Experimental study of evaporating water–ethanol mixture sessile drop: influence of concentration

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Abstract

In this paper we study the evaporation of a drop on a rough polytetrafluoroethylene substrate. A water–ethanol binary drop of few millimetres size is evaporating in a controlled pressure environment. An experimental set up is built to investigate the influence of ethanol concentration and drop profile on the evaporation rate. The measurements were performed using an optical technique. This latter allows measurements of the dynamic contact angle, the drop volume and the base width as function of time. For pure substances (water, ethanol) the evaporation rate and the drop profile are found to have a monotonous evolution with time. For binary water–ethanol mixtures, three stages corresponding to different wetting behaviours are identified. The evaporation rate measurement indicates that the more volatile component evaporates entirely in the first stage while in the last stage the less volatile component is dominantly evaporating. The behaviour of the wetting angle is correlated with the volume of the drop and the ethanol concentration. It was clearly demonstrated that at high ethanol concentration (75%) the wetting contact angle of the drop matches the behaviour of pure ethanol during the first stage and tends to follow the behaviour of pure water during the third stage. This suggests that, as the ethanol evaporates in the first stage it diffuses to the interface where it dictates the surface tension properties and hence the wetting contact angle. Towards the end of the droplet lifetime, the wetting contact angle jumps to join the behaviour of pure water.

1. Introduction and literature survey

Wetting phenomena play a crucial role in a wide range of technological applications. Spreading of liquids on solids involving phase change is encountered in many areas ranging from biological systems to industrial applications. Extensive studies can be found in the literature dedicated to a better understanding of the fundamental aspects of this process. Bourges-Monnier and Shanahan [1] investigated the influence of evaporation on the contact angle. The evaporation of sessile droplets of water and n-decane was observed on various substrates using a projection method. Drop dimensions (height, width volume) and contact angle were measured as a function of time. The variability of the contact angle originates from roughness and chemical heterogeneity. A decrease in evaporation rate was observed with increasing initial contact angle. Hu and Larson [2] experimentally investigated the fluid flow in an evaporating droplet. Their results were compared to the theoretical model of Deegan [3]. Fluid flow within the droplet was measured by suspending small particle tracers within the bulk. The rate of decrease of the contact angle was found to be proportional to the rate of evaporation hence the evaporation of the liquid induces fluid flow in the droplet. The drop volume was found to decrease linearly with time when left to evaporate under a controlled environment thus a constant evaporation rate was observed. The particles were found to move towards

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the edge of the droplet and towards the substrate as evaporation proceeded and the radial and vertical velocities of the particles were calculated. The theory of Deegan [3] gives predictions of radial and vertical velocity that are in reasonable agreement with the experiments. A precise comparison was not possible because of experimental error due to the role of gravity and Brownian motion. In the first phase, the contact line is pinned and the contact angle decreases. In the second phase, the contact line recedes while the contact angle remains very small. The first phase occupies 90–95% of the droplet lifetime, thus Hu and Larson [2] developed their previous study and focussed on the evaporation of a sessile droplet with a pinned contact line.

Bernardin et al. [4] investigated the temperature dependence of water droplets wetting properties on an aluminium surface. They presented an experimental investigation of the temperature dependence of the quasi-static advancing contact angle of water on an aluminium surface. By utilising a pressure vessel to raise the liquid saturation temperature, contact angles were measured with the sessile droplet technique for surface temperatures ranging from 25 to 170 °C and pressures from 101.3 to 827.4 kPa. Two distinct temperature dependant regimes were observed. In the lower temperature regime, below 120 °C, a relatively constant contact angle of 90° was observed. In the high temperature regime, above 120 °C, the contact angle decreased in a fairly linear manner. Aluminium was chosen as the surface because it is the most commonly used metal in industrial processes. Surface finish and impurities heavily influence the contact angle; therefore it is essential to follow the same cleaning programme before each experiment. There is no point using ideal surfaces because these do not exist in practical applications and results could be misleading. The effects of surface roughness have been studied by many researchers using surface roughness factors such as the Wenzel factor. However, these factors all depend on each other, which makes the analysis difficult. Nakae et al. [5] introduced two kinds of models to determine the effects of surface roughness on wettability. The models adopted are hemispherical close-packed model and hemiround-rods closed pack models. Using these models the height of roughness (i.e. radius of hemispheres constituting surface) can be changed without altering the Wenzel roughness factor. Wenzel roughness factor is a function of true and apparent wetted area only. Chow [6] generalised the Young–Dupres equation to include the wetting of rough surfaces, in his paper, Chow presented a theory to describe the wetting phenomena and contact line de-pinning as a function of the microstructure of rough surfaces. Roughness results in local changes in the contact angle and hence the shape of the contact lines. Instead of being a straight line in the case of smooth substrates, the contact line tends to wander on the *x*–*y* plane due to roughness. The inves-

tigation concluded that on rough surfaces the contact angle might change considerably when the contact line is in motion. Thus it may not provide a suitable parameter for comparing different experiments.

Blake and Haynes [7] demonstrated that the technique of molecular dynamics allows a complete study of the dynamics of droplet spreading at the microscopic scale Particular focus was given to the study of the net fluxes inside the droplet during spreading. They concluded that at the molecular level, the mechanism of spreading could be viewed as a competition between a surface tension driving force and friction between the liquid and solid atoms. This result supports the molecular-kinetic theory of wetting as well as the Brochard-Wyart and de Gennes [8] model of spreading. Deegan [3] established that the drop itself can generate one of the essential conditions for ring formation to occur: contact line pinning. Furthermore, when self-induced pinning is the only source of pinning an array of patterns arises from the competition between de-wetting and contact line pinning. The paper provides good information on the self-pinning of droplets. However it mainly refers to liquids with solids in suspension. The model of droplet evaporation can depend on many factors, for example, evaporating liquid, ambient conditions, solid-surface properties etc... Anderson et al. [9] presented a theory based on a two-phase evaporation process for water on a non-ideal solid surface, wherein the first phase the contact angle decreases as the contact line holds until the contact angle reaches a critical value. Thereafter the orientation of the liquid vapour surface tension is large enough that it unbalances the Young–Dupres force balance and the droplet de-pins. In the second phase the contact angle remains constant as the contact line decreases. Although the wetting behaviour of evaporating pure liquids has been extensively investigated by numerous authors. On the contrary many issues related to binary systems remain to be elucidated. Indeed multi-component droplets are present in several industrial applications, such as crop-dusting where the wettability and the evaporation of herbicides on targeted surfaces is crucial. In cooling technologies binary systems are also frequently encountered when using binary refrigerants as cooling fluids. The understanding of wettability associated with phase change behaviour is essential for these applications. The wettability of a solid can be characterised in terms of the contact angle made by the liquid on the solid, at the contact line. The equilibrium contact angle is commonly described using the Young–Dupres relation:

$$\cos \theta_{\mathrm{e}} = (\sigma_{\mathrm{ls}} - \sigma_{\mathrm{sv}})/\sigma_{\mathrm{lv}} \qquad (1)$$

where θ_{e} is the equilibrium contact angle and σ_{lv}, σ_{ls} and σ_{sv} are respectively the liquid–vapour, liquid–solid and solid–vapour surface tensions. However, during the evaporation process the contact angle moves away from

its equilibrium value and adopts a range of apparent (dynamic) contact angles. The dynamic angle depends on the rate of spreading and evaporation. Two main classes of models have been proposed to explain the wetting mechanisms involved and their rate dependence on local conditions: Molecular Kinetic Theory [7] and Hydrodynamic Theory [10].

In this paper we study the evaporation of a sessile drop consisting of a binary ethanol–water mixture. The experiments are performed in a cell with a controlled pressure at ambient temperature. After a description of the experiment and the operating conditions, the evaporation rate, the contact angle and the base width are given with respect to time for different concentrations. A comparison between the pure substances and mixtures is presented. For the mixtures a new behaviour on wetting is found depending on the concentration of the volatile liquid in the drop. A discussion of the experimental results and analysis is proposed.

2. Experimental setup and procedure

The apparatus used includes several parts. A cell where the evaporating droplet is housed connected to a vacuum pump. An automatic injection pump allows the deposition of the calibrated drop on the substrate. An optical system for profile analysis of the drop and a computer for data acquisition. The dimensions of the cell are $70 \times 30 \times 20$ mm^3 (length, height and width) the cell has only one removable base made of aluminium and five other sides made of Perspex (Fig. 1b). This makes it easy to permanently seal the other five sides together with epoxy resin. The surface roughness of the substrate is analysed using an atomic force microscope (AFM). The rms (root mean squared) roughness of the polytetrafluoroethylene (PTFE) substrate is found to be 179 nm. On the top of the cell a needle allows deposition of the droplet on the substrate. On the bottom side a hose is connected to the vacuum pump (see Fig. 1).

A constant volume of liquid is deposited on the PTFE substrate using a programmable injection pump. The pressure inside the cell can be controlled to the desired level using a vacuum pump and a needle valve. The deposited droplet evaporates and its profile is analysed using an FTÅ 200 (First Ten Ångstroms) drop shape analysis software installed on the acquisition computer. The evolution of droplet, volume, contact angle and base width are measured as function of time. For a given imposed pressure, the typical variation of these three quantities with time is measured. The calibration of the optical measurement device allows an accuracy of the drop volume of less than 5%, the contact angle of less than 2°, and the base width of less than 2%. For all experiments, the drop profile is analysed based on a 2D view assuming an axi-symmetric shape of the

drop. The experiments are performed at ambient temperature and atmospheric pressure.

3. Results

The experiments are realised using pure water, pure ethanol and three mixtures of these two components. We present the evolution of the drop volume, contact angle, and base width with time for pure substances then for mixtures.

3.1. Evaporation of pure substances

Pure water is found to have an initial contact angle of 90° on PTFE whereas pure ethanol has an initial contact angle of 30° (Fig. 2).

Results of the variations of contact angle, base width and the drop volume as a function of time are presented in Figs. 3–5. When evaporation occurs, the pure water contact angle decreases continuously with time. At the end of the drop lifetime a sharp decrease is observed due to the entire consumption of the drop.

Similar behaviour is found for pure ethanol with slight differences; however at the end of the drop lifetime where a sudden jump in the contact angle is observed. This behaviour may be explained if correlated to the decrease of the drop base width (Fig. 4). This is related to the depinning of the triple line, which is beyond the scope of this paper. The drop volume for the pure substances is found to decrease continuously with time (Fig. 4), a similar trend is observed for the drop base width (Fig. 5).

3.2. Evaporation of mixtures

The initial contact angle for different drop concentrations ranges between the initial contact angle of the pure substances (water and ethanol) as shown in Fig. 2. The contact angle decreases as the concentration of ethanol is increased.

The drop volume evolves over time through three distinct stages, which depend on the initial concentration of ethanol (Fig. 3). For a small concentration of ethanol the slope of the drop volume differs slightly from that of pure water evaporation. As the concentration of the volatile liquid increases in the drop the curve representing volume versus time deviates from that of the pure water case. These curves exhibit different slopes, the first one with a steeper slope, and the second one with a smaller slope. The transition between the two stages takes place via an intermediate stage where the rate of evaporation is smaller than those during the first and third stage. This indicates that drop evaporation occurs in three distinct stages in mixtures. The deviation of the behaviour of the drop from the pure components one is
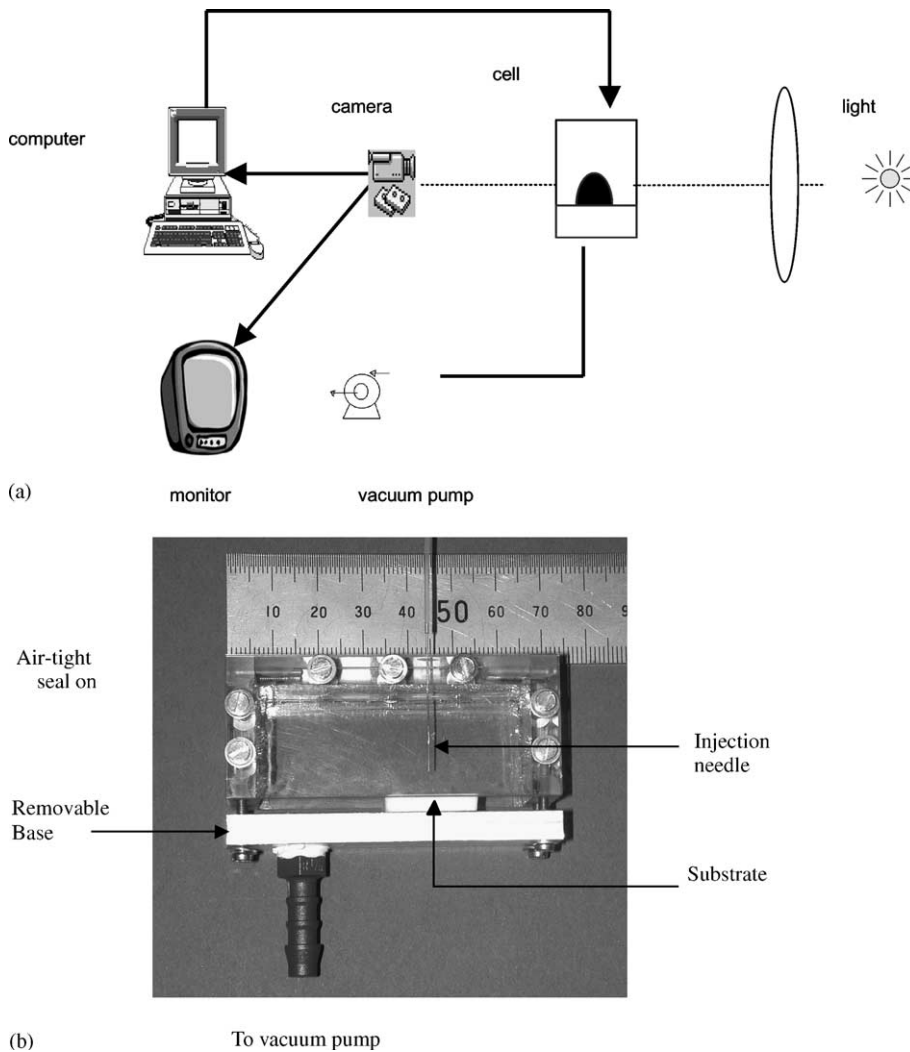
Fig. 1. (a) Schematic diagram of the experimental setup and (b) photograph of the cell.
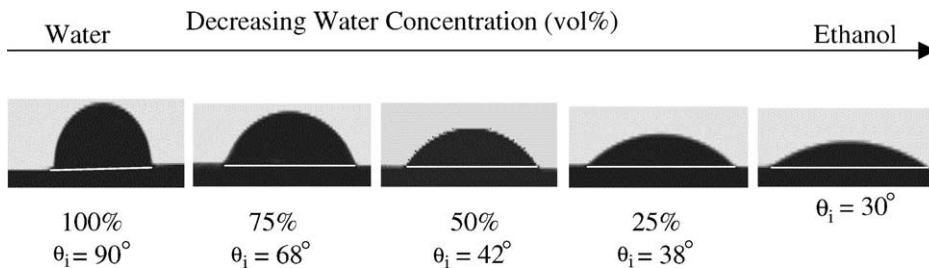

Fig. 2. Initial droplet images for water mixtures at 1 atm.

more pronounced as the concentration of the more volatile liquid is increased. With regards to the behaviour of the dynamic contact angle for mixtures, it is found to be different from that of pure substances. Indeed the contact angle of the mixture sharply decreases in the first stage, and then it increases to reach a maxi-
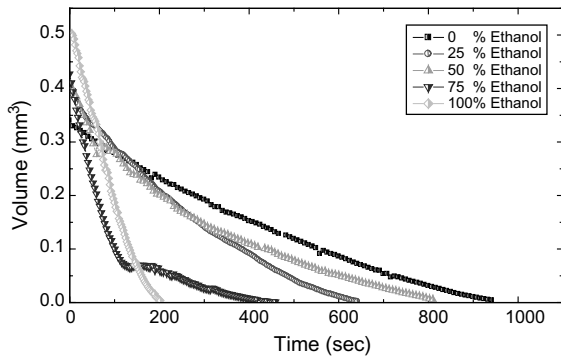
Fig. 3. Drop volume evolution with time for pure substances (water and ethanol) and mixtures for three different concentrations (25% ethanol, 50% ethanol, 75% ethanol).
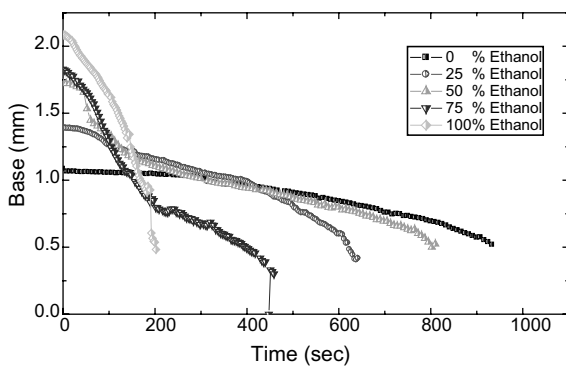
Fig. 4. Base width evolution with time for pure substances (water and ethanol) and mixtures for three different concentrations (25% ethanol, 50% ethanol, 75% ethanol).

mum value and finally decreases towards the end of the drop lifetime. The above-described behaviour is more pronounced as the concentration of the more volatile component is increased. This behaviour is linked to the stages of drop evaporation previously mentioned. It has been observed that the lifetime of the drop decreases as the concentration of ethanol is increased.

4. Discussion

In order to facilitate analysis of our results, data are presented in a non-dimensional 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 normalized curves are given in Figs. 6–8. The normalised curves show two types of behaviour depending on the drop concentration regardless the 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 fact that the evaporation mechanisms for the mixtures differ from the pure ones.

Several authors studied drop evaporation on smooth and rough surfaces for pure liquids (Shanahan [1]). These results allowed the influence of the volatility of the liquids and the surface state on the wetting behaviour of drops to be demonstrated. 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
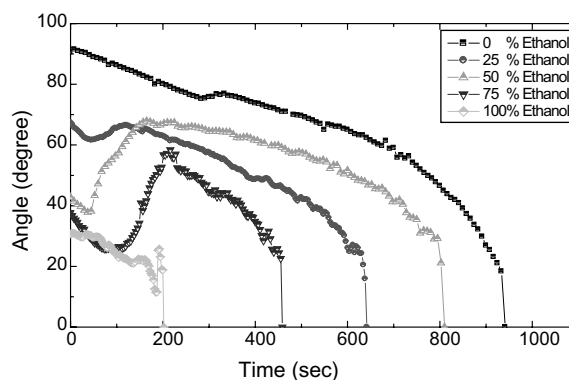

Fig. 5. Contact angle evolution with time for pure substances (water and ethanol) and mixtures for three different concentrations (25% ethanol, 50% ethanol, 75% ethanol).
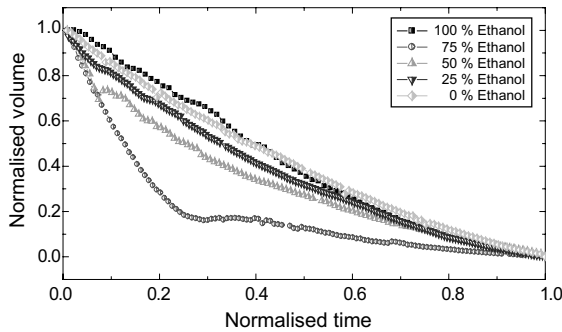
Fig. 6. Normalized drop volume versus normalized time for pure substances (water and ethanol) and mixtures for three different concentrations (25% ethanol, 50% ethanol, 75% ethanol).
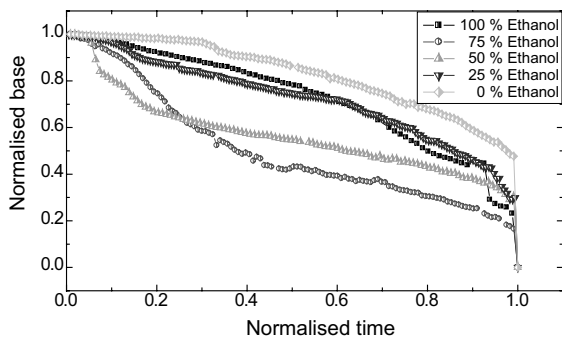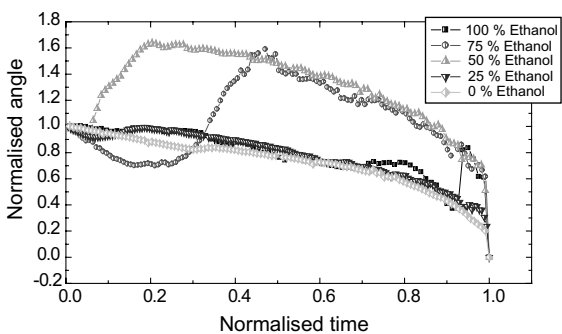

Fig. 7. Normalized base width versus normalized time for pure substances (water and ethanol) and mixtures for three different concentrations (25% ethanol, 50% ethanol, 75% ethanol).

Fig. 8. Normalized contact angle versus normalized time for pure substances (water and ethanol) and mixtures for three different concentrations (25% ethanol, 50% ethanol, 75% ethanol).

with time and that this is due to pinning of the contact line [7]. 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 three-phase evaporation sequence identified, which became more defined as the ethanol concentration increased.

Fig. 9 displays the contact angle, droplet diameter and volume versus time for the same evaporation sequence for a hypothetical ethanol–water mixture droplet. The three phases of evaporation are clearly identified on the graph and the duration of these phases can be distinguished from t_1, t_2 and t_3.

The duration of phase 1 compared to the entire evaporation time, increases with increasing ethanol concentration. The volume evaporated during phase 1 (from A to B on graph (iii) above) appears to be very close to the volume of ethanol in the droplet mixture. This indicates that it is likely that the ethanol works its way to the surface of the droplet and evaporates first. Similarly the duration of phase 3 corresponds to the volume of water in the droplet and evaporates at a much lower rate than phase 1. This corresponds to the evaporation of water.

On Fig. 10 the evaporation rates of phases 1 and 3 identified previously are compared to the evaporation rates of pure components. This comparison shows that on one hand, for the three different concentrations, 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 three 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. As can be seen in Fig. 11 the wetting angle varies continuously with the drop volume for pure substances. For mixtures this behaviour is different. For high ethanol concentration (75%), the contact angle is close to that of pure ethanol for a wide range of drop volumes. The contact angle at some point jumps to the contact angle of pure water and subsequently follows its own behaviour. This pure water analogous behaviour is maintained for the rest of the drop lifetime. From the results presented in Fig. 11 it is clear that the wetting behaviour strongly depends on the initial concentration of ethanol. It is likely that ethanol makes its way to the surface to evaporate during the first phase. This behaviour leads us to conclude that wetting is entirely dictated by interfacial properties (surface tension). During the first phase it is thought that ethanol is concentrated on the liquid–vapour interface, the concentration of ethanol at the interface is such that the surface tension of the drop is virtually that of pure ethanol. Because liquid–vapour surface tension plays a crucial role in dictating the wetting contact angle, this leads to the observed behaviour during the first stage of evaporation. The transition in contact angle is accom-
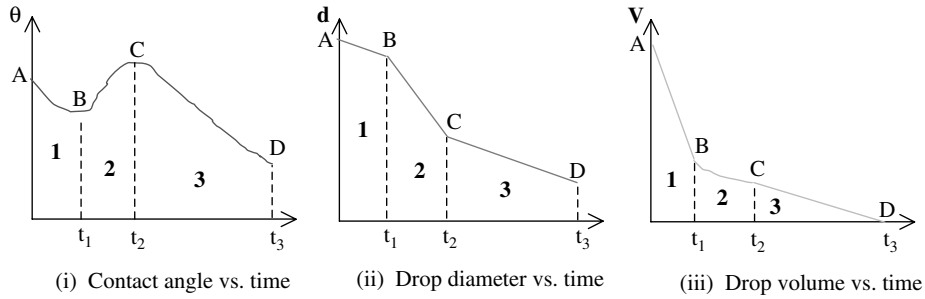
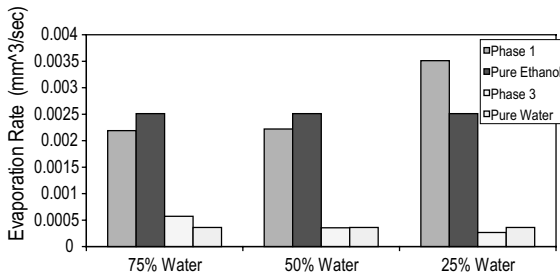Fig. 9. Simplified property vs time graphs for evaporation of ethanol–water mixtures.

Fig. 10. Comparison of phases 1 and 3 evaporation rates with pure water and ethanol evaporation rate.
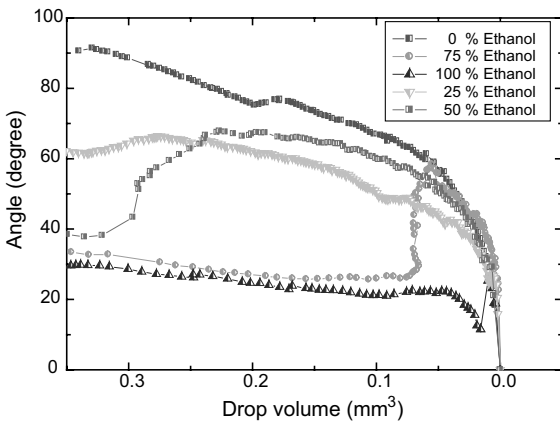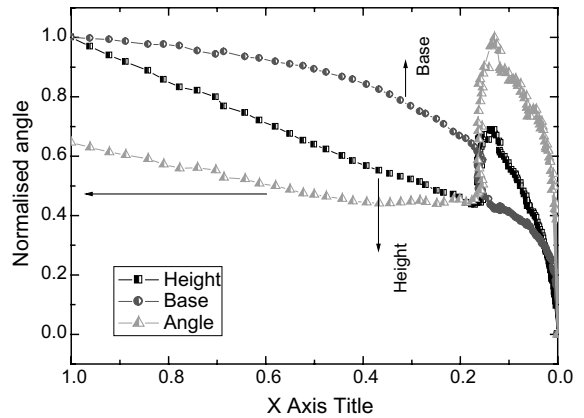

Fig. 12. Evolution of the contact angle, base and height of the droplet as a function of the volume (75% ethanol).

panied by a change of the drop geometry. Fig. 12 shows the height of the drop as well as the contact angle and base width versus the normalised drop volume. During the first stqge, the drop height decreases monotonically. At the same time, as the contact angle jumps to join the behavior of pure water, the drop height increases in the same fashion as the contact angle while the base width decreases sharply during this second stage corresponding to a transitional one.

In the third stage, the contact angle, drop height and base width decrease till to the total drop consumption.
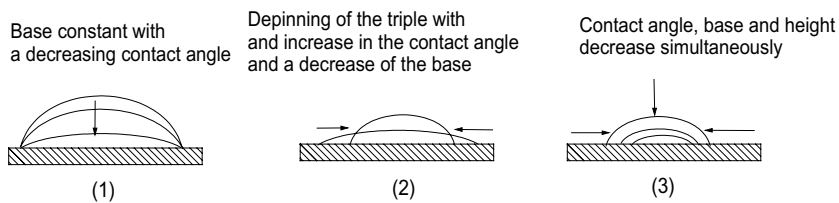

Fig. 11. The dynamic contact angle versus the drop volume for different ethanol concentrations.

Fig. 13. Behaviour of the evaporating drop in different stages.

Fig. 13 shows the schematic sequence of the drop geometry for the three stages.

5. Conclusion

Experiments were performed for studying the drop evaporation of binary mixtures. Results showing the dynamic wetting behaviour of the drop are presented. Drop evaporation of water–ethanol mixtures were found to differ from that of pure substances. The dynamic contact angle, drop width and volume vary according to the concentration of the components. Three stages were found, a first corresponding to the behaviour of the pure volatile substance while the third stage that of the less volatile component. An intermediate (transitional) stage exists where the contact angle varies noticeably, while the volume remains almost constant.

The dynamic contact angle is highly dependent on the concentration of the more volatile component. The next step in this work is to perform a systematic study to establish general behavioural laws and to propose a model to quantify evaporation rate of mixtures.

References

[1] C. Bourges-Monnier, M. Shanahan, Influence of evaporation on contact angle, Langmuir 11 (1995) 2820–2829.

[2] H. Hu, R.G. Larson, Evaporation of a sessile droplet on a substrate, J. Phys. Chem. B 106 (2002) 1334–1344.

[3] R. Deegan, Pattern formation in drying drops, Phys. Rev. E 61 (1) (1998) 475–485.

[4] J.D. Bernardin, I. Mudawar, C.B. Walsh, E.I. Franses, Contact angle temperature dependence for water droplets on practical aluminium surfaces, Int. J. Heat Mass Transfer 40 (1997) 1017–1033.

[5] H. Nakae, R. Inui, Y. Hirata, H. Saito, Effects of surface roughness on wettability, Acta Mater. 46 (7) (1998) 2313–2318.

[6] T. Chow, Wetting of rough surfaces, J. Phys.: Condens. Matter 10 (27) (1998) 445–451.

[7] T. Blake, J. Haynes, Kinetics of liquid/liquid displacement, J. Colloid Interface Sci. 30 (1969) 421.

[8] F. Brochard-Wyart, P.-G. de Gennes, Dynamics of partial wetting, Adv. Colloid Interface Sci. 39 (1992) 1–11.

[9] D. Anderson, S. Davis, The spreading of volatile liquid droplets on heated surfaces, Phys. Fluids 7 (1995) 248.

[10] P.-G. De-Gennes, Wetting: statistics and dynamics, Rev. Mod. Phys. 57 (1985) 827–863.