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Electrowetting of water and aqueous solutions on poly(ethylene terephthalate) insulating films

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The wettability of poly(ethylene terephthalate) (PET) films by water and aqueous solutions is increased by applying a voltage between the water and a rear electrode placed under the polymer film. We show that this electrowetting effect can decrease contact angles by more than 30° under applied voltages of 200 V_{eff}. At low voltage, we observe the expected variation, but for high voltage, the electrowetting saturates, with other polymer films. In the case of PET, the increase in wettability is irreversible but only as a result of modification of the polymer at the edge of the drop, near the three-phase contact line, where the electric field is high and inhomogeneous. At very high fields, we observe that the liquid contour becomes unstable, the liquid drop expelling little droplets around it. We investigate the influence of the composition of the aqueous solution with simple solutes as well as water soluble polymers. In all these cases, the electrowetting effect can help the solutions to wet the solid surface. Copyright © 1996 Elsevier Science Ltd.

(Keywords: electrowetting; poly(ethylene terephthalate); insulating films)

INTRODUCTION

After the comprehensive investigations of Lippmann[1] during the last century into electrocapillarity, it was recognized that electrical phenomena can play a very important role at liquid interfaces. Since that time, several quantitative experiments have been performed on the mercury–electrolyte interface[2], leading to a better understanding of diffuse layers near charged surfaces. In a small number of cases, Froumkine[3] and others measured how the wetting of an electrolyte solution on a metallic surface is influenced by a potential difference applied across the metal–electrolyte interface. These were the first examples of electrowetting, the effect of modification of contact angles by application of a voltage. For a decade, electrowetting has received a renewal of interest with applied physics studies in micromechanics[4] and displays[5,6]. Recently, electrowetting of aqueous solutions on thiol-modified gold electrodes has been the subject of a detailed and interesting study by Sondag-Huethorst and Fokkink[7]. In particular, electroactive species were attached to a monolayer grafted to a gold electrode, increasing the effect noticeably[8,9].

The above studies have mainly dealt with metal–electrolyte interfaces. It was recently shown that the affinity of a liquid for an insulating solid can also be strongly increased when electric charges are brought to the interface[10]. This effect was studied through the wetting of solid polymer films by water. It was shown that electrowetting can decrease the contact angle of water on poly(tetrafluoroethylene) (PTFE) from about 100° to about 30°.

Polymers have low energy surfaces, characterized by the concept of critical surface tension introduced by Zisman and coworkers[11,12]. Polymers are usually hydrophobic, and it is of great industrial importance to control their affinity with water. The control of wettability in a continuous and reversible way is thus a new situation with potential applications. In this paper, we choose to study electrowetting for industrial poly(ethylene terephthalate) (PET) films of 12 μm thickness, which have good natural surface states. The wetting behaviour of water on PET is well known, being characterized by a contact angle hysteresis that varies slowly with time, and which has been attributed to surface molecular reorientations[13].

This paper is organized as follows. After presenting the problem, we recall the formula for the expected reduction in solid–liquid interfacial tension under an applied voltage. We then describe a new experimental set-up used to measure advancing and receding contact angles under the field. We then present and discuss the experimental results.

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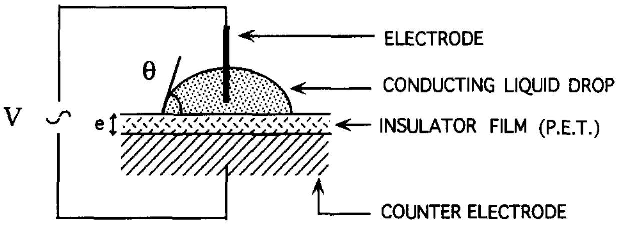

Figure 1 Schematic drawing of electrowetting on a solid insulator film

EXPERIMENTAL SITUATION AND BASIC THEORY

Consider the problem described in *Figure 1*: a liquid drop partially wets a solid insulator film of thickness e and dielectric constant ϵ_r. The liquid is an electrical conductor and a voltage V is applied between the liquid and an electrode underneath (called the counterelectrode). Without an applied voltage, we assume that the solid–liquid interface is not charged. When a voltage is applied, the conducting liquid drop and the counterelectrode form a capacitator of capacitance C. The main contribution to C is proportional to the area S_{SL} at the base of the drop (i.e. the solid–liquid interface)

$$C = \frac{\epsilon_0\epsilon_r}{e} S_{SL} \tag{1}$$

The electrostatic energy stored in the capacitor ($\frac{1}{2}CV^2$) can thus be incorporated into the solid–liquid interfacial energy γ_{SL} to give an effective value[10]

$$\gamma_{SL}(V) = \gamma_{SL}(0) - \frac{\epsilon_0\epsilon_r}{2e} V^2 \tag{2}$$

In the case of partial wetting, the contact angle will be modified according to the Young–Laplace equation[10]

$$\cos\theta(V) = \cos\theta(0) + \frac{\epsilon_0\epsilon_r}{2e\gamma_{LG}} V^2 \tag{3}$$

where γ_{LG} is the liquid–gas surface tension. For an alternating current (a.c.) rather than a direct current (d.c.) field, equations (2) and (3) remain valid if V^2 is replaced by V_{eff}^2. The derivation of equation (2) involves only simple electrostatics. Formally, the situation is no different from the classical electrocapillarity phenomenon at mercury–electrolyte interfaces. The main difference is in the value of the surface capacitance, i.e. the electrical capacitance per unit area of interface. For the mercury–electrolyte interface, made of diffuse layers of ions on a length scale of nanometres, the surface capacitance is several tens of microfarads per square centimetre. In our case, the insulator film has a macroscopic thickness, resulting in a lower surface capacitance of hundreds of picofarads per square centimetre, but it is more efficient for withstanding high electric fields than the spontaneous potential barrier at metal–electrolyte interfaces. One thus expects a stronger reduction of the interfacial tension. Indeed, one expects a wetting transition ($\theta = 0$) for a voltage V_c well below the dielectric breakdown. Equation (3) shows that the electrowetting effect is proportional to V^2/e, whereas the electric field in the insulator film is V/e. As a consequence, for the same electrowetting effect the electric field will be higher when the film thickness is smaller, and breakdown will occur sooner. Indeed, experimentally, these problems occur for thicknesses less than a few micrometres. A related difficulty arises with charge injection in the dielectric film: if one uses d.c. voltages, the reduction of the interfacial tension is a transient effect. It is thus more efficient to use a.c. voltages, although this practice increases resistive losses in the electrolyte. In general, the transport of electric charges in the liquid does not limit the effect of electrowetting (at least with water-based solutions as the conducting liquids).

Let us now consider in more detail the vicinity of the wetting line in the case of partial wetting. It should be noted that equations (2) and (3) neglect edge effects in the capacitor formed by the liquid drop with the other electrode. The field leaks could modify the shape of the drop up to distances from the wetting line of the order of the insulator film thickness. Additional complications might arise on a smaller length scale in the regions where the electrolyte thickness becomes comparable to the Debye–Hückel length. Then the total surface charge on the liquid side of the interface will be lower than that far from the wetting line. These charges will exert an additional disjoining pressure on the liquid–gas interface, thus modifying the liquid profile near the wetting line. In fact, the full determination of the drop shape is a non-local problem and is difficult to perform exactly.

EXPERIMENTAL SET-UP

In this paper, we essentially present contact angle measurements made under high voltages.

Optical set-up

We used the sessile drop method to measure the contact angles. A drop of the aqueous solution under study was deposited onto the polymer film which was applied to a flat, stainless steel disc that acted as the counterelectrode. As usual, the profile of the drop was observed by looking from the side and at a small angle with the horizontal in order to see both the drop and its reflection in the substrate, which acted as a mirror. The sample holder was placed on a motorized rotation stage whose axis was horizontal, almost coincident with the direction of observation. This was used to incline the solid surface, inducing a force on the drop in the downhill direction. We thus measured both the advancing and receding contact angles, θ_a and θ_r. Strictly speaking, the angle of inclination should be large enough to induce a displacement of the drop so as to gain access to θ_a and θ_r. In our case, we could not set an angle of inclination greater than 30°; for higher values, the drop was driven away from the platinum electrode at voltages greater than about 100 V. We thus chose always to work with a 30° inclination only, the consequence being that the measured difference between advancing and receding angles was somewhat underestimated, especially at low voltages. Nevertheless, this problem does not affect the average $(\theta_a + \theta_r)/2$. We checked that there was no systematic error caused by the presence of a platinum wire dipped into the sessile drop.

The images were taken with a Zeiss binocular microscope, a CCD video camera and a tape recorder. The frames of interest were digitized and analysed with a computer.

The method we used here was easy to implement, even with the constraints of using high voltages. Nevertheless, the error in angle determination was a few degrees, but it is not clear if this error came from the method or from hysteresis.

Electrical set-up

We needed to apply high voltages ranging from 10 V to 3000 V at frequencies between 50 Hz and a few kilohertz. The output of a wave generator went to a 100 W hi-fi power amplifier, which delivered power to the primary of a voltage transformer (X1000, specially built by CECLA, La Tour du Pin, Isère, France). This gave a cheap source of excellent quality. The experimenter was protected from high voltage shocks by a relay operated by the closure of the protection box. The whole experiment was enclosed in the box. A resistive voltage divider was installed to allow us to monitor the applied voltage with a voltmeter connected to a computer. The voltage was displayed on the computer screen and superimposed on the video images of the sessile drop. This set-up gave the applied voltage at all times of the video recordings.

Materials

Biaxially stretched PET films of 12 μm thickness were provided by Rhône-Poulenc. The PET molecular weight (M_w) was 44 000. The roughnesses R_Z and R_a were respectively 0.1 μm and 30 nm. The surfaces were not decontaminated, but X-ray photoelectron spectroscopy studies and measurements of contact angles for water and diiodomethane showed that the film surfaces were clean.

The counterelectrode was a polished, stainless steel disc of 35 mm diameter, i.e. much larger than the drop size so that it could be approximated to an infinite electrode. A drop of aqueous NaCl solution was inserted between the counterelectrode and the film to ensure good electrical contact. The electrode dipped into the sessile drop was a platinum wire.

Knowledge of the surface tension was necessary to compute numerical values of $\cos\theta(V)$ from equation (3). Surface tensions were measured by the Wilhelmy plate method[14]. All solutions were made from ultrapure water.

RESULTS

Wettability changes for simple aqueous solutions

The measurement protocol involved a voltage cycle from 0 V to $V_{\max}$ and back down to 0 V. After each voltage change, usually by 50 V steps, the sample holder was tilted by 30° from the horizontal. The direction of tilt was reversed each time such that on average there was no drift of the drop position. At 10 s after tilting, the contact angles on both sides of the sessile drop were measured. *Figure 2a* shows the results of the cosines of the contact angles for a water drop on a PET film as a function of the voltage. At the beginning of the experiment, just after placing the drop, the contact angles are $\theta_a = 66°$ and $\theta_r = 57°$. As explained earlier, these values are different from previous measurements made by Vergelati *et al.*[13] on the same kind of PET film: the difference $\theta_a - \theta_r$ is smaller for experimental reasons, but the average $(\theta_a + \theta_r)/2$ has the same value as given by Vergelati *et al.*[13]. When the voltage is increased both θ_a and θ_r decrease, but a substantial hysteresis persists. For voltages higher than about 150 V, the contact angles cease to vary and remain at $\theta_a = 42°$ and $\theta_r = 30°$. We call this phenomenon 'contact angle saturation'. For a decrease in voltage, the contact angles stay constant, showing a high degree of irreversibility. In *Figure 2b*, we show the average of the cosines of the advancing and

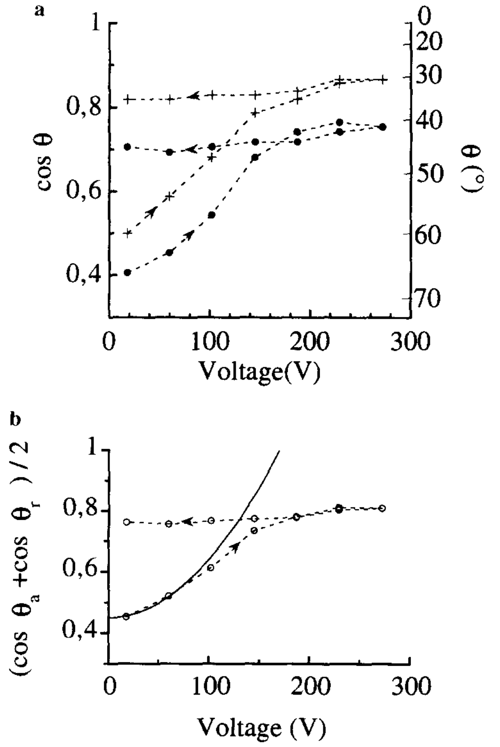

Figure 2 (a) Cosines of the receding (+) and advancing (●) contact angles of pure water on a PET film as a function of the applied voltage. (b) Plot of $(\cos\theta_a + \cos\theta_r)/2$ for the same experiment as in (a). The solid line corresponds to equation (3)

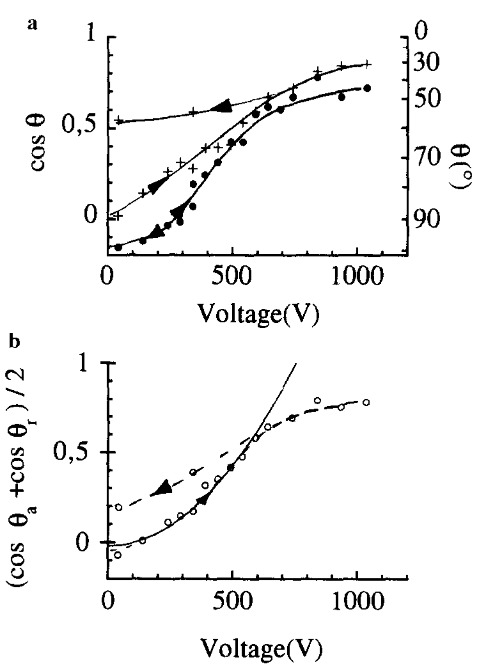

Figure 3 (a) Cosines of the receding (+) and advancing (●) contact angles of pure water on a PTFE film as a function of the applied voltage. (b) Plot of $(\cos\theta_a + \cos\theta_r)/2$ for the same experiment as in (a). The solid line corresponds to equation (3)

receding contact angles for the same experiment as in *Figure 2a*. The solid line corresponds to equation (3) in which we have fixed θ (0) such that it corresponds to the experimental value at zero field: $\theta(0) = 63°$. The parameters used in equation (3) are $\epsilon_r = 3.65$, $\gamma_{LG} = 72\,\mathrm{mN\,m^{-1}}$ and $e = 12\,\mu\mathrm{m}$.

For comparison, we show in *Figure 3a* the cosines of the contact angles for water on a PTFE film of thickness 70 μm. Here, we also see saturation of the wettability for voltages over about 600 V, although in this case the saturation appears more progressive than for PET. For this particular cycle, the advancing contact angle is fully reversible, while the receding angle does not come back to its starting value. *Figure 3b* presents the results of the same experiment in terms of the average of the cosines of the advancing and receding contact angles. The solid line corresponds to equation (3) with $\theta(0) = 91°$, $\epsilon_r = 2$, $\gamma_{LG} = 72\,\mathrm{mN\,m^{-1}}$ and $e = 70\,\mu\mathrm{m}$. As for the case of PET, the hysteresis difference $\cos\theta_a - \cos\theta_r$ seems roughly independent of the voltage, at least for the increasing voltage part of the cycle. The saturation contact angles are $\theta_a = 43°$ and $\theta_r = 32°$, which are close to the values for PET. Indeed, these saturation contact angles show little dependence, if any, upon the frequency, the polymer thickness[10], the nature of the polymer or the dielectric constant (from $\epsilon_r = 2$ for PTFE to $\epsilon_r = 12$ for P(VDF-TrFE) copolymers).

The physical reasons for contact angle saturation are still unclear and remain the major points to be understood about electrowetting on polymer surfaces.

Localization of the irreversibility at the liquid edge

Let us now discuss the origin of irreversibility in the case of PET. There are essentially two possibilities: either the surface of the polymer under the liquid drop is modified irreversibly by the application of the voltage, or there is line pinning such that the three-phase contact line is attached to the position it occupies at high voltage. We now present three arguments in favour of the second explanation.

(1) It can be seen from *Figure 2* that the values of θ_a and θ_r at zero voltage at the end of the cycle are almost identical to the values at high voltage. If there were surface modifications induced by the electric field, the contact angles would be different after the voltage cycle, but there would be no particular reason to get the same results as at high voltage. If, however, the contour line of the drop is immobilized irreversibly at high voltage, then the whole geometry of the drop surface is fixed by this boundary condition, and it is natural to find that the contact angles are 'blocked' upon decreasing the field.

(2) An experiment confirms that there is no modification of the polymer under the drop. First, we measure the contact angles of a small drop on a fresh film of PET ($\theta_a = 66°$ and $\theta_r = 53°$). Then, we deposit a large drop with a much larger base than the previous one. We apply a high voltage (here 350 V) for 5 min, which is comparable to the duration of a typical voltage cycle. We verify that the field is actually applied by checking the contact angle variation at the edge of the drop. We then remove the big drop by suction and at the position of its centre deposit a new small drop. When we measure the contact angles of the small drop, we obtain values of $\theta_a = 66°$ and $\theta_r = 54°$, very similar to the original ones. This procedure proves that if any surface modification of the polymer develops under the drop, it is minor and undetectable with contact angle measurements.

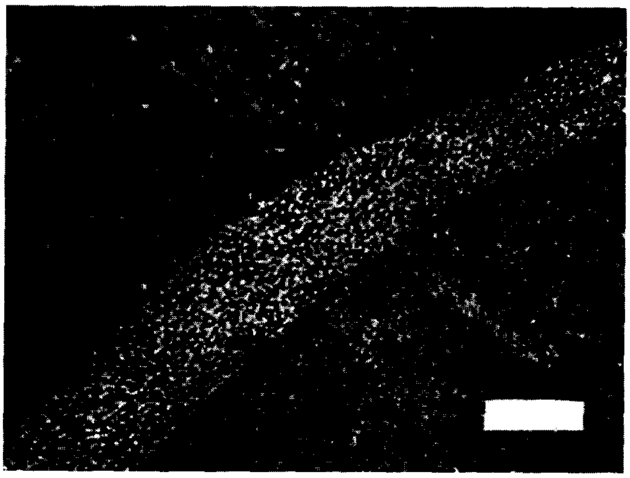

Figure 4 Breath figure of the PET film after the application of 250 V to a drop for 5 min. The drop was removed before taking the picture. The pattern reveals the hydrophilic ring produced at the drop perimeter on the PET film. The bar corresponds to 300 μm

(3) After a high voltage cycle, a hydrophilic ring can be seen. It is formed at the place where the edge of the drop was located when it was under high voltage. *Figure 4* shows a picture of a sample after the voltage cycle, obtained after blowing moist air on the sample (condensation pattern, or breath figure). One can directly see that the polymer has been made hydrophilic only at the previous drop perimeter. Inside the perimeter (i.e. under the drop), the surface is still hydrophobic.

The conclusion of this section is that the electrowetting effect on PET is reversible at moderate voltages. If the voltage is high enough, a hydrophilic ring is irreversibly formed at the edge of the drop. As the voltage decreases, the contour of the drop may still remain attached to this ring, but the surface under the drop recovers its hydrophobic character. There are several possible mechanisms that could lead to this outer hydrophilic ring; for instance, surface reconstruction under an inhomogeneous electric field or chemical surface modification due to some dielectric breakdown may occur. This problem is now under study.

Contour line instabilities

In this section, we describe how under some circumstances the contour line of the liquid drop becomes unstable, the drop eventually expelling little droplets. This phenomenon usually appears with pure water above a threshold voltage V_i, which is usually much higher than the saturation voltage ($V_i \approx 350\,\mathrm{V}$ and $V_{sat} \approx 150\,\mathrm{V}$ for 12 μm PET). When viewing the sample from above, we suddenly see a proliferation of little droplets 'jumping' from the mother drop. These little droplets coalesce very quickly with their neighbours. In some cases, the droplets remain connected to the mother drop by a narrow water bridge, as shown in *Figure 5a*. Exceptionally, at the early stages of this instability the expelled droplets form relatively periodic structures as in *Figure 5b*, obtained from a silanized glass cover slip 170 μm thick. This subject is not well understood, but there are some indications that ejection of the little droplets could be the result of pure electrostatic liquid fragmentation.

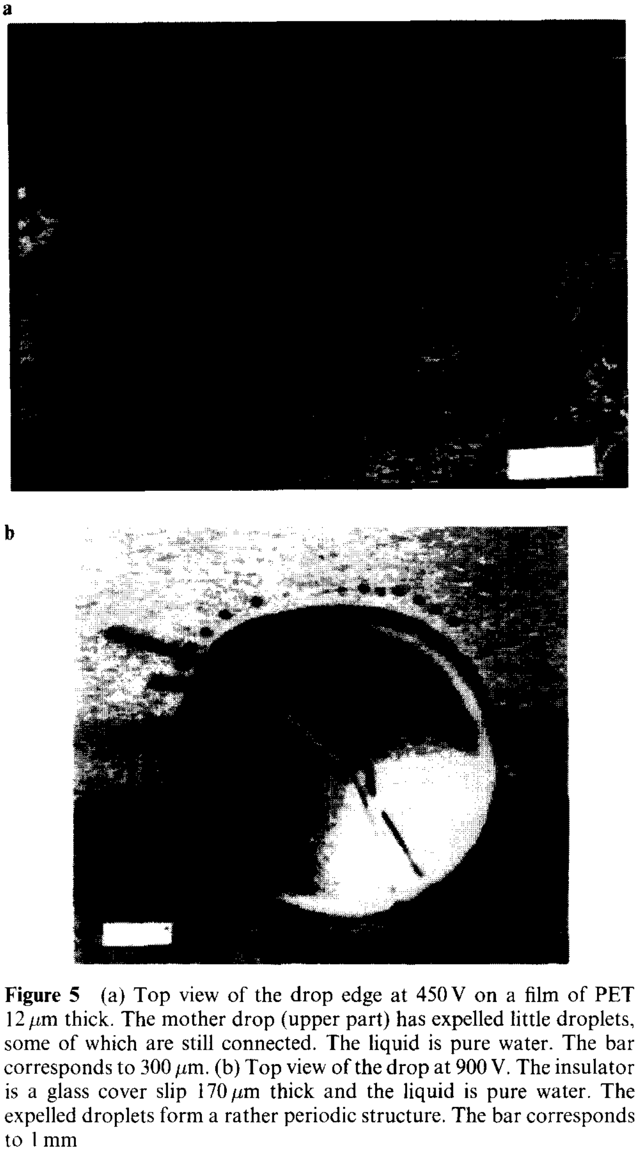

Figure 5 (a) Top view of the drop edge at 450 V on a film of PET 12 μm thick. The mother drop (upper part) has expelled little droplets, some of which are still connected. The liquid is pure water. The bar corresponds to 300 μm. (b) Top view of the drop at 900 V. The insulator is a glass cover slip 170 μm thick and the liquid is pure water. The expelled droplets form a rather periodic structure. The bar corresponds to 1 mm

Droplet ejection is suppressed when a sufficient amount of a salt is dissolved in the water. Above concentrations of about 10^{-2} M Na_2SO_4, the instability is no longer observed. Ethanol, however, added at a concentration of 1 M does not change the behaviour compared to pure water. It is possible that in the case of a mixture of water and a salt, Marangoni effects could suppress the instability by opposing gradients in surface tension (through gradients in concentration). We recall that the dependence of surface tension upon the concentration of solute ($d\gamma/dc$) is positive for Na_2SO_4 and negative for ethanol.

Solutions of water soluble polymers

It is of industrial interest to check if electrowetting works not only with simple aqueous solutions but also with more complex fluids. We have investigated aqueous solutions of some water soluble polymers provided by Rhône-Poulenc. We tried poly(vinyl alcohol) (PVA, degree of hydrolysis 98%) and a statistical copolyester including 10% by weight of sodium 5-sulfoisophthalic acid monomer in a PET structure partially ionized in water. The molecular weight (M_w) of the copolyester was determined by gel permeation chromatography as 64 000.

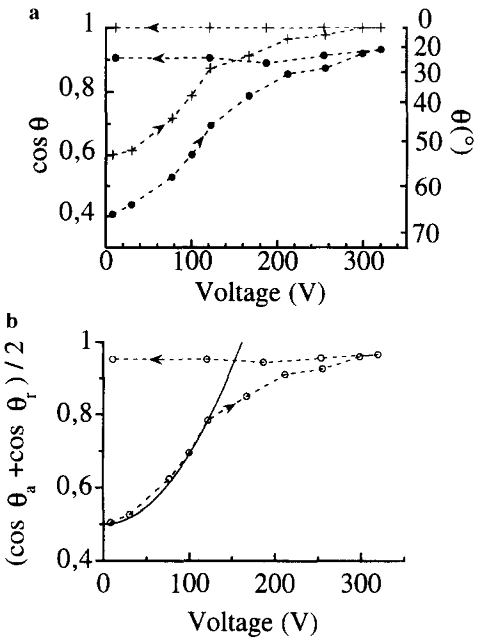

Figure 6 (a) Cosines of the receding (+) and advancing (●) contact angles of a 0.1% copolyester solution in water on a PET film as a function of the applied voltage. (b) Plot of $(\cos\theta_a + \cos\theta_r)/2$ for the

Both give very similar results. *Figure 6* shows the results of a voltage cycle for a 0.1% copolyester solution in water. In *Figure 6b*, the parameters of equation (3) are $\theta(0) = 60°$, $\epsilon_r = 3.65$, $\gamma_{LG} = 72\,mN\,m^{-1}$ and $e = 12\,\mu m$. The overall behaviour is similar to that of pure water. The main difference is the fact that the receding contact angle seems to be 0° for decreasing voltages, i.e. for the second half of the cycle. In this case we observe that a thin liquid film is left behind the receding liquid front.

In fact, in *Figure 6* two effects combine to decrease the contact angles: the applied voltage and the kinetics of copolyester adsorption at the PET–water interface. We did two experiments to separate these effects. In the first experiment, one drop of 0.1% copolyester solution was deposited on a fresh PET film, and the contact angles were found to be $\theta_a = 64°$ and $\theta_r = 52°$. After a delay of 20 min to allow adsorption of the copolyester, the measurements were made again, giving $\theta_a = 41°$ and $\theta_r = 28°$. In the second experiment, instead of waiting 20 min, a voltage pulse of 10 s at 230 V was applied. Just after the voltage was shut down the contact angles were $\theta_a = 40°$ and $\theta_r = 29°$.

The comparison between these two experiments shows that 10 s of voltage can quickly force spreading of the copolyester solution. The spreading would occur spontaneously, even in the absence of an electric field, but on a longer time-scale. Of course, simpler ways exist to force the spreading, and there is no indication that the electric field helps the adsorption in any fashion. The purpose of this section was only to show that electrowetting also works with a great variety of aqueous solutions, even complex ones, as long as they conduct. This might be somewhat different from classical electrocapillarity at metal–electrolyte interfaces, where the diffuse layers in the electrolyte have a major effect on the amplitude of electrowetting.

CONCLUSIONS

We have investigated electrowetting of water and aqueous solutions on PET films 12 μm thick. We have shown that a voltage of 200 V_{eff} across the film can decrease the contact angles of water by more than 30°, which is rather large. During a voltage cycle, the contact angles start to vary as expected from equation (3), but above 150 V the contact angles cease to decrease. As the voltage decreases, the angles stick to the values reached at high voltage. We have shown that this irreversibility is due to the modification of the polymer film at the edge of the drop only, where the film becomes irreversibly hydrophilic. Under the liquid drop, however, the polymer surface stays hydrophobic. This behaviour seems not to be particular to PET but occurs in various types of polymers, such as PTFE. In the latter case, contact angles can be decreased by about 55°, but the lowest contact angles are similar to those of PET.

At high fields (above 350 V for films 12 μm thick), one observes in some cases an instability of the drop contour. The drop ejects little droplets, which sometimes are still connected to the mother drop by a narrow water link. This instability can be understood qualitatively in terms of the natural tendency of a highly charged liquid to fragment, but a quantitative analysis remains to be established.

Electrowetting also works for more complex fluids, such as solutions of polymers in water. We have investigated copolyester and PVA solutions and found that receding contact angles can be very small. Here, spontaneous adsorption of copolyester at the PET–water interface can also decrease the contact angles, as does the applied voltage, so electrowetting may be of interest only for forcing the liquid to spread. Here, the presence of the insulator film makes the electrowetting effect more independent of the liquid composition than in classical metal–electrolyte electrocapillarity experiments.

The present study has dealt with situations close to equilibrium and has exhibited effects of large amplitude. It would be very challenging now to check if the same concepts apply to the dynamics of electrowetting.

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