C_{\text{right}} = \ln \frac{\pi DV_m}{RT} + \left(\frac{-\Delta H_{\text{vap}}}{RT} + K_1 \right) \quad (7)$$

C_{left} contains all the geometric parameters and is a function of time. On the other hand, C_{right} describes effects from intrinsic properties of the liquid (D , V_m , and ΔH_{vap}) at temperature T . Therefore, the in situ shapes of the drop during evaporation are regulated by these intrinsic properties of the liquid in the drop. This relationship should remain constant regardless of the substrate (assuming no adsorption) and drop sizes.

Experimental Section

To test the hypothesis proposed above, we observed the evaporation of drops containing ACS grade acetone, methanol, deionized (DI) water, ethanol, and 1-butanol on different substrates, i.e., the octadecyltrichlorosilane (OTS; Aldrich)-covered hydrophilic silicon surfaces, poly(tetrafluoroethylene) (PTFE or Teflon; Dupont), Parafilm (Pechiney Plastic Packaging), and poly(dimethylsiloxane) (PDMS; Dow Corning). To remove the impurities on the testing surfaces that might affect the experimental results, we rinsed the surfaces in ethanol for 15 min and then dried them with compressed nitrogen gas right before the evaporation experiments. A CAM 200 optical contact angle meter (KSV Instruments Ltd., Helsinki, Finland) was used to observe and record the drying process of the drops. For accurate measurement, the contact radii of the drops were made to be less than the capillary length, $\kappa^{-1} = (\gamma_{\text{LV}}/\rho g)^{1/2}$, where γ_{LV} is the liquid–vapor surface tension and g is the acceleration due to gravity.¹² Room-temperature measurements were carried out at 25 ± 1 °C for all liquids. Observations of water evaporation at higher temperatures (36, 46, 56, 66, and 76 °C) were performed by first preheating the substrate and the liquid to the desired temperatures.

Results and Discussion

Both the size of the drop and the nature of the surface affected the evaporation. In Figure 2, we plot the contact angles, θ , and contact base diameter, W , vs time for acetone, methanol, and water drops of different sizes on various substrates at room temperature. It can be seen that drops composed of the same liquid under different experimental conditions (size and surface) show some diversity in drying behaviors. Size variation apparently affected the contact base diameters. For a given liquid and surface, larger drops had larger initial contact base diameters than smaller ones, despite the fact that their initial contact angles were similar. In addition, the duration of the constant contact

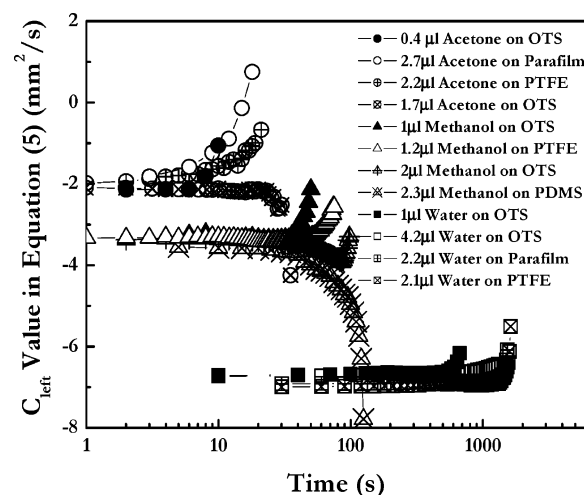


Figure 3. C_{left} values as calculated from eq 6 versus time for acetone, methanol, and water drops with various sizes evaporating on different surfaces at 25 °C and 1 atm.

angle mode lasted longer as the drop size increased. The nature of the surface also had a significant effect on the contact angle. For instance, the contact angles for water on OTS and PTFE were 108° and 97°, respectively. These differences can be attributed to different surface energies of the various substrates used. The contact base diameter curves in Figure 2b,d,f showed no similarity between the drops on different surfaces. All these observations are consistent with previous results.^{1–10}

By analyzing the θ vs t and W vs t curves as illustrated in Figure 2 using eq 6 and $V(t) = \pi W^3(2 - (3 \cos \theta) + \cos^3 \theta)/(24 \sin^3 \theta)$, the relationship between C_{left} (or $\ln(\lambda/2)$) and t can be obtained. In Figure 3 we plot the variation of C_{left} with time for acetone, methanol, and water drops of different sizes on different surfaces. From Figure 3, we see that, regardless of the diversities in the θ and W trends shown in Figure 2, the values of the shape correlation parameter, C_{left} , were similar for all the drops of the same liquid during the primary drying stage, assuming no adsorption happened on the substrate surfaces. The experimentally obtained C_{left} curves for acetone and methanol in Figure 3 differed in value from that of water drops. In Table 1 we list the C_{left} values calculated from experimental data using eq 6 and the C_{right} values calculated from the literature values of D , M , ρ , and ΔH_{vap} ^{13–16} using eq 7. It is seen that C_{left} and C_{right} are close to each other. This and Figure 3 demonstrated our above expectation that λ is a constant determined by the intrinsic properties of the drop liquids irrespective of the surfaces and the drop sizes used.

TABLE 1: Physical Properties of the Liquids, Values of C_{left} , C_{right} , and C_1 , Calculated from Eqs 6, 7, and 8, Respectively, and C_2 Calculated as $C_{\text{left}} - C_1$

liquid	T (°C)	M (g/mol)	ρ (g/mL)	D (cm ² /s)	ΔH_{vap} (kJ/mol)	C_{left} (mm ² /s)	C_{right} (mm ² /s)	C_1 (mm ² /s)	C_2 (mm ² /s)
water	25	18.00	0.9956	0.225	44.0	-6.95 ± 0.06	-7.24	-14.48	7.53 ± 0.06
	36	18.00	0.9922	0.240	43.3	-5.72 ± 0.03	-6.29	-14.45	8.73 ± 0.03
	46	18.00	0.9880	0.253	43.1	-5.22 ± 0.03	-5.67	-14.42	9.20 ± 0.03
	56	18.00	0.9832	0.267	42.7	-4.71 ± 0.04	-5.00	-14.39	9.68 ± 0.04
	66	18.00	0.9778	0.282	42.2	-4.19 ± 0.04	-4.33	-14.36	10.17 ± 0.04
	76	18.00	0.9718	0.297	41.6	-3.68 ± 0.07	-3.67	-14.34	10.66 ± 0.07
methanol	25	32.04	0.7914	0.145	35.2	-3.35 ± 0.08	-3.32	-14.11	10.76 ± 0.08
ethanol	25	46.07	0.7893	0.116	38.6	-4.09 ± 0.09	-4.54	-13.97	9.88 ± 0.09
1-butanol	25	74.12	0.8098	0.090	43.3	-5.73 ± 0.05	-6.15	-13.78	8.05 ± 0.05
acetone	25	58.08	0.7899	0.102	32.7	-2.13 ± 0.04	-2.07	-13.87	11.74 ± 0.04

From the right side of eq 5, we see that C_{right} contains two parts (C_1 and C_2) as

$$C_1 = \ln(\pi D V_m / RT) \quad (8)$$

$$C_2 = -\Delta H_{\text{vap}} / RT + K_1 \quad (9)$$

These two parts represent the two steps of the drop evaporation, i.e., evaporation (C_2) and diffusion of the vapor in the air (C_1).

Figure 4 shows the time dependence of C_{left} as calculated from eq 6, C_1 acquired from eq 8, and C_2 values for water drops evaporated on OTS at a series of temperatures. The C_2 values here are expressed as the difference between C_{left} and C_1 as $C_{\text{left}} - C_1$. At a certain temperature, D and V_m are fixed values, making the diffusion curve, C_1 , a straight line parallel to the x axis. During the prime time of drying, the C_{left} curves turned out to be irrelevant to time also. Thus, their difference, C_2 , was also a constant with time.

Table 1 also displays the C_1 and C_2 values. We can see that C_1 is negative and C_2 is positive for all our tested liquids. Thus, higher D values would accelerate the evaporation loss of liquid, while a higher heat of vaporization, ΔH_{vap} , would slow it down. Using the given M and ρ data of water, we found that V_m is not sensitive to temperature; between 25 and 76 °C, the V_m variation is only 2.5%. However, the diffusion coefficient, D , varied considerably (32%) within the same temperature range. Even so, the influence of D on C_1 is weakened since D is inside the natural logarithm sign. As a result, the variation of C_1 with temperature is very small, which can be seen from the four

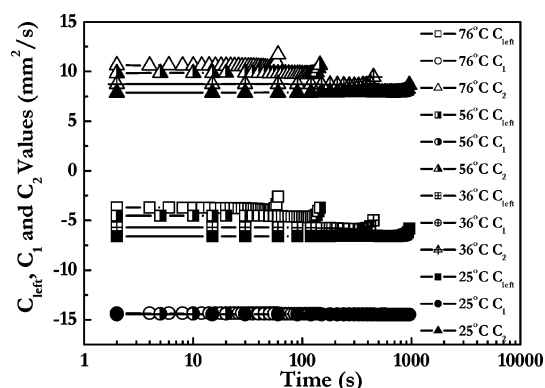


Figure 4. Calculated C_{left} , C_1 , and C_2 values versus time for water evaporating on OTS at various temperatures and 1 atm. C_{left} and C_1 are obtained from eqs 6 and 8, respectively, and C_2 is expressed as $C_{\text{left}} - C_1$.

overlapping C_1 vs t curves in Figure 4. Therefore, the temperature dependence of C_{left} shown in Figure 4 is primarily caused by variations in C_2 . In other words, it is the divergence in ΔH_{vap} that mainly contribute to the variations in drop drying behavior when temperature changes. Additionally, as shown in Table 1, C_2 values for drops of different liquids vary more than the corresponding C_1 values, indicating also that ΔH_{vap} is the dominant factor controlling drop evaporation.

Conclusions

The physical meaning of the drop evaporation constant in the Rowan equation $dV/dt = -\lambda h$ was found to be $\lambda = [2\pi DM \exp(-\Delta H_{\text{vap}}/RT + K_1)]/\rho RT$. The drop evaporation constant, λ , contains contributions from (1) diffusion of the vapor in the air and (2) evaporation. The diffusion is mainly controlled by the diffusion coefficient, D , of the liquid and is not sensitive to temperature or liquid composition. The heat of evaporation, ΔH_{vap} , of the liquid controls the evaporation part and regulates the drop evaporation.

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