ADVANCES IN DYNAMIC WETTING IN COATING FLOWS

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INTRODUCTION

Coating flows present arguably the most fundamental and challenging aspects of all flow processes. They are fast free surface non-Newtonian flows on solid substrates bound to a dynamic wetting line (Figure 1). The non-Newtonian feature is due to applications as coating solutions are fine solids or polymers and binders suspended in a solvent. Ultimately, only the bound solid remains on the substrate and the solvent is evaporated. Clearly coating is a *process* with the coating flow being one unit operation controlling the quality of the product and the rate at which it is produced. Other unit operations in the coating *process* include the preparation of the coating paste and its pumping to the coating head and the drying of the coated film. They too have an influence on throughput and product quality.

As for products issuing from coating processes, it is important to realise that almost *everything* we use nowadays is coated. As a whole, the coating industry is truly phenomenal in its size and it can be argued that coating activity in a country is a good measure of industrial activity-thus prosperity of that particular country. Coating applications are wide and varied and include the coating of paper, plastics, wood, metal and walls, the manufacture of paper, plastic substrates, photographic films, audio and video tapes, electronic substrates, health products (nicotine patch and diabetes test strips for example) and many other products. How fast a coating operation is carried out dictate process efficiency and economics.

The most serious limitation to coating productivity is dynamic wetting, which cannot be sustained and fails above a certain speed and gives way to air entrainment. The air is entrained in the form of very fine bubbles, which mar the integrity and quality of the final product. The resulting waste is significant and very costly throughout the coating industry.

Understanding the physics and chemistry of dynamic wetting and its failure has preoccupied many scientists over the years. As yet no full predictive theory is available and there still remain serious gaps in our knowledge of this phenomenon. This paper will discuss first general features of coating flows, the critical steps in our understanding of dynamic wetting and its failure, exploit these to develop new coating flow situations and present new data to enhance our understanding of some key issues. The ultimate aim is to use this knowledge to postpone dynamic wetting failure to higher speeds than normally achieved and thus push production rate further. This paper deals with continuous coating only on moving substrates.

CLASSIFICATION & FEATURES OF COATING FLOWS

As depicted in Figure 1, a coating flow *brings in* a bulk flow from a source and *transforms* it into a thin film. Various flow configurations are thus possible but they all essentially fit in one of the following four types:

(i) *Free coating flow* - withdrawal of liquid from a pool by a moving substrate (Figure 1a). Clearly in this flow, there a no external control parameters and the thickness of the film will depend on speed and liquid properties.

(ii) *Metering coating flow* - metering an excess amount of liquid in a geometry that gives a uniform film on a moving substrate. The geometry consists of a metering gap formed between the substrate usually driven by a roller and stationary or moving wall(s), which may be rigid or flexible (Figure 1b). Unlike free coating, the geometry and dynamics of the metering gap provide extra variables to control film thickness.

(iii) *Metered coating flow*- delivering by means of a flow geometry the exact amount of liquid to form a film which then is transferred to a moving substrate. The geometry generally consists of a film issuing from a die falling onto the moving substrate (Figure 1c). Here, the die sets the flow and the film thickness is merely controlled by the substrate speed.

(iv) Print or gravure coating flow - in which a moving substrate wipes a proportion of a coating trapped in the cells on a printed or engraved roller (Figure 1d). Here the geometry of the cells will play an important role in controlling flow and film thickness.

The classification described above is based on film delivery only. As depicted in Figure 1, all coating flows will *begin* at a region when the incoming solid substrate first meets the liquid- the *dynamic wetting line* where the three phases (solid-liquid-air) coexist. Clearly there will be a speed V_{ae} above which this line cannot be maintained; it will fail (*dynamic wetting failure*) and let in air with the liquid being entrained in the substrate. The exact mechanism is described below. Another limit of this flow is the quality of the surface finish, i.e. the stability of the free surface, which leads to the formation of the film. Clearly it will be prone to waves, ribs and other rippling effects, which must be controlled by the flow conditions and liquid properties, viscosity (μ) and surface tension (σ). As expected the surface tension of the liquid will have a dominant effect and this is expressed in the capillary number (ratio of viscous forces to capillary forces), $Ca=\mu V/\sigma$. Coating flows are thus delimited by a window of operation, which provides the range of operating conditions leading to the production of an air free, rib free film.

MECHANISM OF DYNAMIC WETTING FAILURE

As inferred earlier the origin of dynamic wetting failure lies in the inability of the dynamic wetting line to remain stable- straight above a certain a speed. Experiments to study this phenomenon have been largely conducted with plastic substrates in dip coating (Figure 1e) which is the simplest coating flow. They show that as the speed of the substrate is increased, the wetting line moves downward and the *contact* *angle* increases until it approaches 180° at the critical velocity V_{ae}. At this speed, the dynamic line break into a sawtooth (vvv) shape line with air bubbles attaching themselves to the trailing vertices and becoming entrained by the substrate (Figure 2). Deryagin and Levi (1964) were the first to report this mechanism described since in greater details by many investigators in dip coating and other coating flows (Benkreira (2004)). The bulk of the data are however limited to dip coating and they all show that viscosity is the main controlling factor with surface tension and density playing a very minor role. One correlation widely used is that due to Gutoff and Kendrick (1982) with V_{ae} expressed in cm/s and μ in mPa.s:

$$V_{ae} \approx 5.11\,\mu^{-0.67} \qquad [1]$$

Such correlations do not consider the effect of non-Newtonian behaviour, which must be important since viscosity is the dominant property. Remember that wetting is a surface phenomenon and viscosity being dependent on shear rate will vary throughout the flow. Shear rate very near the surface will be comparatively larger and could lead to very low viscosities especially when the coating liquid is highly shear thinning. Another feature feature however becomes important. Non-Newtonian fluids are also by definition made up of small molecules (solvent) and larger molecules (solids) and it is likely that it is the smaller molecules (the solvent) that are the more active. Clearly the non-Newtonian effect will be complex and rheological properties alone will not describe it.

When we consider dynamic wetting, the substrate topography (roughness) or wettability should a-priori, have an effect on air entrainment. Indeed early studies by Buonoplane *et al.*(1986) showed that substrate roughness leads to higher critical velocities in some tests by a factor as much as 12 in comparison with smooth substrates but surface wettability has little or no effect. The fact that roughness postpones V_{ae} to higher values could be inferred (Scriven (1982)) because roughness presents a path for the air to escape. The present paper shows however that this argument is not absolute and roughness, depending on its magnitude, can postpone as well as hasten air entrainment.

The most fundamental observation, which provides a mechanism for the break-up of the wetting line into a sawteeth pattern, is that made by Blake and Ruschak (1979). They observed the geometry of the vvv shaped wetting line at speeds higher than V_{ae} and established that the component of the speed normal to the straight-line segments of the wetting line (Figure 2) is independent of the substrate velocity. They defined this component, the *maximum speed of wetting,* V* which they assumed is the maximum speed at which the wetting line can advance normal to itself. They observed that the substrate could be wet at speeds V higher than V* only if the wetting line slanted so that the speed of the solid normal to it did not exceed the maximum speed of wetting. More specifically, they found that the wetting line segments adopted the minimum possible inclination Φ such that:

$$\cos \Phi = V^*/ V \qquad (V \geq V^*), \qquad [2]$$

One important corallary of this observation, not verified experimentally by Blake and Ruschak, is air entrainment can be postponed to velocities V_{ae} larger if the substrate enters the liquid at angle such that the wetting line becomes not perpendicular to the direction of substrate motion. The present paper will present data to test this hypothesis and exploit the findings to develop new faster coating flow situations.

Another aspect and may be the most fundamental to dynamic wetting is with regard to its nature. As yet no theory is available that can describe it fully. Molecular-kinetic theories (Blake (1993) for example) by their essence are limited because they disregard macroscopic hydrodynamic effects. At best they can describe dynamic wetting at very low speeds and usually predict a finite maximum speed of wetting even if the displaced phase is inviscid. In other words, according to molecular-kinetic theories, the viscosity of air plays no effect in its entrainment by the liquid. Hydrodynamic theories (Cox (1986) for example) are also limited because they only consider viscous effects- interactions of large numbers of molecules (fluid elements) and the effects this interaction produces on a macroscopic length scale. Their other most serious drawback is they do not have a physical rationale to handle the variation of the dynamic contact angle with coating speed. Recent developments (Shikhmurzaev (1993, 1997)) are being made to resolve this crucial feature using flow-induced surface tension gradients along the wetting line. Such approach predicts a maximum speed of wetting when the displaced phase is viscous. In the absence of air or with an inviscid gas and for perfectly flat chemically homogeneous solids an infinite maximum wetting speed is predicted. However, no experiments have been carried out to assess the fundamental effect of air viscosity on dynamic wetting failure. This paper will present unique data for this purpose.

EXPERIMENTAL METHODS

Here we present the experimental methods relating to the three crucial aspects of dynamic wetting discussed above: effect of roughness, wetting angle and air viscosity. These three effects were studied using the dip coater depicted in Figure 2. It is a simple device consisting of a transparent tank (20cm x 20cmx 20cm) holding the coating liquid and a rollers-drive system to plunge a narrow substrate 50mm wide and 25 microns thick into the liquid at constant speed. This speed was measured with an optically triggered digital tachometer mounted on one of the rollers. To reduce any static charges, all the rollers were grounded. The substrate exited the tank through a narrow slit. The liquid level in the tank was maintained constant by topping up with fresh liquid.

In order to assess the effect of wetting angle the following technique was used. The whole system, including the tank and the motor, which was no more than 60 cm high, was mounted on a solid frame that could pivot sideways. This allowed a vertical plane to be maintained whilst allowing the wetting angle to be varied and measured in increments of 5° from 0° to 55°. The height of the tank ensured that the depth of the liquid was at least 5 cm even at the maximum wetting angle investigated.

In order to assess the effect of air viscosity, the whole set up was placed in a stainless steel vacuum chamber (80cm x 40cm x 40cm) with walls 1cm thick and three viewing glass windows. For the vacuum experiments, the drive system was changed with the substrate winder roller being driven from the outside by a geared motor via a labyrinth type vacuum seal. A remote sensor placed inside the vacuum chamber measured the substrate speed. The viscosity of the air in the chamber was decreased by decreasing the pressure from atmospheric down to 6.5 mbar, the minimum we could attain with our pump.

For the experiments at atmospheric conditions, lubricating oils and glycerine-water solutions were used and their viscosities were in the range 40-733 mPa.s with a surface tension of 30-65 mN/m. In the vacuum experiments, silicones were used to prevent boiling at low pressures. They had viscosities in the range 9 to 194 mPa.s and a surface tension of 19 mN/m. Note that the coating liquids were thoroughly characterised for their viscous properties, with a Bohlin CVO variable shear rate viscometer. As expected these solutions are Newtonian and the viscosities measurements are within an accuracy of ± 5%. The surface tension of the coating liquids were measured using the pendent drop method to an accuracy of ± 2 %.

The effects of non-Newtonian behaviour were also assessed using glycerine-water solutions of various viscosities mixed with small amounts of either polyacrylamide (PAA) or carboxymethyl cellulose (CMC). The molecular weights of the PAA and the CMC were 5×10^6 and 7×10^5 g/mol respectively. All the polymer solutions tested presented measurable degrees of shear thinning and in the case of PAA, measurable elasticity. Details on the preparation procedure and rheological measurements can be found in Cohu and Benkreira (1998).

Now as for the measurement of air entrainment speed, visual observation under good illumination are very effective in detecting the critical speed at which the wetting line changes from a straight line into a sawteeth shape. During this programme, repeat experiments by three observers showed that the discrepancies between individual and averaged data was always found to be less than ± 10%, being even less than ± 7% in most cases. It must be noted that we have assumed that the break-up of the wetting line and the onset of air entrainment are confounded. Air entrainment appears of course after dynamic failure but in practice and our observations confirm it, it occurs almost so immediately that it is difficult to distinguish between the two speeds (Burley, 1992; Veverka and Aidun, 1997). Strictly therefore our data refer to dynamic wetting failure, which of course is the fundamental measurement.

This programme of experiments also required an accurate measurement of the roughness of the substrates used. We used for this purpose a specialised equipment, the MicroXam surface-mapping microscope at AG Electro-Optics (Tarporley, Cheshire, UK), checked against gross data obtained from a Talysurf and intricate data from an atomic force microscope.

EXPERIMENTAL RESULTS & DISCUSSION

Roughness Effect on Dynamic Wetting

Two important observations were made from all the data. The first is that depending on the value of viscosity and roughness, V_{ae} with a rough substrate can be larger or smaller than V_{ae} with a smooth substrate of the same material. In other words for any given roughness a *switch* is observed with viscosity and this illustrated in the data in Figure 3a. The second observation is in relation to the mechanism of dynamic wetting failure in the two regimes. At viscosity lower than a critical value, the classical vvv failure is observed with the rough side entraining air at lower speeds than the smooth side. This is consistent with the concept of maximum speed of wetting in that the wetting line must move a greater distance across a rough surface than a flat surface of equivalent length. Above the critical viscosity the reverse was observed, the rough side entraining air at higher speed than the smooth side. The air entrainment in such a case was sudden and intense and not preceded by a vvv line. A new mechanism is occurring with the liquid film *skipping* over the peaks of the rough surface and suddenly breaking above a critical speed allowing air to gush in with the substrate.

The data showed clearly that this switch is observed only when the roughness is above a critical value, observed to be about 1.5-3 microns. The data also show that the critical viscosity is very sensitive to roughness and a slight increase in roughness (8%) can push the critical viscosity by a much larger order of magnitude (311%). This is very useful in practice as it implies that higher solid content formulations (higher viscosity) can be coated faster by increasing the roughness of the substrate but not so substantially as to weaken its strength. Remember that the push in coating productivity is to coat not only faster but also with higher solid content, which is synonymous to higher viscosity.

Wetting Angle Effect (β) on Dynamic Wetting

Here the objective was to verify experimentally the corollary of Eq. (2)- that V_{ae} can be increased by a factor $1/\cos\beta$ if the substrate enters the liquid at angle (β) such that the wetting line becomes not perpendicular to the direction of substrate motion. The data shown in Figure 3b clearly prove that this is indeed true. They provide experimental evidence of the existence, for a given solid / liquid / gas system, of a maximum speed of wetting understood as the maximum speed at which a dynamic wetting line can advance normal to itself in dip-coating experiments. The data also can be exploited practically. As far as dynamic wetting failure and air entrainment are concerned it is not the velocity of the substrate, which is relevant but the component normal to the wetting line. Tilting the dip coater by an angle of 55° as we did has led to a 75 % increase in the coating speed. Similar gain can be achieved in other coating flows by realising the same wetting condition. We have verified this in a curtain coater rotated in the horizontal plan (Benkreira and Cohu (1998)).

Air Viscosity Effect on Dynamic Wetting

This is probably the most testing effect to help theoretical development of dynamic wetting failure. The data in Figure 3c conclusively stress the importance of the viscosity of the air on its entrainment by the substrate. They show that as the pressure is reduced -that is as the viscosity of the air is reduced the speed at which dynamic failure increase rapidly.

Whether a zero viscosity would lead to an infinite dynamic wetting failure velocity still remains an unanswered experimental challenge. The data points towards this but remember that substrate surface always have a roughness even if it is microscopic. Also they are rarely chemically homogeneous throughout their surface. Molecular and surface effects will thus in practice always play their part. Whether their contribution in the absence of air is more effective or the mechanism different, we do not know.

CONCLUSIONS

Dynamic wetting is a complex phenomenon yet some simple experiments, carried out only recently, have began to unravel its complexities. Challenging issues still remain but the vacuum experiments described here with a tilting dip coater can provide a fundamental experimental basis to help our understanding of this phenomenon, which occurs in nature and in many engineering processes. What is required is to build on these experiments with well-defined substrate under extreme vacuum.

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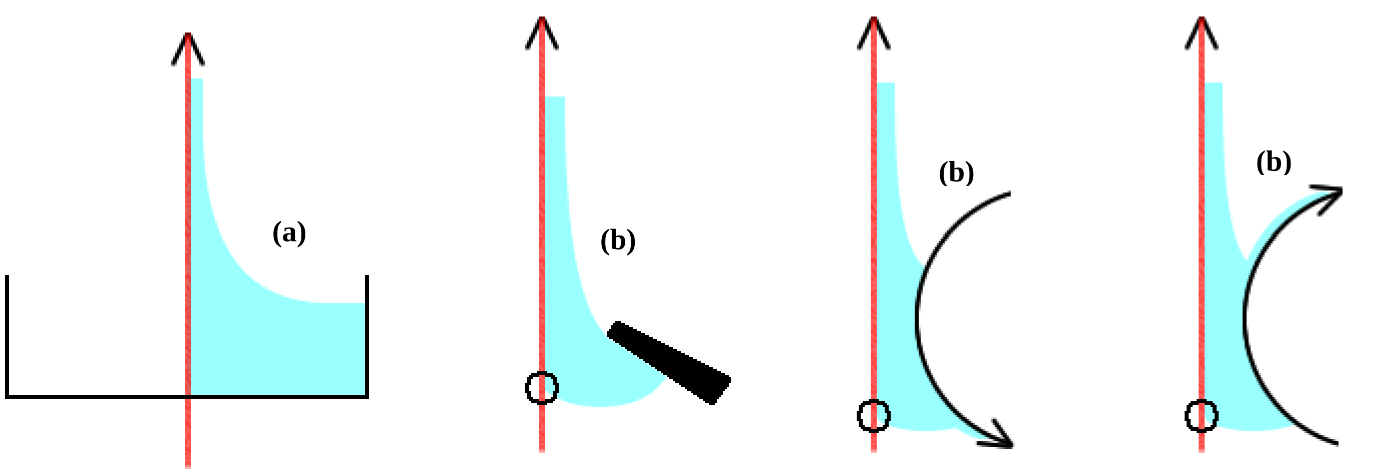

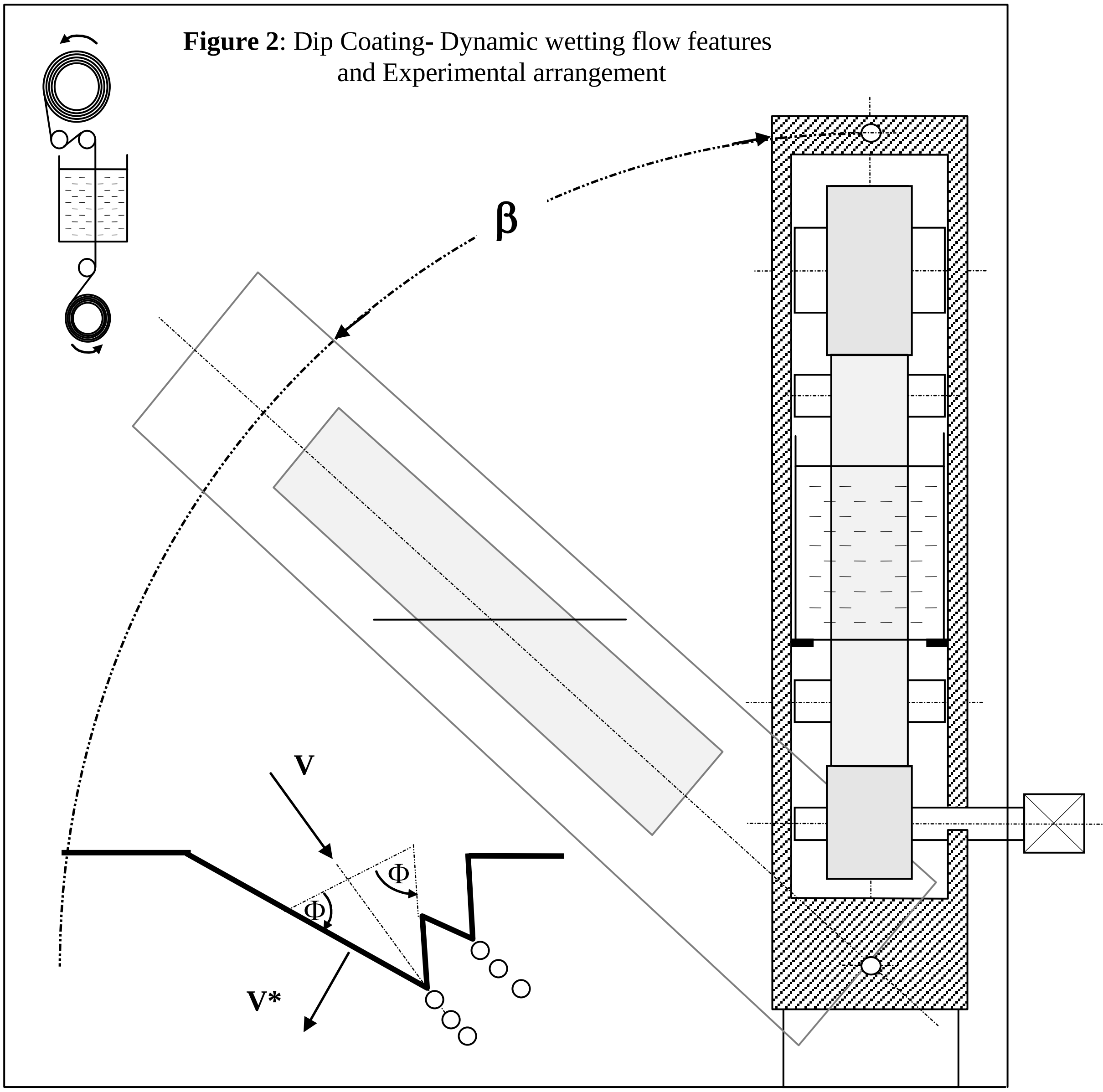

Figure 2: Dip Coating- Dynamic wetting flow features and Experimental arrangement

Figure 3a: Effect of Roughness (O : Smooth Side)

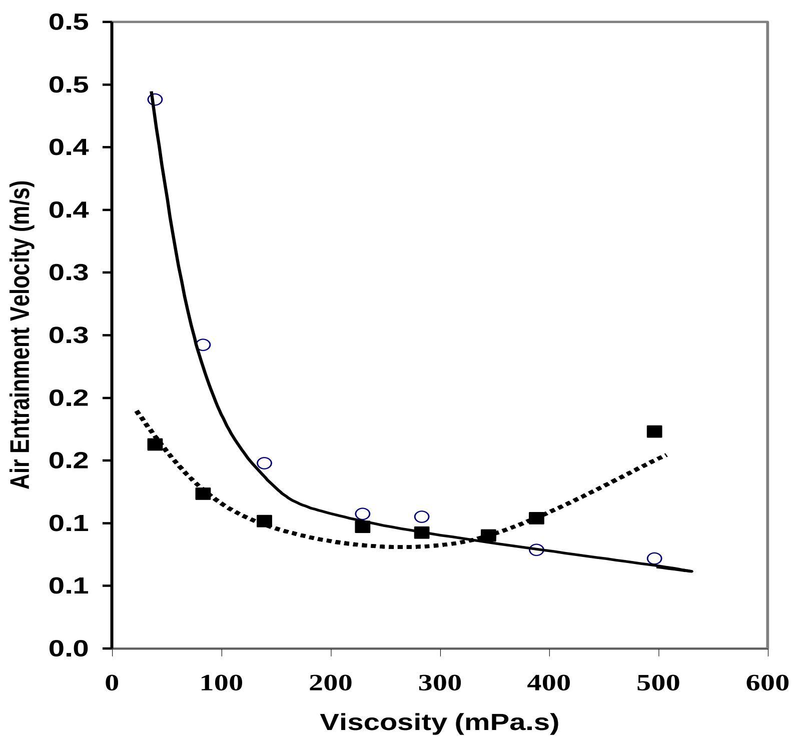

Figure 3b: Effect of Wetting Angle

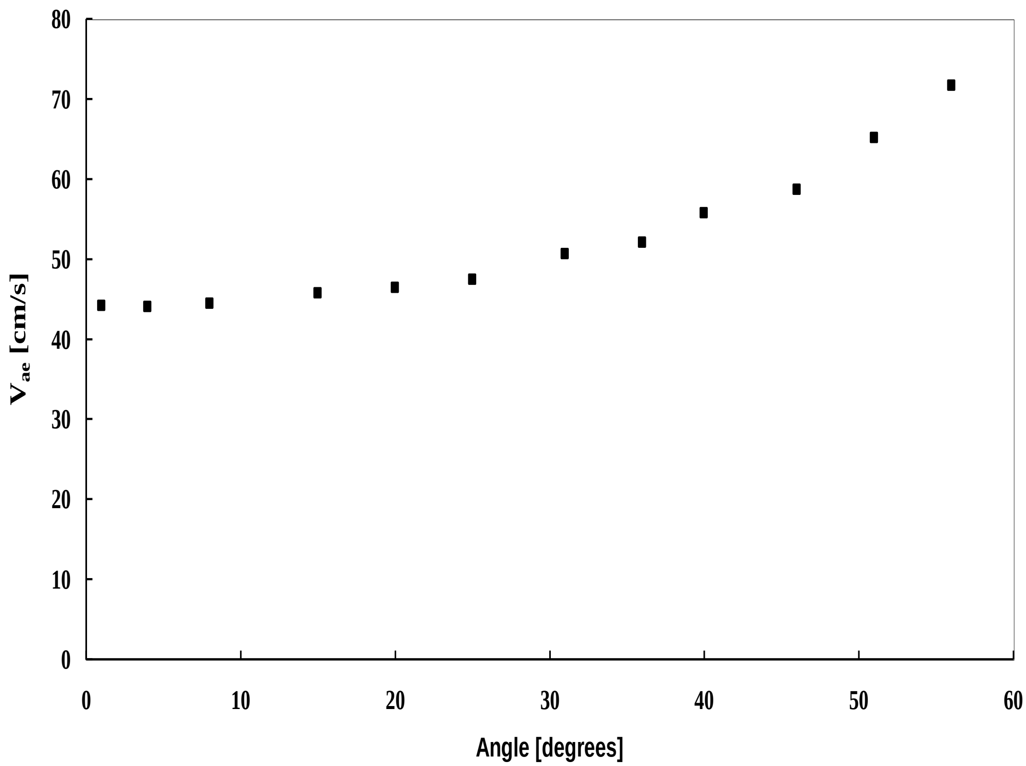

Figure 3c: Effect of Reduced Pressure at various viscosities