From Single Drop to Falling Film. An Insight Into the Hydrodynamic and Geometry of a Falling Water Film Under Elevated Pressure of Carbon Dioxide

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Abstract

A better design of process engineering plants with respect to heat and mass transfer can be achieved by improving the understanding of wettability of liquids on solid surfaces. In this study an attempt was made to measure the wettability of a single liquid drop on a horizontal surface under elevated pressure of carbon dioxide. A comparison with calculated contact angles can be made only if the so called interaction parameter is able to describe the relation between cohesion in the bulk phases and adhesion between the phases at the given conditions.

In case of dynamic wetting of a falling film the forces of gravity, buoyancy and shear stress on the free surface area should be considered along with the wetting phenomena. Assuming that the cross sectional area of the falling film normal to its flowing direction has the geometry of a circular segment, the triple line contact angle of the film can be obtained by measuring the thickness and the width of the film. This value can be compared with the contact angle value of a sessile drop. Furthermore several approaches were made to calculate the velocity profile in this cross sectional area. A comparison between the obtained mean velocity of the falling film and the experimental value was performed.

1 Sessile Drop: Wettability and Solid Surface Tension

If a liquid does not completely cover a solid surface, the liquid intersects the solid surface at the triple line and forms a finite contact angle. The parameters which characterize the wetting behaviour of a sessile liquid drop on solid surfaces can be found in the Young equation:

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cos \theta . \tag{1}$$

Liquid surface tension σ_{lv} and equilibrium contact angle θ can be obtained through experimental measurements, but the solid-vapour surface tension σ_{sv} and the solid-liquid surface tension σ_{sl} cannot directly be measured. In order to solve the Young equation a so called molecular interaction parameter Φ_{sl} was introduced [1, 2, 3]. This parameter is defined as the ratio of Helmholtz free energy of adhesion and cohesion. According to the theory of Good, Girifalco and Elbing [1, 2, 3], the value of this parameter should be close to unity when the cohesive forces within each separate phase and the forces acting across the interface are of the same type. On the other hand when the predominant forces within each bulk phase are different and when there are no specific forces across the interface, low values of Φ_{sl} are to be expected. This parameter can be estimated with help of the molecular properties of the substances in each phase as follows

$$\Phi_{ab} = \frac{\frac{3}{4}\alpha_a \alpha_b \frac{2 I_a I_b}{I_a + I_b} + \frac{1}{2}\left(\alpha_a \mu_b{}^2 + \alpha_b \mu_a{}^2\right) + \frac{1}{3}\frac{\mu_a{}^2 \mu_b{}^2}{kT}}{\left[\left(\frac{3}{4}\alpha_a{}^2 I_a + \alpha_a \mu_a{}^2 + \frac{1}{3}\frac{\mu_a{}^4}{kT}\right)\left(\frac{3}{4}\alpha_b{}^2 I_b + \alpha_b \mu_b{}^2 + \frac{1}{3}\frac{\mu_b{}^4}{kT}\right)\right]^{\frac{1}{2}}} \tag{2}$$

where α is the polarizability, I the ionization potential and μ the dipole moment. The mole fractions of the involved substances are used to calculate the molecular properties in order to take the miscibility between the phases into account. Provided that the liquid surface tension σ_{lv}, the equilibrium contact angle θ and the interaction parameter Φ_{sl} are known, the solid surface tension can be estimated

$$\sigma_{sv} = \sigma_{lv}\left(\frac{\cos\theta + 1}{2\Phi_{sl}}\right)^2 . \tag{3}$$

1. 1 Experimental Setup

Surface tensions of water and ethanol were measured according to the pendant drop method. Contact angles of these liquids on PTFE, glass and stainless steel were measured according to the sessile drop method. All measurements were performed in a high pressure view cell. The analysed liquid was introduced into the view cell through a stainless steel capillary with an outer diameter of 1/32" for pendant drop method and 1/16" for sessile drop method. A special magnetic construction was designed to allow the rotation of the solid surface in the view cell under high pressure conditions in this way, that more than one drop can be placed and measured on the solid before depressurization needs to be carried out in order to clean the solid surface. The measurements were performed under elevated pressure of carbon dioxide at temperatures up to 373 K and at pressures up to 27 MPa.
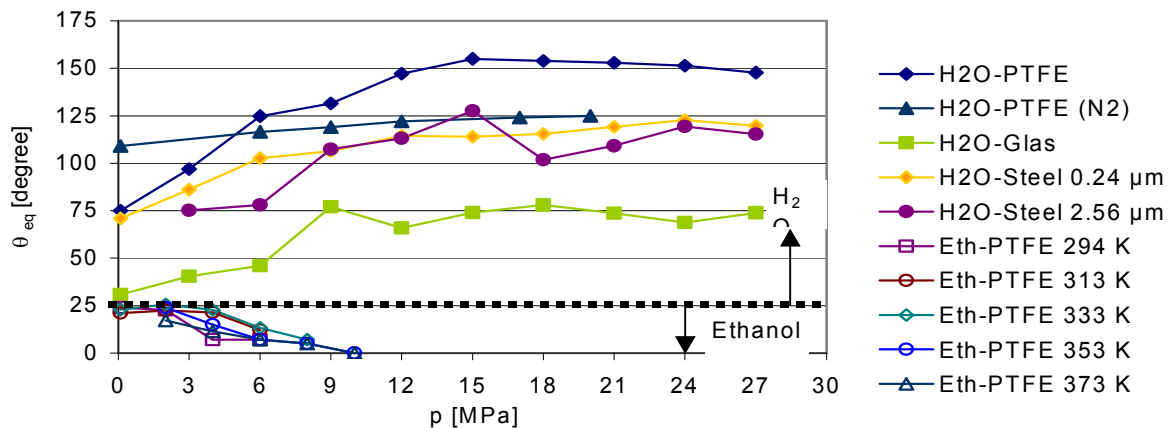
1. 2 Results and Discussion

Figure 1: Wetting behaviour of liquids on several solids under elevated pressure of carbon dioxide and nitrogen [4]

The results of contact angle measurement are shown in fig. 1 as a function of pressure. A comparison of the wettability of water on several solid surfaces in carbon dioxide and nitrogen atmosphere at 313 K is made. The Wettability of water on PTFE under elevated pressure of nitrogen [4] is better than under carbon dioxide atmosphere. In all cases the wettability decreases with increasing pressure, i. e. the contact angle increase initially linear or nearly linear until it reaches an asymptotic value. A further pressure increase does not influence the contact angle anymore. It remains more or less constant. The worst wetting behaviour is to be found on PTFE, steel follows and the best wetting appears on glass surface. This agrees good with the predicted and reported wetting phenomena in the literature. Both examined stainless steel surfaces are 1.4305, the roughness values are 0.24 µm and 2.56 µm respectively. Little discrepancy in the value of contact angle is noticed concerning the effect

of surface roughness. The wettability of water on steel surface with greater roughness appears to be better than on the smooth one. Regarding surface roughness, the apparent contact angle is not always equal to the real one. Provided that the liquid's surface tension is low enough to allow it filling the gussets on the rough surface, the apparent wettability of this rough surface can be better than that of a smooth one. Increasing the pressure of carbon dioxide means decreasing the liquid surface tension, so that actually the wettability should be far more better, but at the same time there is a competition between the compressed (supercritical) carbon dioxide and water to fill the gussets. The results show that carbon dioxide can fill them better, so that along with increasing pressure, the discrepancy of the contact angle values concerning the roughness decreases. At pressure above 20 MPa both surfaces show nearly the same wetting behaviour.

On the contrary to water, ethanol wets PTFE surface better with increasing pressure at all temperatures observed. The reason for the better wetting characteristic of ethanol is the lower surface tension of the pure liquid phase. The surface tension decreases further with increasing pressure due to the higher solubility of carbon dioxide in the liquid phase. Contact angle measurements for this system over 10 MPa are impossible not only because the excellent wetting behaviour of ethanol but also because ethanol and carbon dioxide form a homogenous phase at these conditions. Ethanol spreads completely on glass and steel at 313 K.
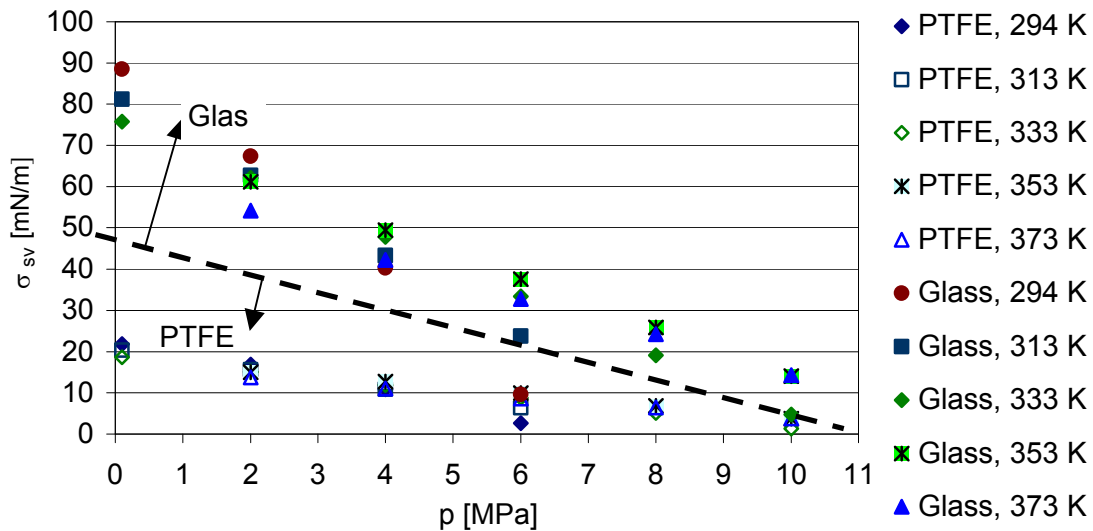
Figure 2: Solid surface tension as function of pressure

Using equation 2 the interaction parameters Φ_{sl} for glass and PTFE are calculated. The values Φ_{sl} for the system PTFE-H_2O-CO_2 range from 0.75 to 0.78 and for PTFE-Ethanol-CO_2 from 0.95 to 0.97. Calculation of PTFE surface tension was carried out with equation 3 and the wetting parameter, surface tension and contact angle of ethanol. The results are shown in fig. 2 as a function of temperature and pressure. The effect of a variation in temperature on surface tension of PTFE is not significant. Increasing the pressure means decreasing the surface tension. In the observed conditions PTFE surface tension vary from 22 mN/m to 1 mN/m. Using this surface tension data contact angles of water on PTFE are estimated and compared with the experimental data as shown in fig. 1. The discrepancy between calculated and measured contact angles is in the range of $\pm 10°$, which is excellent for a contact angle prediction because of the moderate reproducibility of the measurements.

For the system glass-H_2O-CO_2 the values of Φ_{sl} range from 0.6 to 0.65 and for glass-Ethanol-CO_2 from 0.95 to 1. These values lead to glass surface tensions which cannot be

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applied for useful contact angle prediction. A correction of Φ_{sl} need to be done. For the system glass-H_2O-CO_2 the values 0.85-0.89 and for ethanol 0.5 are assumed. The calculated glass surface tensions from the system glass-Ethanol-CO_2 are shown in fig. 2. Making use of these values, contact angles prediction for water on glass with $\pm 15°$ precision can be achieved.

2 Falling Film: the Geometry, Velocity Profile and Shear Stress

The aim of this investigation is to compare the dynamic wettability of liquids to the static one particularly under the influence of compressed and supercritical carbon dioxide. The questions that need to be answered are: how is the triple line contact angle of liquid on vertical surface if the effect of gravity and buoyancy are to be considered, which simplifications and models can be applied to estimate the velocity profile and thus the mean velocity of the film and finally, how is the magnitude of the shear stress on the free surface.

2. 1 Experimental Setup

The experiments were carried out in a high pressure view cell with 95 mm long and 14 mm wide windows. A capillary with an outer diameter of 1/16" was used to introduce the liquid on a solid surface, which was placed vertically in the view cell. The required magnification in measuring the film thickness allows only a max. length of 6.6 mm measurement zone whereas for the specific wetting area a length of 33.55 mm was available. The measurements were carried out at the bottom side of the view zone so that the liquid was given enough distance to reach a hydrodynamic fully developed flow. Glass-H_2O-CO_2 system was investigated for the case of falling film at 313 K up to 27 MPa.
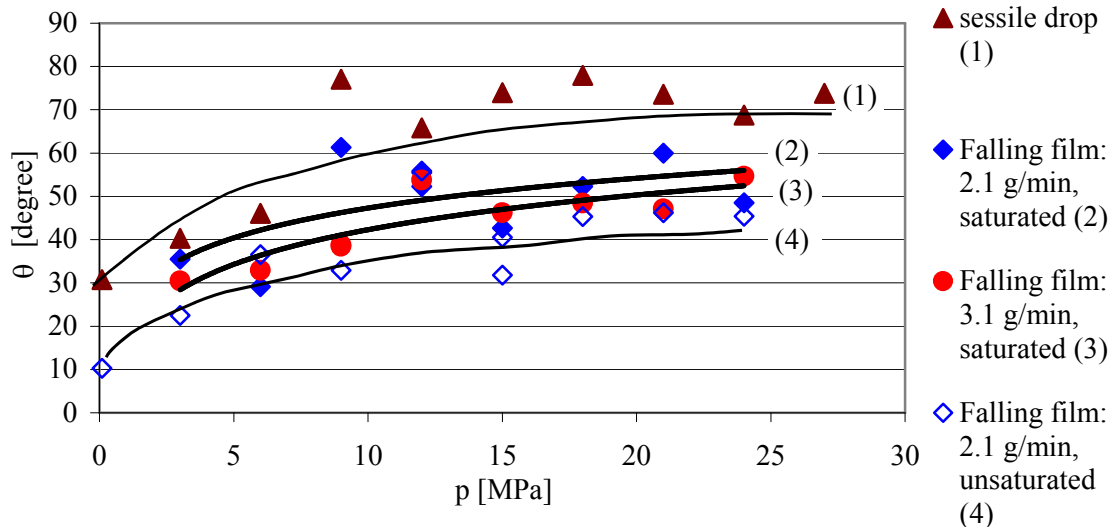
2. 2 Results and Discussion

Figure 3: A comparison between falling film and sessile drop contact angles of water on glass surface

Assuming the cross section area normal to flow direction has the geometry of a circular segment [5], the triple line contact angle can be estimated with help of film width and thickness data. A comparison of film width and thickness gives information about the wetting behaviour, whether the contact angle is greater, equal or less than 90°. Saturating water with carbon dioxide causes a larger contact angle and a smaller circle radius (fig.3). The mean circle radius of unsaturated water is about 1.55 mm, the one of saturated water is 1.3 mm.

Applying contact angle of sessile drop to the case of falling film causes an overestimation because in the latter case gravitation, buoyancy and shear stress cannot be neglected. Generally it can be said, that the wetting behaviour of liquid on a vertical surface is better than that of a sessile drop.
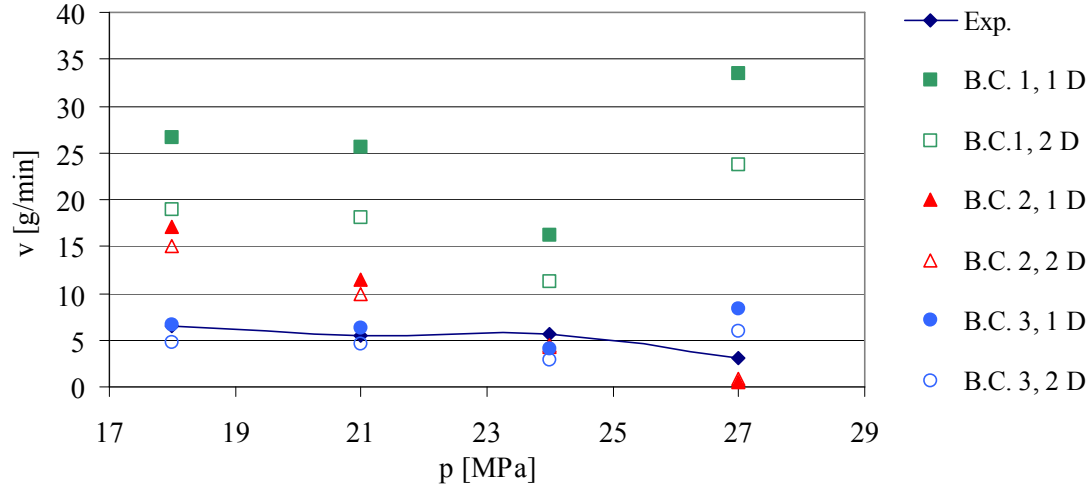
Figure 4: Mean velocity of falling film with the mass flow 3.1 g/min at 313 K. A comparison between the experimental results with the calculated one using three different boundary conditions.

The velocity of the falling film can be estimated using the mass flow and cross section area of the film by applying the continuity equation. If the liquid velocity is not large (laminar flow) and the film is thin, the velocity can also theoretically be estimated making use of the Nusselt's film condensation theory

$$\eta_L \cdot \frac{\partial^2 w}{\partial y^2} = -(\rho_{L-}\rho_G) \cdot g \ . \tag{4}$$

To solve equation 4 two boundary conditions are required. On the wall y=0, the velocity is v=0. Furthermore assuming the flow is stationary, there exists another boundary condition on the free surface:
1. shear stress exerted by the vapour on the film is negligible
2. shear stress exerted by the vapour on the film surface is finite
3. shear stress on the film is so large, that the velocity is equal zero.

In addition, the film can be assumed as one dimensional, i.e. velocity profile exists just along the thickness of the film, the surface curvature and the three line contact angle are neglected, or two dimensional i. e. the curvature of the arc of the cross sectional circle segment must be considered. For the theoretical mean velocity there exist three boundary conditions with one or two dimensional model, so that there are six models to be considered. In fig.4 a comparison between the experimental and calculated values are carried out. The assumption that on the surface no shear stress exists lead to an overestimation of the mean velocity. There exists definitely a finite shear stress on the surface. The assumed shear stress made by boundary condition nr. 2 appeared to be too low for pressures up to 23 MPa but a little too high for pressures above it. In the last boundary condition, the liquid velocity on the surface was set to zero. The theoretical prediction of the velocity profile and thus the mean velocity is excellent. The calculated values agree with the experimental ones well. It is also shown, that the one dimensional approximation always leads to a bigger mean value than that of the two dimensional one. Mathematically it can be shown, that depending on the magnitude of the

contact angle, the ratio of the two to one dimensional mean velocity varies from 68.58% to 93.75%. At 90° the ratio is exactly 75% and increases continually up to 180°. An attempt to calculate the free surface shear stress is also made. For this purpose the velocity on the surface was derivated with respect to the thickness (y). The results are shown in fig.5, where the calculated shear stresses according to the boundary condition nr. 2 and 3 are compared. The measurements at pressures between 3 MPa and 9 MPa were not very precise because in this range the ratio of density to temperature change is relatively large. Therefore, small temperature gradients cause great fluctuations in density and thus schlieren in the view cell which complicated the optical measurement. This is the main reason which causes that the shear stresses calculated with the different boundary conditions do not coincide with each other. Above 10 MPa all three approximations agree well with each other.
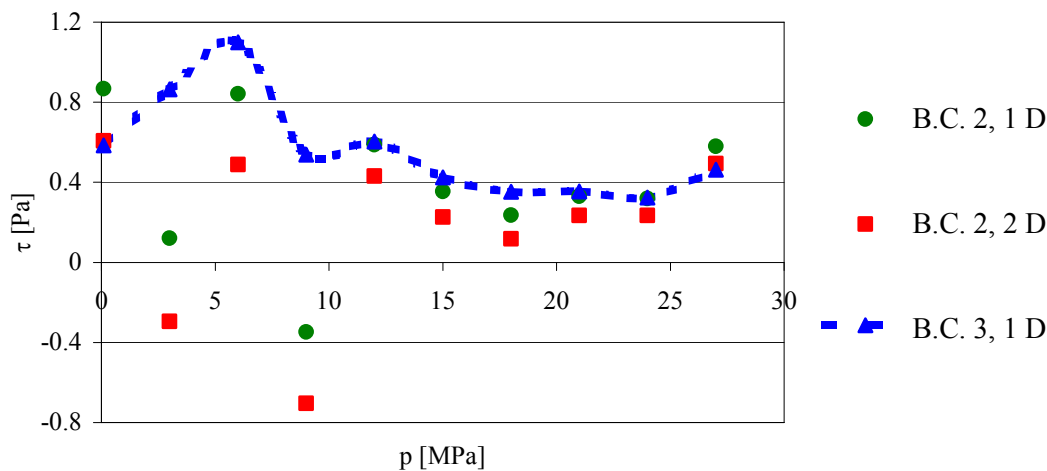

Figure 5: Shear stress on free surface area, estimated with boundary conditions 2 and 3

3 Conclusions

Surface tensions of PTFE and glass were calculated according to the method of Good, Girifalco and Elbing. The calculated surface tensions of PTFE were successfully used to predict the contact angle of water on this surface in accuracy of $\pm 10°$. Using corrected values of interaction parameters, the glass surface tensions were successfully applied to predict the contact angle of water on this surface in an accuracy of $\pm 15°$. The investigation of falling film leads to the knowledge, that buoyancy and shear stress on the film surface are large enough to slow down the liquid velocity to zero. Along with liquid and gas properties and the geometry of falling film, models to calculate the velocity profile and thus the mean velocity were developed. The calculated value agree well with the experimental one.

4 References

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