

On the Dynamic Capillary Effects in the Wetting and evaporation process of Binary Droplets

K. Sefiane ¹

Abstract: In this paper recent experimental results on the wetting behaviour of volatile binary sessile drops are reported. The evaporation rate is varied through the control of the ambient total pressure. The dynamic wetting contact angle of an evaporating Water-Ethanol drop is investigated at various sub-atmospheric pressures. The wetting properties (contact angle, shape and volume) are monitored in time using a drop shape analysis instrument. The results show that the evaporation of the binary droplet takes place in two stages: a first stage where the wetting behaviour is very similar to the pure ethanol case and a second stage where it is very close to the pure water case. The effect of varying the evaporation rate is found to shift the observed transitional stages. The analysis of these results shows that in the first stage mostly the more volatile component evaporates and in the second one mostly the less volatile component evaporates. It appears however that during these processes there can be an evaporation of both components in different proportions. This is clearly influenced by the total evaporation rate and the diffusion from the bulk to the interface.

keyword: Wetting; Evaporation, Diffusion, Concentration gradients, Capillary effects

1 Introduction

Wetting phenomena play a crucial role in a wide range of technological applications (see, e.g., Lappa (2005a, 2005b)). Spreading of liquids on solids involving phase change is encountered in many areas ranging from biological systems to industrial applications. Ring formation from evaporating drops and its use for thin films coating, Deegan (1998), and DNA chains elongation using a drying sessile droplet are examples of new developments and identify a need for the understanding of the process of evaporating droplets, Hu (2002). Exten-

sive work can be found in the literature dedicated to understanding the fundamentals of this process, Pickenet (1977), De Gennes (1985), Blake (1969), Shanahan (1995).

Although wetting and evaporation of binary mixtures is an important case to many applications, little work has been done to investigate the fundamentals of the problem. There are many possible applications to which understanding of evaporation and wetting behaviour of binary mixtures can be applied.

In wastewater treatment plants, knowledge of surface tension behaviour is used to monitor concentrations of volatile organic compounds such as benzene, toluene and trichloroethylene (TCE) to ensure that levels do not exceed safety limits. In the microelectronics field, recent trends towards technologies with high power dissipation and density have resulted in the need for the design of more effective thermal management systems. The traditional methods of air cooling and direct immersion cooling may no longer provide a sufficient level of heat removal from the circuitry. A promising solution to the cooling of high density microelectronic applications is the process of spray evaporative cooling. This involves the spraying of a dielectric liquid directly onto the circuitry. The liquid will absorb the heat from the circuitry, and then evaporate, thereby cooling the electronic components. The evaporative process and therefore the effectiveness of cooling will be governed by the wetting behaviour of the sprayed liquid. In a study by Rowan et al. (2000) the wetting behaviour of a 1-propanol and water mixture were observed. Contact angle and base width measurements of the droplet were made for a variety of compositions at 21C and ambient pressure. The results of this paper show two distinct trends of wetting behaviour: one for mixtures with mole fractions of less than 0.39 propanol and one for mixtures with mole fractions more than 0.39 propanol. For mixtures containing more than 0.39 mole fraction propanol, it was found that the contact angle decreased at a steady rate for the period

¹ School of Engineering and Electronics, University of Edinburgh, Kings Buildings, Mayfield road, Edinburgh EH9 3JL, UK. Email: ksefiane@ed.ac.uk

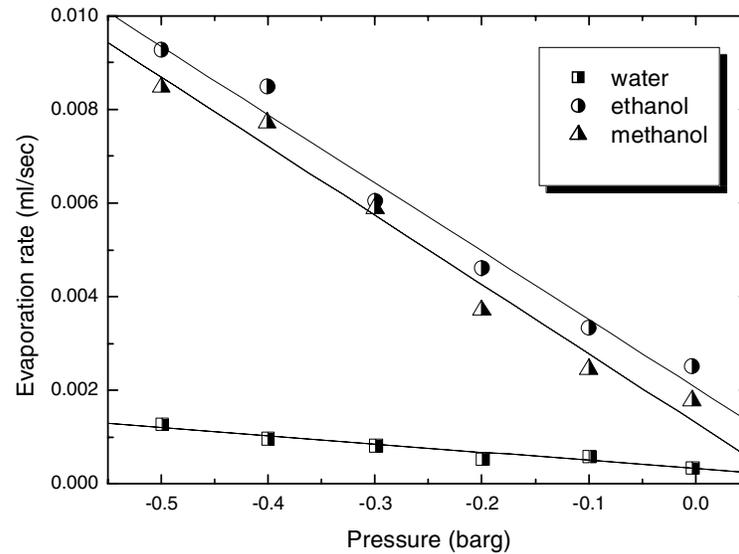


Figure 1 : Evaporation of water droplet on aluminium and PTFE substrates

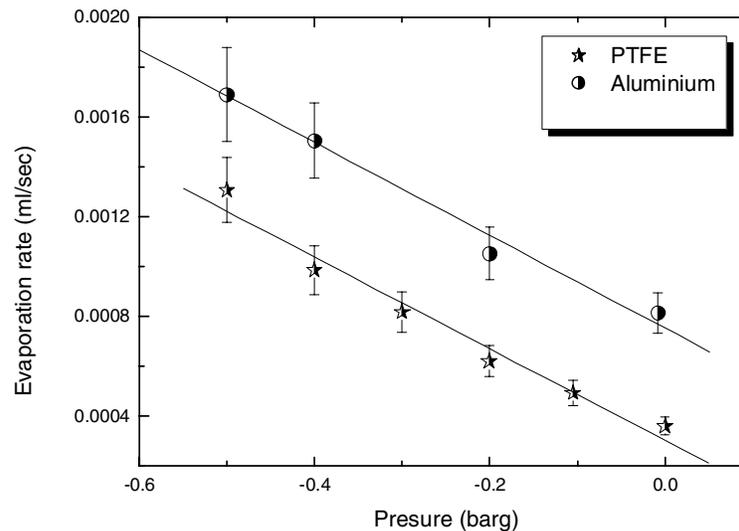


Figure 2 : Evaporation of water droplet on aluminium and PTFE substrates

required for total evaporation (90 s), whereas the base width measurement was steady for about 60 s before decreasing at a fast rate. Additionally, the droplet maintained a rough spherical cap-type shape throughout the evaporation process. For mixtures containing less than a 0.39 mole fraction of propanol, the behaviour observed was markedly different. Initially, for a short period of time, the contact angle decreased. After this however,

contact angle measurements were found to be unobtainable due to instabilities around the droplet periphery. The droplet was then observed to spread and break into several smaller droplets, eventually leading to the formation a single new droplet.

A likely explanation for this behaviour has to do with the azeotropic nature of the propanol/water mixture. The azeotropic composition at the conditions of the experi-

mental studies was externally verified to be 0.41 which is so close to the margin at which the trend of wetting behaviour changes. Therefore, when the mixture contains a water in excess of the azeotropic composition ($x_{\text{propanol}} < 0.41$), evaporation will result in a residual liquid that tends to pure water as the propanol is preferentially absorbed at the interface. The combined effects of the preferential absorption of propanol and also the cooling caused by evaporation induce local surface tension minima and maxima, leading to the instabilities observed. When most of the propanol has evaporated, the dynamic surface tension observed will tend to that of pure water, which is verified by the higher contact angles detected in the latter stages of the experiment.

Again, although a quantitative reasoning is given to explain the dynamic surface tension behaviour of the propanol/water droplet, it is essential to produce a more rigorous physical approach which will include mathematical modelling of the absorption and evaporation dynamics to verify the experimental findings. The aim of this paper is to present the findings of an experimental investigation of the evaporation and wetting behaviour of ethanol/water droplets. The effect of concentration and evaporation rate has been investigated and the role of diffusion in the liquid and gas phases is discussed.

2 Experimental Setup and Procedure

The experimental equipment used to carry out the evaporation of sessile droplets under various pressures consists of:- a computer with FTA200 package (contact angle analysis software), a CCD camera, a cell of dimension 4x4x3 cm, an injection pump, an aluminium/PTFE substrate of dimension 2.5x6cm. The FTA200 package evaluates the contact angle, volume, height, diameter and surface tension of the sessile drops. The sessile drop and its contact angle is highly influenced by the surface finish and the presence of impurities on the substrate. For that reason, surface preparation techniques such as polishing, and cleaning in ultrasound bath were used, prior to the experiments, in an attempt to obtain a clean and homogeneous surface. Substrates were pictured by the Atomic Force Microscope, (AFM). The analysis performed by the AFM was completed by the use of a Zygo profilometer to evaluate the roughness of the substrate. The resulting profile indicated that the PTFE substrate can be considered as relatively rough.

Some preliminary exploratory tests have been performed

in order to select the binary system as well as the substrate. In order to select a binary mixture to demonstrate the coupling between volatility and surface tension, water, ethanol and methanol were investigated independently.

The evaporation of the three liquids under reduced pressure has been investigated (Fig. 1). For these pure substances, evaporation rate increased linearly with decreasing pressure, with water having a much lower rate and pressure dependence than ethanol or methanol, which is consistent with its lower vapour pressures. Water and ethanol were chosen for the experiments with mixtures because pure water and pure ethanol have similar contact angle trends with time during evaporation. The liquids used are pure liquids purchased from Aldrich Chemicals, ethanol and methanol are used as received, 99.9% purity. Water is pure distilled deionised water.

Fig. 2 shows evaporation of a water droplet on both the PTFE substrate and Aluminium substrates. The evaporation rate is higher for the Aluminium substrate because the droplet spreads more on this surface, giving rise to a larger surface area. The PTFE substrate has lower thermal conductivity which could have reduced heat transfer for the energy required for evaporation in addition to the spreading effect.

However, the slopes of both lines are similar, indicating that heat transfer limitation is unlikely. The PTFE substrate was chosen because its high surface energy gave rise to larger and hence more readily measurable contact angles for ethanol.

3 Results

Evaporation rates for pure water and pure ethanol and a range of mixtures of these are given in fig 3. at various concentrations of ethanol in water in volume fractions. various (sub)atmospheric pressures. The evaporation rate is observed to increase linearly with decreasing pressure for each substance. Increasing the ethanol concentration increases the overall evaporation rate consistently. In order to facilitate analysis of our results, some further data are presented in dimensionless form. The contact angle, base width and drop volume are normalized to the initial values, while time is normalized to the lifetime of the drop.

The normalised curves show two types of behaviour depending on the drop concentration regardless the pa-

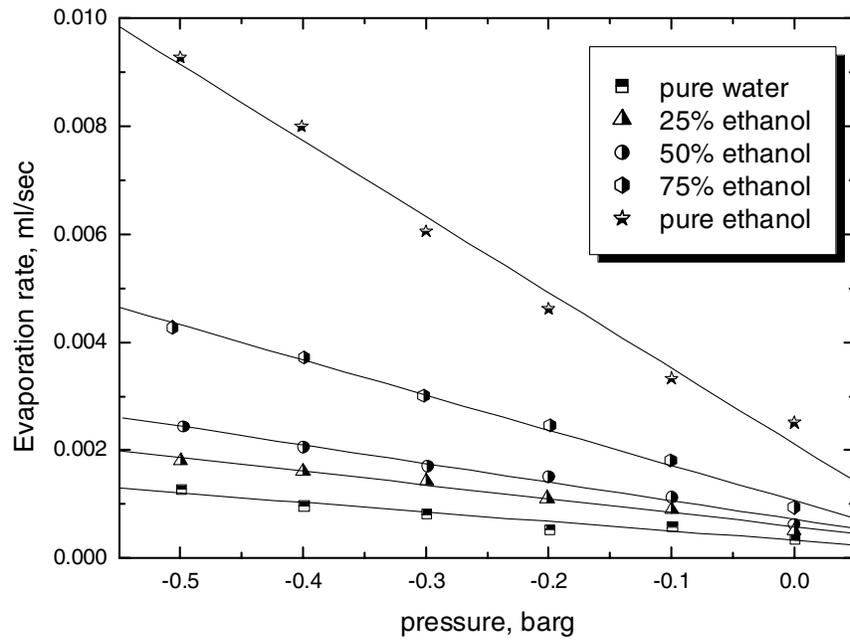


Figure 3 : Overall evaporation rates of pure and mixtures at various sub-atmospheric pressures.

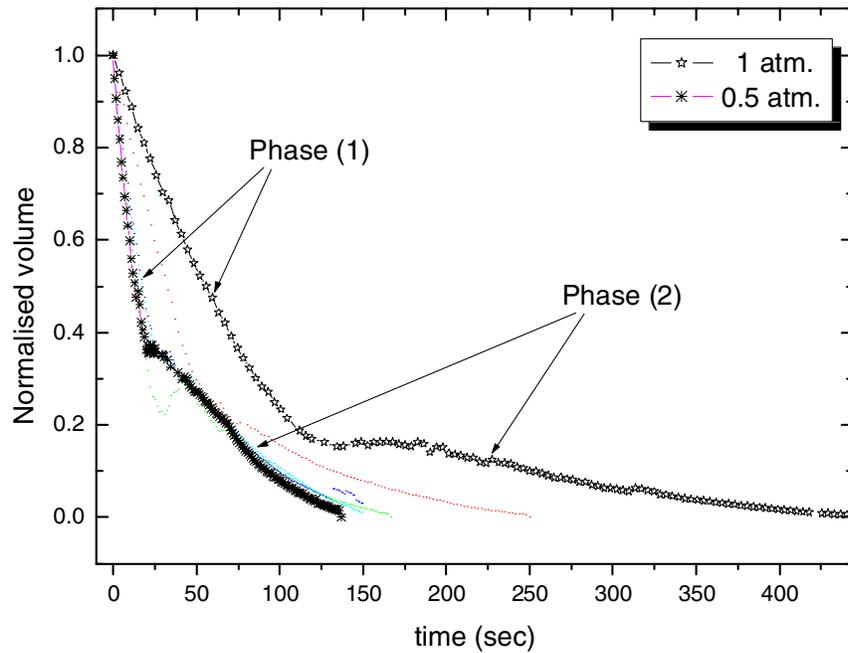


Figure 4 : Identification of the two stages in the evaporation of water-ethanol mixtures at two pressures.

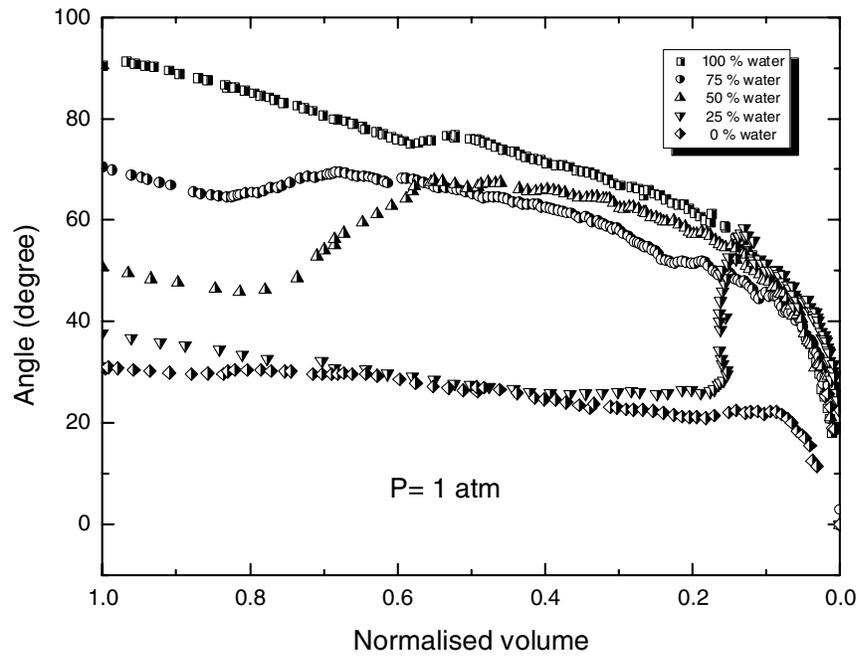


Figure 5 : Evolution of the contact angle versus the drop volume for various initial concentrations at P= 1 atm.

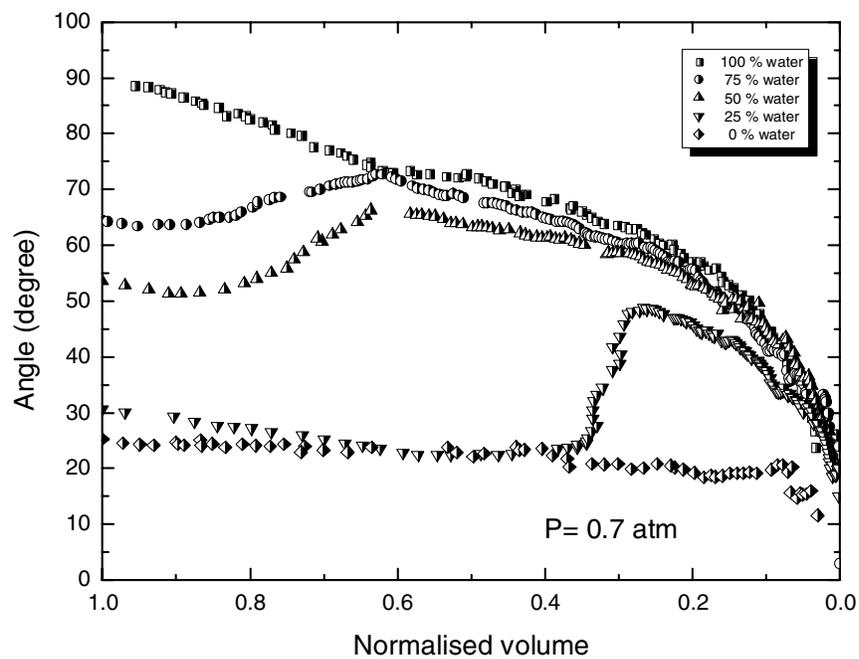


Figure 6 : Evolution of the contact angle versus the drop volume for various initial concentrations at P= 0.7 atm.

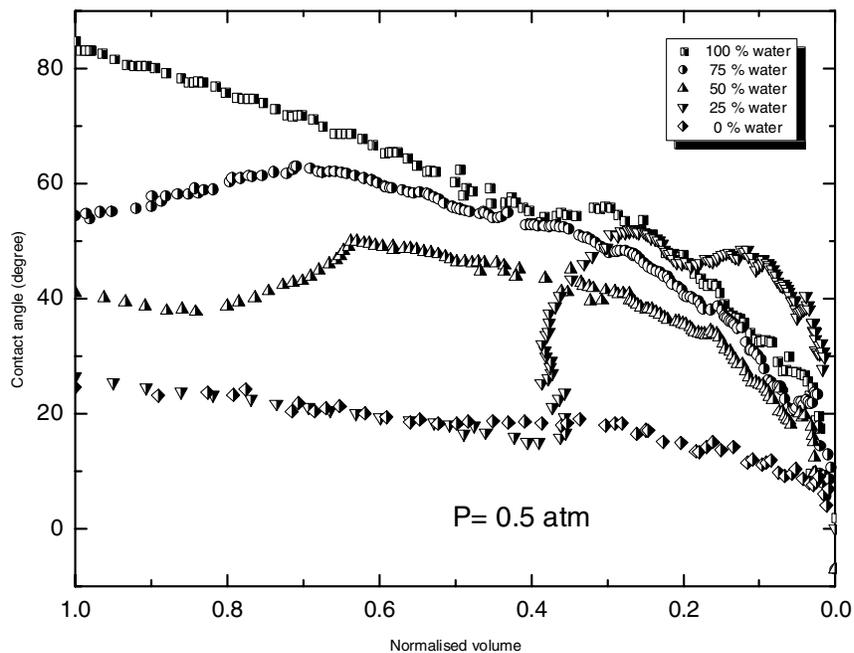


Figure 7 : Evolution of the contact angle versus the drop volume for various initial concentrations at P= 0.5 atm.

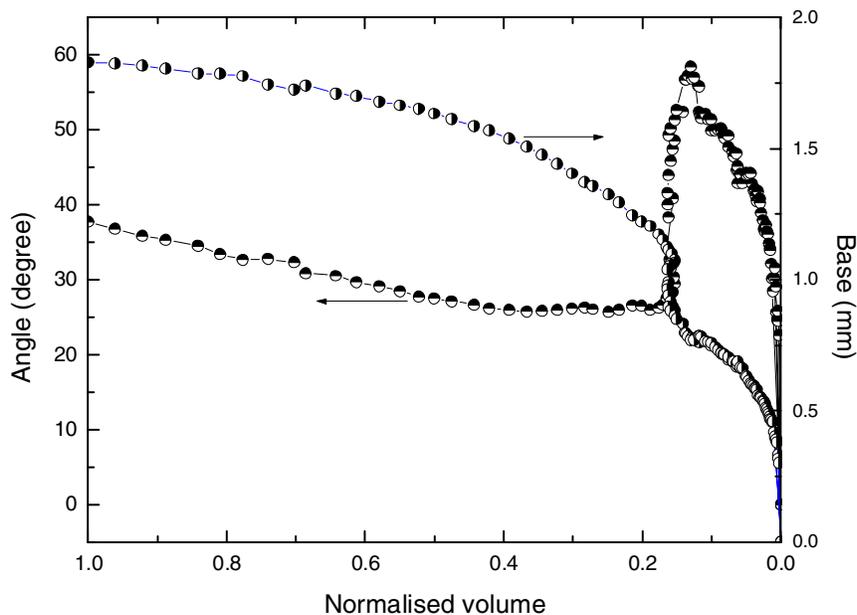


Figure 8 : Depinning of the contact line during contact angle jump.

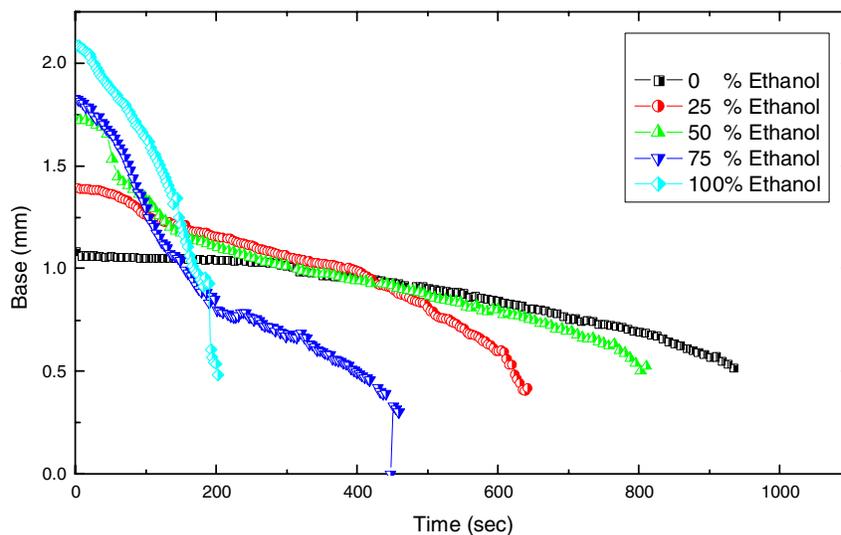


Figure 9 : Evolution of the drop base versus time for various initial concentrations at P= 1 atm.

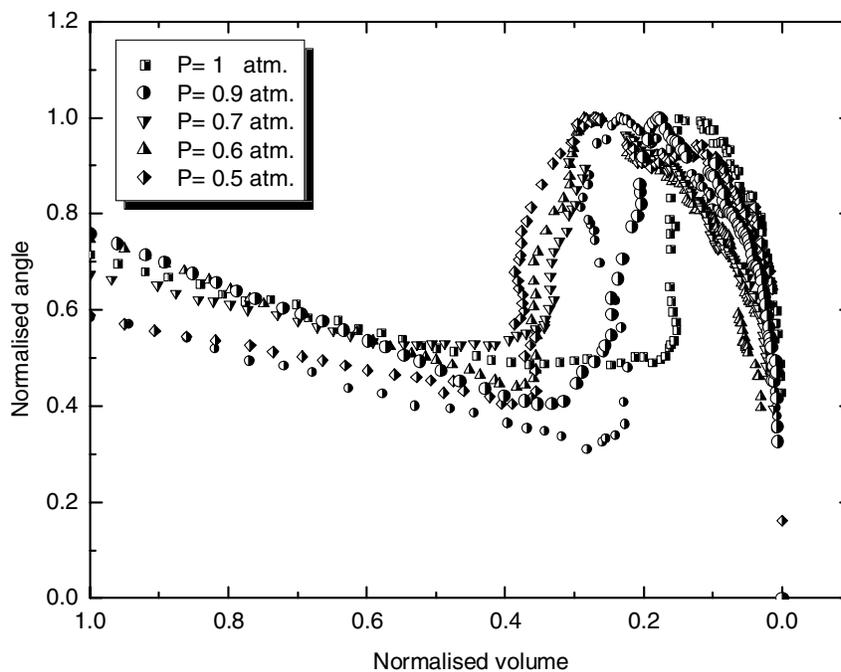


Figure 10 : Evolution of the contact angle versus the drop volume for an initial concentrations of 75% ethanol at various pressures.

parameter studied (drop volume, contact angle, drop base width). For pure substances, the normalised curves show almost a similar trend. The drop volume and the base width decrease monotonically for all the evaporation duration. For mixtures, the normalised curves reveal different behaviours from the pure substances. For small concentration (25%) of the volatile liquid, the droplet characteristics evaporation is globally close to pure substances. As the volatile liquid concentration increases in the drop, the drop volume variation deviates significantly from the pure substances. This leads to the observation that the evaporation mechanisms for the mixtures differ from the pure ones. The present results show that for binary mixtures the wetting behaviour of evaporating drops deviates from the known pure component trends. In all performed experiments we found that on the rough surface we used, the contact angle decreases which suggests that pinning of the contact line may occur; however, base width measurements (Fig. 9) show a slow decrease for all tests except that of pure water. The evaporation sequence of an ethanol-water droplet did not display similar characteristics to either of the two pure components. There was a well defined two-phase evaporation sequence identified, which became more defined as the ethanol concentration increased (see Fig. 4). If pinning occurs an initial extra phase is observed – see Sefiane (2003).

The duration of phase 1, compared to the entire evaporation time, increases with increasing ethanol concentration. The volume evaporated during phase 1 appears to be very close to the volume of ethanol in the droplet mixture. This indicates that it is likely that the ethanol, with its higher vapour pressure evaporates preferentially, though some small amount of water will evaporate too. Similarly the duration of phase 2 corresponds to the volume of water in the droplet and evaporates at a much lower rate than phase 1. This corresponds roughly to the evaporation of almost pure water.

The evaporation rates of phase one and phase two identified previously are compared to the evaporation rates of pure components. This comparison shows that on one hand, for the mixtures, the magnitude of the evaporation rate of phase one is very close to the one of pure ethanol. On the other hand the magnitude of the evaporation rate of phase two is close to the one of pure water. This corroborates the idea that the more volatile component evaporates mainly during the first phase while the less volatile one evaporates in the last phase.

When the evaporation occurs, the dynamic contact angle is correlated to the drop volume. The wetting angle varies continuously with the drop volume for pure substances. For mixtures this behaviour is different. For high ethanol concentration (75%), the initial contact angle is close to that of pure ethanol for a wide range of drop volumes. The contact angle at some point increases rapidly to the contact angle of pure water and subsequently follows the behaviour of pure water for the rest of the drop lifetime. This ‘jump’ in contact angle is a key feature of evaporation of rich mixtures of ethanol. There is a corresponding reduction in base width of the droplets (see fig 8) and the drop height also increases.

The location of the jump in contact angle varies with reducing pressure, occurring at progressively lower normalised volumes, as shown in figures 5, 6, 7 and 10. From the results presented it is clear that the wetting behaviour strongly depends on the initial concentration of ethanol.

4 Discussion of Mechanism

For mixture droplets, the overall rate of the evaporative process can be thought of as consisting of the following stages in series:

1. Diffusion (or more generally mass transfer) of the more volatile component to the surface of the drop;
2. Evaporation of both species from the surface according to their vapour pressures and droplet surface phenomena;
3. Diffusion of both species through quiescent air above the droplet in the cell.

The energy loss brought about by evaporation must be accounted for in stage (2) and, if not provided for entirely by heat transfer through the substrate, this heat transfer limitation must be modelled too.

Diffusivities of ethanol in water are significantly lower than those of either ethanol or water vapour in air. An estimate of the diffusive flux of ethanol from the base of the drop to the surface is much lower than the observed evaporation rate. This indicates that there are other mass transfer processes occurring in the drop. Circulation within evaporating drops has been observed, Hegseth (1996) and it appears that this, which would replenish

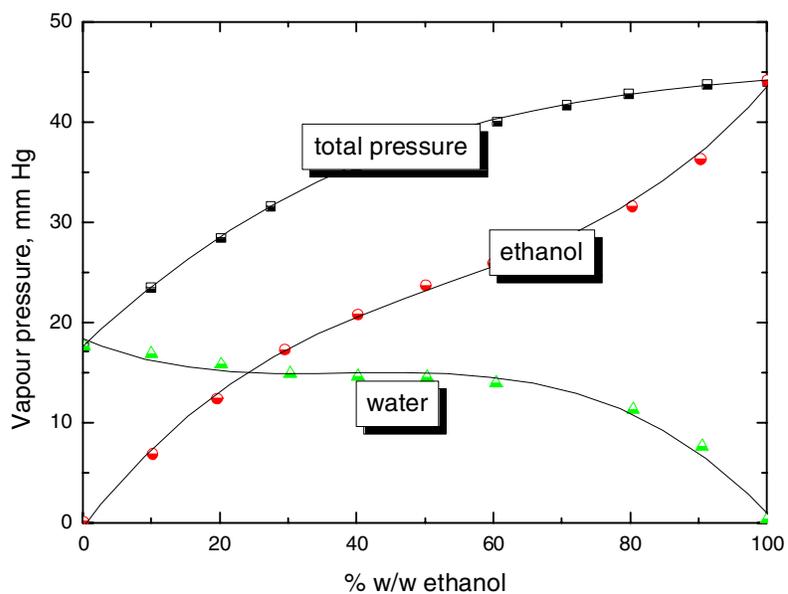


Figure 11 : Vapour pressure of ethanol-water mixture, [8].

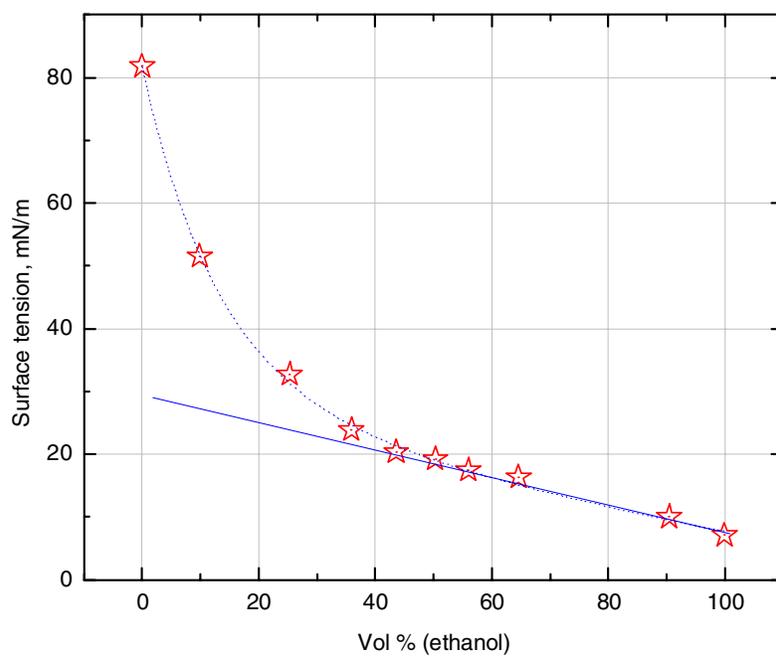


Figure 12 : Surface tension of ethanol-water mixture.

lost surface ethanol, is sufficient to keep the surface layer as ethanol rich as possible during preferential evaporation. Over time the ethanol concentration will decline. The contact angle is fairly insensitive to changes in concentration until the ethanol concentration has reduced to about 20% (see Fig. 11), see Vasques (1995), where after a rapid change in contact angle with further evaporation of ethanol would be expected; this appears to be the cause of the jump in contact angle seen. This insensitivity to ethanol concentration for rich mixtures also explains why the initial contact angle for these mixtures is close to that of ethanol.

The variation of location of the contact angle jump with pressure may be explained when considering the effect of pressure on evaporation of the mixture. The vapour pressure data (see Fig. 11 and O' Hare (1992)) suggest that the effect of reduced pressure is proportionately greater on ethanol evaporation than on that of water, leading to a transition to phase 2 earlier in normalised time the lower the system pressure.

The effects of dynamic surface phenomena on the evaporation rate have not yet been considered nor any surfactant-type behaviour. Incorporation of an energy balance into a model of the mass transfer phenomena explained above would be needed to accurately represent the system as would the dynamics of depinning of the droplet. Evaporation is not expected to be uniform along the surface.

Many investigators see e.g. Deegan (1998), have demonstrated that evaporation is larger near the contact points. This is a complicated system to represent accurately though the preliminary explanation provided here is in agreement with major observations.

5 Conclusions

An experimental investigation of the wetting and evaporation of sessile drops under sub-atmospheric pressures is presented. The role of surface tension of the a binary (water-ethanol) mixture in the wetting process is investigated. It appears that the mechanisms which govern the evaporation of a binary sessile droplet are coupled mass transfer and evaporation together with surface-tension-determined contact angle and depinning. Ethanol evaporates preferentially during the first phase whereas second phase evaporation is similar to that of water. For initially ethanol-rich mixtures there is an observable jump in con-

tact angle, which occurs earlier at lower system pressures and can be explained by surface tension phenomena.

References

- Deegan, R.** (1998): Pattern formation in drying drops. *Physical Review E*, 61(1): pp. 475-485.
- Hu, H. and Larson R.G.** (2002): Evaporation of a Sessile Droplet on a Substrate. *Journal of Physical Chemistry B*, 106: pp. 1334-1344.
- M. Lappa** (2005a): Coalescence and non-coalescence phenomena in multi-material problems and dispersed multiphase flows: Part 1, a critical review of theories. *FDMP: Fluid Dynamics & Materials Processing*, 1(3): pp. 201-211.
- M. Lappa** (2005b): Coalescence and non-coalescence phenomena in multi-material problems and dispersed multiphase flows: Part 2, a critical review of CFD approaches. *FDMP: Fluid Dynamics & Materials Processing*, 1(3): pp. 213-234.
- Picknett, R. and Bexon R.** (1977): The Evaporation of Sessile or pendant drops in Still Air. *Journal of Colloid and Interface Science.*, 61(2): pp. 336-350.
- De-Gennes, P.** (1985): Wetting: statistics and dynamics. *Rev. Mod. Phys.*, 57: pp. 827-863.
- Blake, T. and Haynes J.** (1969): *J. Colloid Interface Sci.*, 30: pp. 421.
- Shanahan, M. and Carre A.** (1995): Viscoelastic dissipation in wetting and adhesion phenomena. *Langmuir*, 11: pp. 1396-1402.
- Rowan S. M., Newton M.I., Driewer F.W., McHale G.** (2000): Evaporation of microdroplets of azeotropic liquids, *J. Phys. Chem. B*, 104, pp. 8217-8220.
- Vasques G., Alvarez E., Navaza JM.** 1 Surface tension of Alcohols+water from 20 to 50 C, *J. Chem. Eng. Data*, pp. 611-614.
- Hegseth, J.J., Rashidnia N., and Chai A.** (1996): Natural convection in droplet evaporation. *Physical Review E*, 54(2): pp. 1640-1644.
- O' Hare KD., Spedding PL.** (1992): *the Chemical Engineering Journal*, 48, pp. 1-9
- Sefiane K., Tadrist L., Douglas M.** (2003): *Int J. of Heat and Mass Transfer*, 46, pp. 4527-4534.