WITHDRAWAL OF A CONICAL PIN FROM A POOL OF LIQUID

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ABSTRACT

The development of biochips leads to a straightforward, fast and cost effective method to obtain valuable genetic information. A key element of the emerging biochip technology is a microarray system, which fabricates high-density samples on solid materials of a microscopic area. In particular, dots of test liquid are printed on solids by a system of pins constituting a microarray. At present, however, the technique cannot make dots of arbitrary equivalent and controllable size. On the other hand, printing pins in microarrays represent themselves as a particular example of dip coating. In the experiments of the present work, a model of tapered stainless steel needle was withdrawn from different glycerine-water mixtures. Thicknesses and volumes of the withdrawn liquid films were measured as a function of the needle geometry, immersion depth, withdrawal rate, and physical parameters of the liquid. The experimental data are analyzed as a function of the capillary number Ca based on the withdrawal speed and compared to the predictions of the modified Landau-Levich-Deryagin (LLD) theory. The results show that for $Ca < 10^{-2}$ the thickness and the volume of the liquid follow the $Ca^{2/3}$ -scaling, while for $Ca > 10^{-2}$ — the $Ca^{1/2}$ -scaling, as it is expected from the LLD theory. Flow visualization is utilized to resolve the detail flow structure. The results put the key element of the pin-printing technology exploited in microarrays into a familiar hydrodynamic context of dip coating. This allows one to expect that under appropriate operational conditions, high-precision sampling could be attainable.

Keywords : Conical pin, Withdrawn liquid, Flow visualization.

1. INTRODUCTION

Microarray biochip is a newly developed technology, which combines the parallel processing of test samples and the minimization of large-scale instruments. This microarray technology allows setting more than thousands of biological samples, such as cDNA, oligonucleotide, polypeptide, *etc.*, on a small glass slides or plastic membranes. These biological materials cause a specific biochemical reaction with the test fluids, and the signal following the reaction can be quantitatively analyzed [1~5]. Because of the small volume of biochips, the amount of the reagent required for reaction is minute and the reaction is rapid, which fit well the trend of medical and pharmaceutical development.

Three primary technologies used at present in microarray manufacture include photolithography, injection, and microspotting [6]. The last is most

commonly used in the laboratories and also in industry due to its extraordinary simplicity and cost efficiency compared to the other manufacture processes. The process of microspotting technology consists of four stages: sampling, deposition, washing and drying [7]. The microspotting technique, however, suffers from some drawbacks. For example, the sample size is fixed and controllable sampling of arbitrary dot size is unattainable. There are no systematic methods to determine the appropriate operating conditions in the sampling technique. The subject of the present work is focusing on the sampling technique of microspotting. To reach the goal of handling this technique completely, we decided to investigate the parameters of the liquid films withdrawn by the printing-pin surface. The aim of this work is to obtain a relationship between the amount of liquid withdrawn by a printing-pin and various governing parameters.

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The present research concentrates on the immersion of a printing-pin into a liquid sample, pause, and withdrawal leading to entrainment of a liquid film attached to the pin surface. This stage is a key element in further determining the spot size on the chip and how many spots can be continuously printed after each sampling process. The withdrawal of a liquid film by a pin is due to the action of the viscous forces overbearing gravity and surface tension. In this sense, the present situation is kindred to the familiar process of dip coating of plates and fibers [8~13]. Theoretical understanding of dip coating dates back to the seminal works of Landau, Levich and Deryagin (LLD in short later) [14~16]. The LLD theory establishes itself as a relevant theoretical background for data processing in the present work. However, it should be emphasized, that we are unaware of any solution for the case of withdrawal by a conic surface, which is the topic of the present work.

Section II contains a brief description of the theoretical background of dip coating relevant to the present context. Section III describes the experimental setup and procedures. In Section IV, the experimental results on withdrawal film are presented. They are discussed in Section V in comparison to the theory. Transient character of flow in the pool is described in Section VI. Conclusions are drawn in Section VII.

2. THEORETICAL BACKGROUND OF DIP COATING

2.1 For a Flat Plate

In the case of dip coating, the liquid film is withdrawn by, for example, a flat plate being pulled from a deep pool filled with liquid. The film adheres to the plate due to the action of viscous forces, which overbear counteraction of gravity and surface tension. The first theoretical calculation for the thickness of the vertically withdrawn film far away from the horizon of liquid pool, denoted as h_∞ , was given in the seminal work of Landau and Levich [14] (also Levich [15]) as

$$h_\infty = 0.9458 a_c Ca^{2/3} \quad \text{for } Ca \ll 1. \quad (1)$$

Here a_c is the capillary length and defined as

$$a_c = \sqrt{\frac{\sigma}{\rho g}} \quad (2)$$

with ρ and σ being the liquid density and surface tension, and g the gravity acceleration. Also the capillary number

$$Ca = \frac{\mu U}{\sigma} \quad (3)$$

is the dimensionless withdrawal velocity with U being the vertical velocity of the plate, and μ the liquid viscosity.

On the other hand, for $Ca \gg 1$, the film thickness h_∞ should be independent of the surface tension σ , and can be written as,

$$h_\infty = \frac{2}{3} a_c Ca^{1/2} \quad \text{for } Ca \gg 1 \quad (4)$$

according to Deryagin and Levi [16].

2.2 For an Inclined Flat Plate

In the case of an inclined flat plate steadily withdrawn from a pool with velocity U , the thickness of the film given by Eq. (1) should be modified by a factor $(1 - \cos \theta)^{-1/2}$, where θ is the angle of the plate inclination to the horizon [13,16].

2.3 For a Circular Cylinder

In the case of dip coating of fibers for low capillary numbers (this is the most real manufacturing case), the dependence of $h_\infty \sim a_c Ca^{2/3}$ in Eq. (1) is replaced by $h_\infty \sim a_f Ca^{2/3}$, where a_f is the fiber cross-sectional radius [12].

2.4 For a Tapered Rod/Pin

In the present work, the model of a tapered rod/pin is used to simulate the printing pin as shown in Fig. 1. The coating on a cone is however hydrodynamically different

Fig. 1 The model printing pin used in the experiments of the present work. All the dimensions are given in mm and $\theta = 84.3^\circ$. The printing pin is connected to the traversing unit at the top end with $\phi 7.5$. L and AA' show the immersion depth and the free surface of the liquid in the pool before withdrawal has begun. BB' shows the instantaneous free surface of the liquid pool during withdrawal process.

from the above-mentioned cases of plates, cylindrical fibers, and even the inclined plate. This is due to the fact that the meniscus region near the cone, which moves not only upwards but also inwards, is always transient in distinction from the steady-state flows in this region in comparison with the withdrawal of plates and cylindrical fibers. (The transient character of the flow in the pool accompanying pin withdrawal is discussed in detail in Section VIB.) Even if the inertial effects accompanying the transient flow in the pool could be neglected (which is justified for low capillary numbers), withdrawal of a cone is still theoretically intractable in the framework of the LLD approach due to the geometrical complexity of the situation. Generally, when an almost vertical solid object is withdrawn at a constant speed, its lateral surface remains covered by a uniform liquid layer [15]. In this respect, the LLD theory yields a reliable estimate of liquid mass withdrawn per unit surface area. Then, a coarse extrapolation of the LLD theory on the case of a tapered cone could be done as the following. If the tapered printing pin is withdrawn vertically with velocity U_0 , then by using $U = U_0 / \sin\theta$ and substituting into Eq. (1), the film thickness can be approximated as

$$h_\infty = 0.9458 \frac{\sin^{-2/3} \theta}{(1 - \cos\theta)^{1/2}} a_c Ca_0^{2/3} \quad (5)$$

in the case of $Ca_0 \ll 1$, where the capillary number

$$Ca_0 = \frac{\mu U_0}{\sigma} \quad (6)$$

In the case of withdrawal of a cone with a high capillary number, Eq. (4) should be modified by a factor of $\sin^{-1/2}\theta$ [16]. For a tapered pin still $U = U_0 / \sin\theta$, and the film thickness can be approximated by

$$h_\infty = \frac{2}{3} \frac{1}{\sin\theta} a_c Ca_0^{1/2} \quad (7)$$

If a conical pin is immersed to a depth L (cf. Fig. 1), the surface area of the submerged part S is given by

$$S = \frac{\cos\theta}{\sin^2\theta} \pi L^2 \quad (8)$$

Combining Eqs. (5) and (8), we obtain the withdrawn liquid volume on a cone in the form of

$$V = 0.9458\pi \frac{\cos\theta}{\sin^{8/3}\theta} \frac{1}{(1 - \cos\theta)^{1/2}} a_c L^2 Ca_0^{2/3} \quad (9)$$

for $Ca_0 \ll 1$.

Similarly, by using Eqs. (7) and (8) in the case of $Ca_0 \gg 1$, we obtain

$$V = \frac{2}{3} \pi \frac{\cos\theta}{\sin^3\theta} a_c L^2 Ca_0^{1/2} \quad (10)$$

It is worthy to mention here that the approximate results of Eqs. (5), (7), (9), and (10) still do not account for the characteristics of the favorable pressure gradient resulting from the capillary pressure near the cone. This component leads to an additional liquid suction into the film withdrawn by the cone, and thus h_∞ might become L -dependent. This effect will dominate in the cases where the pin has not been deeply immersed at the beginning. It is discussed in detail in Section V. For the cases with deep initial immersion, the scalings with the capillary number in Eqs. (5), (7), (9), and (10) are expected to be reliable, since they stem from the basic force balance. Reliability of the scalings is supported by the experimental data of Section 4. On the other hand, the numerical factors before $a_c Ca_0^{2/3}$ and $a_c Ca_0^{1/2}$ in Eqs. (5) and (7), as well as before $a_c L^2 Ca_0^{2/3}$ and $a_c L^2 Ca_0^{1/2}$ in Eqs. (9) and (10), can still be affected by secondary geometric details. The factors will be discussed in Section V.

3. EXPERIMENTAL SETUP AND PROCEDURES

The model pin used in the present work is shown in Fig. 1, where all the dimensions (in millimeter) are also presented. A test flat-plate of the length 100mm, the width of 10mm and the thickness of 0.1mm was also used for comparison. Both the model pin and the plate were made from stainless steel.

Glycerine-water mixtures of 20, 50, and 70% weight concentration of glycerine were used as liquid samples. The advantages of glycerine are in its complete mixing with water at any concentration and in its relatively low volatility. The mixture of glycerine and water was contained in a 150mm (length) $\times$ 100mm (width) $\times$ 150mm (height) acrylic vessel. The density and viscosity of the working fluids were measured before each series of experiments to determine the capillary number accurately. The viscosity of the glycerine-water mixture was measured by a viscometer (Brookfield, model DVII+); the density was determined by direct division of fluid weight by volume. An electronic weight (Excell, EKW-6) was used to measure the weight; the volume was measured by a graduated cylinder.

A high speed video camera (FASTCAM-super 10K) was used to record the withdrawal process. The frame speed was set as 1,000 ~ 3,000FPS and the resolution of each frame was set as 256 $\times$ 120 pixel. To obtain the mass of the liquid withdrawn by the pin, a high precision balance with the accuracy of 0.0005g was used to measure the gained weight of the medicinal cotton bud, which was used to wipe off all the withdrawn liquid of the model pin. Each cotton bud was used only once to avoid the reduction of absorption performance that influences the experimental repeatability.

To withdraw the pin, a three-axial traversing unit (Isel automation) was initially used. The preliminary tests showed some problems at a small velocity range of

$U_0 = 0$ to 50mm/s due to the vibrations of the system. It was then replaced by a highly stable traversing unit (YAMAHA, model BPS-450). The whole experimental set up is sketched as shown in Fig. 2. The one-axial traversing unit, which used a servomotor to draw the whole model unit with a special designed rubber timing belt, was operated in the speed range of $U_0 = 1.2$ to 1,200mm/s. The vibration of the traversing unit is satisfactory small.

To visualize the flow below the free surface of the liquid sample, a small amount (about 0.1g) of PSP (Polymer Seeding Particle, about 50 micrometers in diameter) tracers have been added to the working fluid and premixed in the acrylic vessel. A laser sheet (about 1mm thickness), emitted from a 1W coherent argon ion laser, was introduced through the bottom surface of the vessel as shown in Fig. 2. The test model (flat plate or pin) was initially immersed in the vessel 60mm deep and then withdrawn at a constant lower ($Ca_0 = 0.0087$ or $U_0 = 24$ mm/s) and higher ($Ca_0 = 0.0424$ or $U_0 = 117$ mm/s) velocity, respectively. The flow visualization was collected by a digital camera (Nikon, model Coolpix 990).

4. EXPERIMENTAL RESULTS

The main factors affecting the thickness of the withdrawn liquid film on the pin surface are the withdrawal velocity, the physicochemical properties of the liquid, the immersion depth and the shape of the printing pin. The effects from each influential factor are investigated below, separately. The data obtained from the model of printing pin are also compared to those from a model plate.

4.1 The Calibration of the Actual Withdrawal Velocity

Denote the nominal withdrawal velocity set to operate the uniaxial traversing station by $U_{0,set}$. The actual value of the withdrawal velocity in the experiment, denoted as $U_{0,act}$, was recorded by the high-speed video camera. The time dependencies of the ratio $U_{0,act} / U_{0,set}$ are depicted in Fig. 3 for several $U_{0,set}$ -values. The time period from the start of pin motion till the instant of the pin tip leaving the free surface of liquid vessel is defined as t_s and is used as the time scale for the normalization. It is observed that the duration of the transient stage could reach more than $0.5t_s$ in the high speed region. Both unloaded and loaded (with pin model) cases have been calibrated and the results are the same within current measurement uncertainties. In the successive analysis of the experimental data, the withdrawal velocity U_0 is associated with the time-averaged values of $U_{0,act}$, i.e., the integral area under the $U_{0,act}-t$ plot divided by the total period.

4.2 Effects of the Model Material

Four different materials (stainless steel, iron, copper,

Fig. 2 The sketch of the experimental setup.

Fig. 3 The ratio of the actual withdrawal velocity to the nominal one.

and aluminum) have been used as the test material of the model. With the present glycerine-water mixtures used in the experiments, all the four materials led to the similar trend. Therefore, only the experiments done by using the stainless steel pin (SUS304) were shown and discussed in this paper.

4.3 Results of the Model Flat Plate

By calculating the total accumulated liquid volume on the pin model (mass is actually measured and then divided by the density) divided by the immersed area, the averaged thickness of the film on the model could be derived and denoted as h . Further define h' as h/a_c , where a_c is the capillary length. Figure 4 shows the experimental h' -data of a flat plate that is vertically withdrawn from a pool. The immersion depth of pin model was 60mm. The working fluid were mixture of (a) 70% glycerine-30% water, (b) 50% glycerine-50% water and (c) 20% glycerine-80% water (by weight), respectively. It shows that all the data from different liquids collapse excellently together in Fig. 4. The data

Fig. 4 Normalized thickness of the film withdrawn by a vertical plate versus the capillary number. The experimental data are shown by symbols. The fitting curves: 1- $h_{\infty}' = 0.9545 Ca^{0.6781}$ ($R^2 = 0.9977$), and 2- $h_{\infty}' = 0.4371 Ca^{0.5091}$ ($R^2 = 0.9975$).

in Fig. 4 are fitted by the dependences 1: $h_{\infty}' = 0.9545 Ca^{0.6781}$ and 2: $h_{\infty}' = 0.4371 Ca^{0.5091}$ corresponding to the ranges $Ca < 10^{-2}$ and $Ca > 10^{-2}$, respectively. The corresponding root-mean-square errors are 0.0023 and 0.0025, respectively. The scalings agree with those of Eqs. (1) and (4). The factor of Eq. (1) also agrees with the experimental data, while that of Eq. (4) overestimates them.

4.4 Effect of the Immersion Depth L of the Pin Model

In the rest of the present section, we shall concentrate on the experiments with the pin model. The data acquired for the printing pin model for different immersion depths are presented in Fig. 5. The mixture was 70% glycerine-30% water. They show that the thickness is independent of L for all the data ($L > 10\text{mm}$). This is consistent with the prediction of the LLD theory. The model printing pin used in industry, e.g. the conical part of the printing pin of TeleChem, is 2.1mm long and has a base of 0.16mm in diameter. Dependence of the thickness h_{∞} on L could become dominating for these short pins. It stems from the favorable gradient of the capillary pressure in the conical film, and will be explained in Section 5.

4.5 Effect of the Withdrawal Velocity of the Model Printing Pin

In the experiments, the withdrawal velocity U_0 was varied in the range of 3 to 300mm/s. The data were acquired for the immersion depth of $L = 60\text{mm}$ where the thickness of the withdrawn film h_{∞} has been proven to be L -independent. The mixture of 70% glycerine-30% water was used as the test fluid. The experimental results on the withdrawn liquid volume V are depicted in Figs. 6(a) and (b) by symbols, and the corresponding data calculated by Eqs. (9) and (10) are shown as solid lines and dashed lines, respectively. The comparison

Fig. 5 Normalized thickness of the withdrawn liquid film on the pin at different immersion depths. 1- $L = 10\text{mm}$, 2- $L = 20\text{mm}$, 3- $L = 30\text{mm}$, 4- $L = 40\text{mm}$, 5- $L = 50\text{mm}$, 6- $L = 60\text{mm}$, 7- $L = 70\text{mm}$.

Fig. 6 Volume of the liquid withdrawn by the model pin. The experimental data and theoretical results are shown by symbols and curves, respectively. (a) 1- $Ca_0 = 0.0011$ ($U_0 = 3\text{mm/s}$), 2- $Ca_0 = 0.0022$ ($U_0 = 6\text{mm/s}$), 3- $Ca_0 = 0.0043$ ($U_0 = 12\text{mm/s}$), 4- $Ca_0 = 0.0087$ ($U_0 = 24\text{mm/s}$), 5- $Ca_0 = 0.0130$ ($U_0 = 36\text{mm/s}$), 6- $Ca_0 = 0.0174$ ($U_0 = 48\text{mm/s}$), 7- $Ca_0 = 0.0261$ ($U_0 = 72\text{mm/s}$), 8- $Ca_0 = 0.0424$ ($U_0 = 117\text{mm/s}$), 9- $Ca_0 = 0.0786$ ($U_0 = 217\text{mm/s}$), 10- $Ca_0 = 0.1087$ ($U_0 = 300\text{mm/s}$), solid and dashed curves are calculated from Eqs. (9) and (10), respectively.

in Fig. 6(a) shows that the theory describes the data rather accurately for $Ca_0 < 0.01$. The results show that the withdrawn volume increases with the withdrawal velocity U_0 . This is to say, the sampling quantity can be well controlled by changing the withdrawal velocity. However, in the intermediate range $0.01 < Ca_0 < 0.1087$ the results still deviate from the limiting formula for $Ca_0 \gg 1$. It was also found that when the withdrawal velocities were extremely low, corresponding to the range of $Ca_0 < 10^{-4}$, liquid slipped off the pin after it had been withdrawn. This phenomenon will be explained in Section 5 later. Liquid slip off caused difficulties in measurements, increased errors, and made the sampling process less controllable.

4.6 Cumulative Data for the Model Printing Pin

The cumulative data for the model pin versus the capillary number are plotted in Fig. 7. The immersion depth was $L = 60\text{mm}$ and the liquid were 20%, 50%, and 70% glycerine-water mixture. It is seen that the dependences 1: $h_\infty' = 0.9908 Ca_0^{0.671}$ and 2: $h_\infty' = 0.4165 Ca_0^{0.495}$ fit the experimental data in the ranges $Ca_0 < 10^{-2}$ and $Ca_0 > 10^{-2}$, respectively. The root-mean-square errors are 0.0077 and 0.0046, respectively. It should be noted that these dependences are rather close to those found in subsection 4C for the films withdrawn by a flat plate, especially in the regime of low capillary number that the microarrays are commonly operated. The results put the sampling process of the modern pin-printing technology exploited in the microarrays into a predictable and familiar hydrodynamic context of dip coating. This allows us to expect that high precision sampling could be attainable under appropriate operation conditions, instead of the commonly used trial and error process.

Fig. 7 Normalized thickness of the film withdrawn by the model pin versus the capillary number. The experimental data are shown by symbols. The fitting curves: 1- $h_\infty' = 0.9908 Ca_0^{0.671}$ ($R^2 = 0.9923$), and 2- $h_\infty' = 0.4165 Ca_0^{0.495}$ ($R^2 = 0.9954$).

5. DISCUSSIONS OF THE EXPERIMENTAL DATA IN COMPARISON WITH THE THEORY

First, consider the data obtained for a plate withdrawn vertically from different glycerine-water mixtures (20%, 50%, and 70%-glycerine, cf. Fig. 4). Experiments were carried out at 20°C . Therefore the density, viscosity and surface tension of the mixture were $\rho = 1.188\text{g/cm}^3$, $\mu = 0.223\text{g/(cm}\cdot\text{s)}$ and $\sigma = 65.2\text{g/s}^2$, respectively. Then from Eq. (2) we obtain $a_c = 0.237\text{cm}$. Thus Eq. (1) predicts

$$h_\infty' = 0.9458 Ca_0^{2/3} \quad (11)$$

Comparing this result with the corresponding experimental fit (cf. Fig. 4)

$$h_\infty' = 0.9545 Ca_0^{0.6781} \quad (12)$$

we find that, the LLD theory agrees excellently with the experimental data for a plate at low values of the capillary number. Similarly, for high values of the capillary number we obtain from Eq.(4) that

$$h_\infty' = 0.667 Ca_0^{1/2} \quad (13)$$

which slightly overestimates the corresponding experimental fit (cf. Fig. 4)

$$h_\infty' = 0.4371 Ca_0^{0.5091} \quad (14)$$

In the case of the model printing pin ($\theta = 84.3^\circ = 1.47$, cf. Fig. 1), then we obtain from Eq. (5) that

$$h_\infty' = 1.00 Ca_0^{2/3} \quad (15)$$

for low values of Ca_0 . The corresponding experimental fit equation (cf. Fig.7) is rather close, namely

$$h_\infty' = 0.9908 Ca_0^{0.671} \quad (16)$$

For high values of Ca_0 , Eq. (7) predicts

$$h_\infty' = 0.667 Ca_0^{1/2} \quad (17)$$

which slightly overestimates the corresponding experimental fit (cf. Fig. 7)

$$h_\infty' = 0.4165 Ca_0^{0.495} \quad (18)$$

Summarizing, we can state that the theoretical formulae (5) and (7) yield a rather accurate predictive tool for the case of a model printing pin. Comparison of the theoretical formulae for the withdrawn volume, Eqs. (9) and (10), with the experimental data in Fig. 6 shows that the theory predicts excellently the experimental data for lower capillary number ($Ca < 10^{-2}$) and qualitatively correctly represents the trend of the withdrawn volume $V(L)$ for higher Ca -values (i.e. $Ca > 10^{-2}$), albeit overestimates the experimental values.

Consider now how the thickness of the withdrawn film on the pin could become dependent on L at low immersion depths L , namely to increase as L decreases. The explanation of this phenomenon is as follows. The capillary pressure of the liquid on a cylindrical surface $p_{\text{cap},c}$ is given by

$$p_{\text{cap},c} = \frac{\sigma \cot \theta_c}{r} \quad (19)$$

where θ_c is the half-angle of the cone (refer to Fig. 1, here $\theta_c = 5.7^\circ = 0.0994$ radian in the present case), and r is the radial coordinate along the generatrix; $r = 0$ at the apex. Therefore the capillary pressure in the film is actually

$$p_{\text{cap}} = p_{\text{cap},c} + f(h) \quad (20)$$

where f is a function of the local film thickness h .

The LLD theory accounts for $f(h)$ and its gradient over the solid surface. On the other hand, the component $p_{\text{cap},c}$ is absent there, since $p_{\text{cap},c} = 0$ corresponds to the plate case. However, in the present case of a cone the component $p_{\text{cap},c}$ can become a dominating favorable factor for withdrawal competing with the counteraction of the gravity and surface tension in the meniscus in the pool. Indeed, the pressure drop related to $p_{\text{cap},c}$

$$-\frac{\partial p_{\text{cap},c}}{\partial r} = \frac{\sigma \cot \theta_c}{r^2} \quad (21)$$

is positive. Therefore it pumps the liquid upwards. On the other hand, the counteracting factors are given by ρg and σ/a_c^2 . By using Eq. (2), we obtain $\sigma/a_c^2 = \rho g$. Therefore the pumping effect described in Eq. (21) can be neglected only if

$$\frac{\sigma \cot \theta_c}{r^2} \ll 2\rho g \quad (22)$$

Given the fact that r can be estimated as $r = L / \cos \theta_c$, Eq. (22) yields the condition

$$L \gg \sqrt{\frac{\sigma \cos^3 \theta_c}{2\rho g \sin \theta_c}} \quad (23)$$

If it is satisfied, the additional suction becomes insignificant, and h_∞ should become independent on L . Taking for the estimate $\sigma = 65.2 \text{ g/s}^2$, $\rho = 1.188 \text{ g/cm}^3$ and $\theta_c = 0.0994$, we obtain from Eq. (23) $L \gg 5.3 \text{ mm}$. This agrees with the condition established experimentally: at $L > 10 \text{ mm}$ the thickness h_∞ on the model pin became independent of L .

It should be emphasized, however, that the right-hand side of Eq. (23) does not scale down with the pin size. Therefore the thickness h_∞ on the printing pin used in industry e.g., TeleChem (2.1 mm long), will be variable with L for any immersion depth.

The film slip off the pin at extremely low values of the capillary number $Ca_0 < 10^{-4}$ found in subsection 4.5 can be attributed to the dynamics of the receding contact line on top of the withdrawn film.

6. FLOW VISUALIZATION

6.1 Flow Visualization of a Finite Plate near the Free Surface

The effect of the flow in the meniscus was neglected in the LLD theory. Most of the previous experiments were focused on the meniscus profile in the case of withdrawal of an infinitely long flat plate from liquid pool. The flow under the free surface can influence the withdrawn film to some extent. As to our knowledge, the time dependent pattern of the flow in the meniscus in the withdrawal process of a finite plate was not investigated experimentally yet. A kindred literature deals with vortex ring interactions with the free surfaces [17–20]. The main object of this subsection is to visualize the transient vortex structure during the withdrawal process.

Figures 8(a) and 8(b) show the flow visualization in the case of a plate withdrawn at velocities of 24 mm/s and 117 mm/s, respectively. The immersion depth was $L = 60 \text{ mm}$ and the liquid was 70% glycerine-water mixture. The photos in Fig. 8(a) were taken by a digital camera with the aperture of 5.6 and a shutter-speed of 1/4 second. On the other hand, an aperture of 4 and 1/8 second shutter-speed were used in Fig. 8(b). The sequence photos (1) to (6) in Fig. 8(a) show that the fluid near the plate is entrained in a closed vortex pair. Also, an induced liquid flow, which could not approach the plate, results in two circulation cells near the free surface with vorticity of the opposite sign to that of the primary vortex. In order to distinguish these two vortex pairs, we denote the original vortex near the plate as the primary vortex pair, and the other one as the secondary vortex. The evolution of these vortices is similar to that of the vortex ring vertically approaching a plane wall studied in Walker *et al.* [18]. Before the plate is withdrawn from the liquid pool, two symmetric primary vortices are fairly stable and growing up as being observed in photos (1) to (5) of Fig. 8(a). The secondary vortex pair seems to play no role in the fluid dynamics close to the plate, since it is displaced by the primary vortex pair to a significant distance from the plate. After the plate has been withdrawn from the pool (at about $t = 2.5$ seconds), the secondary vortex pair rolls downwards about the outer rim of the primary vortex pair. When the primary vortex pair has a sufficient strength, a third vortex pair, referred to as the tertiary vortex, might be induced near the free surface. The tertiary vortex pair has the vorticity of an opposite sign to that of the primary vortex. The whole process could be schematically depicted as in photos (1) to (3) of Fig. 9(a).

On the other hand, Fig. 8(b) shows the plate withdrawn at a faster velocity ($Ca_0 = 0.0424$, $U_0 =$

Fig. 8 Flow visualization in the vicinity of the flat-plate at different stages of withdrawal at (a) low capillary number ($Ca_0 = 0.0087$, $U_0 = 24\text{mm/s}$), and (b) high capillary number ($Ca_0 = 0.0424$, $U_0 = 117\text{mm/s}$). Liquid level of the horizon is shown as the dashed line.

117mm/s) than that of Fig. 8(a). A similar scenario of formation of the primary and secondary vortices is clearly observed in photos (1) to (4) of Fig 8(b), although the sizes of all the vortices are relatively

smaller in comparison to those in Fig. 8(a). It is worthy to note that a regular shedding of vortex street following the withdrawn plate was observed in photos (3) and (4) of Fig. 8(b). Moreover, after the plate has been

Fig. 8 (continued).

withdrawn from the pool (at about $t = 0.52$ seconds), the secondary vortex pair had moved relatively quicker downwards due to the smaller size of the primary vortex and thus had a relatively stronger interaction with the liquid flow in the layer near the plate. The above-mentioned process is depicted schematically in photos (1) to (3) of Fig. 9(b). No formation of tertiary

vortex ring was observed in the experiments at higher capillary numbers.

6.2 Flow Visualization of the Model Pin near the Free Surface

The transient character of flow in the pool accompanying pin withdrawal is discussed in the present

Fig. 9 Sketch of the flow in the withdrawal process for flat-plate at (a) low and (b) high Capillary number, respectively.

subsection. Figures 10(a) and 10(b) show the photos during the pin withdrawal at the capillary number of $Ca_0 = 0.0087$ ($U_0 = 24\text{mm/s}$) and 0.0424 ($U_0 = 117\text{mm/s}$), respectively. The immersion depth was $L = 60\text{mm}$ and the liquid was 70% glycerine-water mixture.

The formation of the primary and secondary vortex rings in the case of the model pin withdrawn at a capillary number of $Ca_0 = 0.0087$ (cf. photos (1) to (6) of Fig 10(a)) is basically similar to that of the plate at the same withdrawal velocity, except that the primary

Fig. 10 Flow visualization in the vicinity of the model pin at different stages of withdrawal at (a) low capillary number ($Ca_0 = 0.0087$, $U_0 = 24\text{mm/s}$), and (b) high capillary number ($Ca_0 = 0.0424$, $U_0 = 117\text{mm/s}$), respectively.

vortex is axisymmetric and relatively smaller in the former case. Because the withdrawal of the model pin had induced the inward motion of the liquid to the pin

axis, shrinkage of the primary vortex ring was caused. As a result, the inner diameter of the toroidal vortex ring decreased. After the pin had been withdrawn from the

(4)

(5)

(6)

(a)

(b)

Fig. 10 (continued).

liquid pool, the interaction between the primary and secondary vortex ring suppressed the strength of the primary ring, cf. photos (5) and (6) of Fig. 10(a). No tertiary vortex is observed in the pin withdrawal process. The overall process is depicted schematically in photos

(1) to (3) of Fig. 11(a).

Photos (1) to (6) of Fig. 10(b) show the withdrawal snapshots for $Ca_0 = 0.0424$ ($U_0 = 117\text{mm/s}$). Similar to the case of flat-plate, the sizes of all vortices are relatively smaller in comparison with those in Figs. 10(a).

Fig. 11 Schematic diagram of the flow during withdrawal process of model pin at (a) low and (b) high Capillary number, respectively.

No regular shedding of vortex street following the withdrawn pin was observed. After the pin has been withdrawn from the pool, the interaction between the primary and secondary vortex rings weakens the primary one. The secondary ring springs and continues to orbit from the bottom of the primary vortex ring towards the outside perimeter of the primary ring. The corresponding overall process is depicted schematically in photos (1) and (3) of Fig. 11(b).

The photographs in Fig. 10 show that the circulation pattern near the withdrawn model pin is time-dependent, as was expected in Section 2. This is a basic difference in the meniscus zone as compared to a steady-state circulation pattern near the withdrawn plate photographed in Ref. [11]. The effect of this difference should be enhanced at higher withdrawal rates. This, however, cannot be the reason for the fact that Eq. (17) overpredicts the data of Eq. (18), since a similar

overestimation was found for plate withdrawal (cf. Eqs. (13) and (14)).

7. CONCLUSIONS

1. It was shown that in the range of the capillary number (based on the withdrawal velocity of the pin) $Ca_0 < 10^{-2}$, the thickness of the withdrawn film h_∞' on a conical printing pin closely follows the Landau-Levich-Deryagin (LLD) law $h_\infty' \sim Ca_0^{2/3}$ if the immersion depth L was large enough. Under the same condition, in the range of $Ca_0 > 10^{-2}$ the thickness h_∞' on the pin follows the $Ca_0^{1/2}$ scaling, also expected from the LLD theory modified for a cone.

2. It was demonstrated that at relatively small values of the immersion depth L , significant qualitative deviations from the LLD theory begin. In particular, the thickness of the withdrawn film h_∞ becomes L dependent (increases as L decreases). This phenomenon was explained in the present work by an additional pressure drop arising in the case of a cone, which results in additional fluid suction into the film. The theoretical estimate showed that this effect could be neglected only for $L \gg 5.3\text{mm}$. The experiment revealed that for $L \geq 10\text{mm}$ the film thickness h_∞ on the model pin is independent of L . Since the threshold does not scale down with the pin size, the film thickness on the smaller industrial pins could be L dependent.
3. By changing the withdrawal velocity of the printing-pins makes it possible to control sampling quantity.
4. The film slips off the pin at low capillary numbers $Ca_0 < 10^{-4}$. This phenomenon can be attributed to the motion of the receding contact line on top of the pin.
5. As long as the governing parameters are controlled properly, it is possible to attain a high accuracy of sampling using printing pins.
6. The results of the present work can be of interest not only for development of microarray biochips, but also for dip-pen lithography recently developed for nanofabrication technology, where the tip of atomic force microscope is used [21].

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