Experimental study of dynamic contact angles in liquid-liquid microfluidic plug flow with partial wetting

A V Kovalev, A A Yagodnitsyna and A V Bilsky

Kutateladze Institute of Thermophysics SB RAS, Russia

Abstract. Partial wetting of walls by immiscible liquids in microfluidic flows is a crucial parameter for heat and mass transfer applications. Dynamic contact angles, which characterize wettability, are studied experimentally for different liquid-liquid sets in microchannels with 200x400 µm and 120x240 µm cross-sections. An appropriate algorithm is chosen for meniscus shape approximation. Cox-Voinov law is found to predict correctly advancing contact angles in liquid-liquid flow. The generalized version of Cox-Voinov law is proposed for the liquid sets with different physical properties. Based on experimental data, new dependences of receding contact angle on contact line velocity are provided for the systems with concave and convex rear meniscus of a plug.

1. Introduction

In recent years microfluidic devices were found to be a very prospective tool for analytical chemistry, biology, pharmaceuticals, and other applications [1,2]. Microfluidics provides precise control and safety of processes along with the intensification of heat and mass transfer rates due to the high surface-to-volume ratio. In most of the applications, gas-liquid or liquid-liquid flows are utilized inside microfluidic devices either to generate droplets/plugs or to perform processes in continuous flow regimes. In such microscale two-phase flows with interfaces, the phenomenon of wetting is of great importance, because interfacial tension and adhesion dominate gravity and inertia forces. For example, heat and mass transfer in plug flow depends on the contact line presence between the plug and channel walls and its thickness [3,4], which in turn is defined by wall wettability. Wetting is described by values of contact angles, which depend on liquid velocity for moving contact line (dynamic contact angles). Partial wetting of channel walls by dispersed phase in the case of a liquid-liquid flow in microchannels strongly affects plug formation and velocity [5] and even leads to specific flow regimes like plugs with V-shaped contact line and microdroplets breakup [6]. Therefore, understanding of wetting phenomena and derivation of contact angle dependencies are essential for correct description and modeling of two-phase flows in microchannels.

The problem of moving gas-liquid interfaces in capillaries and contact angle dependence on liquid capillary number (Ca = U·µ/σ, where U is the characteristic velocity, µ is the liquid dynamic viscosity, and σ is the surface tension) was studied thoroughly by many researchers. One of the first comprehensive experimental research was conducted on air-liquid moving interfaces in capillary tubes by Hoffman [7]. Five different liquids were used. The author distinguishes flow regimes depending on predominant forces in the system. Viscous and interfacial forces play a key role in this problem formulation, while inertia is negligible. A generalized form of advancing contact angle dependence on the contact line velocity was proposed based on the shift factor, which depends only on static contact angle. The form of the dependence is \( \theta_m = f(\text{Ca} + f^{-1}(\theta_s)) \), where \( \theta_m \) is the measured dynamic contact angle and \( f^{-1}(\theta_s) \) is a shift factor acquired from the master curve. The master curve was obtained experimentally for different...
liquids and is in good agreement with data from the literature. A correlation between contact angle and Ca was derived based on Hoffman’s experimental data in [8]. This correlation allows for avoiding a calculation of a shift factor based on the master curve. From a comparison of the correlation with literature, the authors concluded that the latter is independent of macroscopic geometry. Thus macroscopic contact angle must be the same in different geometries for keeping all other parameters constant. The equation for \( \theta_m (\text{Ca}) \) proposed by Hoffman with a shift factor calculated using correlation similar to Jiang et al. but modified for high Ca is also referred to in the literature as Kistler’s law, which is often used in numerical simulations [9]. When Ca < 0.1 the correlations based on Hoffman’s data reduce to form nearly equivalent to \( \theta_m = \theta_0 + \alpha \text{Ca} \), where \( \theta_0 \) and \( \alpha \) depend on the fluid pair [10]. The dependence \( \theta_m = \alpha \text{Ca} \) was obtained by multiple researchers through the theoretical treatment of a moving interface problem [11–13], and further in the current work, we will refer to this dependence as Cox-Voinov relation similarly to [5]. Another approach developed by Shikmurzaev and Blake et al. consists in considering dynamic contact angle as not a property of system materials and contact line velocity, i.e., equation \( \theta = f(U_{cd}, a, b, c, \ldots) \) is invalid. For the given system at the same contact line velocities, a dynamic contact angle is deemed to depend on the liquid flow rate or flow field, which results in a more complicated implicit relationship between \( \theta_m \) and Ca [14].

Despite extensive theoretical and experimental investigations on wetting phenomena, the understanding of underlying processes is still incomplete. For instance, analytical models for dynamic contact angles developed for gas-liquid flows fail for the fluids with different physical properties [15]. There are only a few works on partial wetting in the case of plug flow in microchannels. Important features, such as dewetting and transition from the contact line to the thin film were investigated, but a little attention was paid to the contact angle [5, 16]. Another poorly explored problem is a contact angle hysteresis, i.e. the difference between advancing and receding angles, especially in microfluidic plug flow.

In the present work, experimental research of dynamic contact angles formed by dispersed phase plug menisci in liquid-liquid-surface line inside a microchannel with a rectangular cross-section is performed. Advancing and receding contact angles are measured for different liquid-liquid systems and compared with existing correlations. Cox-Voinov relation is shown to be suitable for advancing contact angles description and its generalization for the case of different liquids is proposed. The difference between trends for advancing and receding contact angles is discussed.

2. Experimental setup

The pairs of kerosene-water, paraffin oil-water, and ionic liquid-water were used as liquid-liquid systems for experiments. In all these liquid sets contact line was clearly observed at low Ca between plugs of a dispersed phase and channel walls. Microchannels were made of SU-8 polymer by microLIQUID (Spain) using a photolithography procedure. The roughness of the walls did not exceed 1 µm. The cross-section of microchannels had a rectangular shape with deviations within 3%, and dimensions of cross-sections used were 200x400 µm, 120x240 µm. High-speed CMOS camera with 500 Hz frame rate and an inverted microscope Zeiss Axio Observer.Z1 with magnification lenses up to 63x were employed for flow visualization. Advancing and receding dynamic contact angles were measured as shown in Figure 1 for the kerosene-water system.

![Figure 1](image.png)

**Figure 1.** Image example of aqueous plug in kerosene inside the microchannel, red lines schematically show the measurement of receding and advancing contact angles.
Three different algorithms were tested for the approximation of plug menisci: circle/ellipse, solution of Young-Laplace equation for a droplet of equivalent shape [17], and cubic B-spline [18]. Eventually, the B-spline method was chosen as the most precise one. As shown in Figure 2, this method captures local curvature near the wall better than two others. When Ca increases and meniscus shape starts to deviate from spherical, circle/ellipse and solution of Young-Laplace give an inadequate approximation. In all experiments, the resulting values of the contact angle and contact line velocity were obtained by averaging over 10 to 25 points. Velocity standard deviation was less than 2% for every studied flow rate, and the standard deviation of contact angles is shown as error bars at corresponding graphs below.

![Figure 2. Approximation of advancing meniscus shape by different methods: a – circle/ellipse, b – solution of Young-Laplace equation, c – B-spline.](image)

### 3. Results and discussion

Using the technique of interface form approximation based on cubic B-spline, advancing and receding contact angle dependencies on plug velocity were obtained for kerosene-water, paraffin oil-water, and ionic liquid-water systems in microchannels with different cross-section sizes. Figure 3 a,b presents the plots of advancing and receding contact angles depending on contact line velocity for kerosene-water and paraffin oil-water in the channel with 200x400 um cross-section. Both advancing and receding contact angles grow with the contact line velocity increase, but the trends are different. The available correlations for dynamic contact angles from the literature were compared with the experimental data. It was found that the equation in the form of the Cox-Voinov law (1) mentioned above, describes the data for the advancing contact angles well (Fig. 4 a). Equation (1) was obtained independently by Cox and Voinov based on solving hydrodynamic equations with free boundary conditions, and this equation also describes well Hoffman’s experimental data for gas-liquid systems.

\[
\theta_m^3 - \theta_0^3 = \alpha \cdot Ca
\]  

where \(\theta_0\) is the dynamic contact angle, \(\theta_m\) is the microscopic contact angle, which is usually assumed to be equal to the equilibrium contact angle at zero velocity of the contact line, Ca is the capillary number and \(\alpha\) is the phenomenological coefficient that depends on the properties of a surface and liquids. The values of the equilibrium contact angles \(\theta_0\) for the kerosene-water and paraffin oil-water systems were obtained at \(Ca = 0\) from the approximation of \(\theta_{adv}(Ca)\) dependencies corresponding to equation (1). The obtained values of the equilibrium contact angles coincide with good accuracy with the values measured at zero velocity of the contact line in the channel, as well as with the average values of static angles obtained by the sessile drop method on a substrate made of the microchannel material (the difference between the obtained values is less than 5°). In the case of receding contact angles, equation (1) no longer provides an adequate approximation of the \(\theta_{rec}(Ca)\) dependence. None of the existing models in the literature provide a good description of this data. However, \(\theta_{rec}(Ca)\) corresponds to the form \(\theta_{rec} \sim \ln(Ca)\) with high accuracy. Here, the difference in capillary numbers constructed for continuous and dispersed (water) phases consists only in the dynamic viscosity coefficient, and dependence is still logarithmic. Therefore, the logarithmic form of \(\theta_{rec}(Ca)\) is not attributed to the inappropriate choice of
variables. This type of dependence of the contact angle on the velocity was not described earlier and requires additional study and justification, taking into account the phenomenon of hysteresis in systems with partial wettability.

![Figure 3](image_url)  

**Figure 3.** Dependence of contact angles on contact line velocity for kerosene-water and paraffin oil-water: a – advancing contact angle, b – receding contact angle.

Similar dependencies of advancing and receding contact angles on the contact line velocity were obtained for the ionic liquid-water system in the channel 120x240 µm and are shown in Fig. 4. As for the two previous systems, the advancing contact angle is well placed on the theoretical curve given by equation (1). While the receding contact angle is no longer described as \( \theta_{\text{rec}} \sim \ln(Ca) \) and degenerates into \( \theta_{\text{rec}} \sim Ca \). This fact is also related to the contact angle hysteresis and different wall adhesion in comparison with two previous liquid sets. In this case, the condition \( \theta_{\text{rec}} < 90^\circ \) was always met, even at critical contact line velocities close to the onset of a thin film of the continuous phase and contact line vanishing between plugs and channel walls. The curvature of the rear meniscus of the plug had the opposite sign compared to the front meniscus in contrast with the cases of kerosene-water and paraffin oil-water. Apparently, for the cases, \( \theta_{\text{rec}} < 90^\circ \) and \( \theta_{\text{rec}} > 90^\circ \) the physics of the process is determined by different mechanisms, which requires further study.
Figure 4. Dependence of contact angles on contact line velocity for ionic liquid-water in the microchannel with 120x240 μm cross-section.

It was found that to generalize equation (1) to the liquid-liquid case and to correctly describe sets of liquids of different viscosities, the capillary number constructed based on the viscosity of the aqueous phase must be replaced with a dimensionless complex \((Ca_{d}Ca_{c})^{0.5}\), which leads equation (1) to the form:

\[
\theta_{m}^{3} - \theta_{0}^{3} = \alpha \cdot (Ca_{d}Ca_{c})^{1/2}
\]

(2)

where \(Ca_{d}\) is the capillary number of the dispersed phase, \(Ca_{c}\) is the capillary number of the carrying phase. All the obtained data for different systems of liquids, constructed according to equation (2), are shown in Fig. 5. It can be seen that equation (2) provides data generalization for the liquids with different viscosities; the coefficient of determination of the approximating curve R-squared is equal to 97.8. It is worth noting that the coefficient \(\alpha\) for all liquid-liquid sets is significantly higher than predicted by the theory, which is explained by the additional forces required for the movement of the contact line in liquid-liquid systems compared to gas-liquid ones. Another important consequence of the equation (2) applicability to data sets from channels of different cross-sections is the independence of advancing contact angle on channel hydraulic diameter.
Conclusion
Experimental study on advancing and receding contact angles in liquid-liquid flow in microchannels with different cross-section sizes is carried out. It is shown that the cubic B-spline algorithm can be successfully utilized to approximate meniscus shape. The Cox-Voinov law was found to predict correctly advancing contact angles in liquid-liquid flow. A dimensionless complex was constructed to generalize the Cox-Voinov law for the liquid sets with different physical properties. Based on experimental data, new dependences of receding contact angle on contact line velocity were provided for the systems with concave and convex rear meniscus of a plug.

Acknowledgments
This work, performed in the Kutateladze Institute of Thermophysics SB RAS, is supported by a grant from the Russian Science Foundation (project No 16-19-10519).

References
[1] Samiei E, Tabrizian M and Hoorfar M 2016 A review of digital microfluidics as portable platforms for lab-on-a-chip applications Lab Chip 16 2376–96
[2] Maeki M 2018 Microfluidics for pharmaceutical applications (Elsevier Inc.)
[3] van Baten J M and Krishna R 2004 Chem. Eng. Sci. 59 2535–45
[4] Dai Z, Guo Z, Fletcher D F and Haynes B S 2015 Chem. Eng. Sci. 138 140–52
[5] Jose B M and Cubaud T 2014 RSC Adv. 4 14962–70
[6] Kovalev A V, Yagodnitsyna A A and Bilsky A V 2018 Chem. Eng. J. 352
[7] Hoffman R L 1975 J. Colloid Interface Sci. 50 228–41
[8] Jiang T S, Soo-Gun O H and Slattery J C 1979 J. Colloid Interface Sci. 69 74–7
[9] Malgarinos I, Nikolopoulos N, Marengo M, Antonini C and Gavaises M 2014 212 1–20
[10] Berg J 1993 Wettability of Surfactant Science vol 49 (CRC Press)
[11] Voinov O V. 1976 Hydrodynamics of wetting Fluid Dyn. 11 714–21
[12] Tanner L H 1979 J. Phys.-D. 12
[13] Cox R G 1986 J. Fluid Mech. 168 195–220
[14] Blake T D, Bracke M and Shikhmurzaev Y D 1999 Phys. Fluids 11 1995–2007
[15] Heshmati M and Piri M 2014 Langmuir 30 14151–62
[16] Khodaparast S, Atasi O, Deblais A, Scheid B and Stone H A 2018 Langmuir 34 1363–70
[17] Stalder A F, Melchior T, Müller M, Sage D, Blu T and Unser M 2010 A Physicochem. Eng. Asp. 364 72–81
[18] Stalder A F, Kulik G, Sage D, Barbieri L and Hoffmann P 2006 A Physicochem. Eng. Asp. 286 92–103