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SHORT COMMUNICATION

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Electrowetting: a model for contact-angle saturation

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Abstract Electrowetting (EW) involves the application of an electric potential across a solid–liquid (SL) interface, which modifies the wetting properties of that interface by reducing the SL surface energy and induces a contact-angle change without altering either the bulk liquid or solid properties. Reversible contact angles are achieved at low potentials, while the application of high potentials results in contact-angle saturation and system instabilities. In the present work, an EW system consisting of a substrate (plate or rod) coated with a thin Au underlayer, a dielectric (parylene) layer of various thickness and a 100-nm layer of fluoropolymer (Teflon AF1600) is studied both theoretically and experimentally. A theoretical consideration of the EW effect, taking into account the detailed structure of the electrical double layer, and a model for the saturation of the contact angle observed at high applied potentials are presented. The theoretical treatment presented here confirms that the EW effect is, in the most part, due to polarization of the dielectric, as opposed to purely a rearrangement of the double layer, and explains why no dependence of the EW effect on the electrolyte concentration has been observed. The theory is only applicable over a limited potential range, and we have developed a model that predicts the potential at which this limit occurs. This is the potential at which the SL surface energy becomes zero. The limiting potential is dependent only on the bulk liquid and solid properties and is thus fixed for a given system. Experimentally, the limiting potential corresponds to the onset of contact-angle saturation, although variations in the exact angle of saturation are not uncommon due to the kinetic effects involved in a real system as opposed to a strict thermodynamic analysis. The model predicts that for an EW device in which an aqueous droplet can be forced to completely wet a hydrophobic surface, a surface with basically the same surface energy as the liquid is required.

Key words Electrowetting theory · Contact-angle saturation · Parylene dielectric · Fluoropolymer AF1600

Introduction

It is well known that electric charge plays a significant role in the wetting phenomenon [1]. In the past decade, interest in the possibility of changing the wettability of solids by applying an electric potential between the solid and the liquid has been renewed. The phenomenon, referred to as electrowetting (EW), was studied with self-assembled thiol monolayers [2, 3], poly(tetrafluoroethylene) [4] and poly(ethylene terephthalene) [5] thin films deposited on metal electrodes and a significant change in the wettability of the solids was reported. Recently, a reversible EW effect has been observed when two different dielectric layers (parylene and AF1600) are deposited onto a metal electrode [6, 7].

The theory of EW was developed by Berge [4] and Vallet et al. [5] and recently in more detail by Verheijen and Prins [8]. Generally, the surface energy of the solid–liquid (SL) interface is corrected for the electrostatic energy, W ($= CV^2/2$), stored in the capacitance, C, of the dielectric layer:

$$\cos\theta = \cos\theta^0 + \frac{CV^2}{2\gamma_{\mathrm{LV}}} \ , \tag{1}$$

where θ is the contact angle measured through the liquid phase at an applied electric potential, V, and θ^0 is the contact angle with no applied potential. The presence of a double layer (DL) at the SL interface and the detailed structure of the dielectric layers are neglected in Eq. (1) [4, 5, 8]. These assumptions are perfectly justified from an electrostatic point of view for the systems studied, but limit the applicability of the theory to other experimental systems, for instance, systems with dielectric multilayers, different electrolyte concentrations and nonaqueous liquids. The theory explains very well the change in the wettability observed at low electric potentials but fails to explain the saturation of the contact angle observed at high potentials.

Here, we present a more detailed theoretical consideration of the EW effect, taking into account the detailed structure of the DL. Also a model for the saturation of the contact angle observed at high applied potentials is presented.

Materials and methods

The system studied here consists of a 1-mm diameter glass rod coated with a thin Au underlayer, a dielectric (parylene) layer of various thickness and a 100-nm layer of fluoropolymer (Teflon AF1600). The sample preparation is described in detail elsewhere [6–8]. The dielectric layer provides the significant potential drop necessary for a large EW effect, and the hydrophobic fluoropolymer gives the desired wetting characteristics of a large contact angle and smooth homogeneous surface. The potential is applied between the metal underlayer and a counter electrode in the bulk solution.

Contact angles were measured using the Wilhelmy balance technique [9]. The system used can determine changes in contact angles of less than 0.2°. Static water advancing and receding contact angles were measured at 15 separate positions along a 3-cm length of rod for each applied potential. The equilibrium contact angle was taken as the average of the cosines of the average advancing and receding contact angles [5].

Theory

For simplicity, the theoretical expressions are derived for a case of a flat EW system. Consider a flat metal electrode covered with a dielectric layer of thickness d_1 and capacitance C_1 in contact with a partially wetting liquid. In the absence of an applied potential an electrical DL will form at the SL interface due to the charge present on the solid surface. The DL formation will cause a rearrangement of the charge in the metal electrode and polarize the dielectric. As a result a potential difference will be established between the bulk solution and the electrode. The SL interface can be represented as two capacitors, C_1 and C_{DL}, in series, where C_{DL} is the capacitance of the DL. When a DL is formed and/or an electric potential is applied across the SL interface between the metal electrode and a counter electrode in the solution the SL surface energy can be formally written as [10]

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SL}}^0 + \Delta F \ , \tag{2}$$

where γ_{SL} is the total free energy per unit area of the SL interface, γ_{SL}^0 is the chemical part of that energy (and equals γ_{SL} at the point of zero charge, PZC) and ΔF is the electrostatic part. We acknowledge that the applied potential will cause not only polarization of the dielectric layer but also rearrangement of the DL. Consequently

$$\Delta F = \Delta F_{\mathrm{diel}} + \Delta F_{\mathrm{DL}} \ , \tag{3}$$

where ΔF_{diel} is the free energy of polarization of the dielectric layer and ΔF_{DL} is the free energy of the DL. From simple electrostatics [4]

$$\Delta F_{\mathrm{diel}} = -\frac{C_1 V_1^2}{2} \ , \tag{4}$$

where $C_1 V_1^2/2$ is the electrostatic energy stored in the dielectric layer and V_1 is the potential drop across the layer. The term ΔF_{DL} can be expressed as [10]

$$\Delta F_{\mathrm{DL}} = -\int_0^{V_{\mathrm{DL}}} \sigma_{\mathrm{DL}} \mathrm{d}V + \Delta F_{\mathrm{conf.DL}} \ , \tag{5}$$

where V_{DL}, σ_{DL} and $\Delta F_{\mathrm{conf.DL}}$ are the surface potential, surface charge density and the configurational entropy contribution for the DL. Here, the assumption is made that the potential in the bulk of the liquid is zero. If Eqs. (2)–(5) are substituted into Young's equation, with the assumption that both the solid–vapor (γ_{SV}) and liquid–vapor (γ_{LV}) surface energies do not depend on the presence of charge on the SL interface, one can obtain

$$\cos\theta = \cos\theta^0 - \frac{\Delta F}{\gamma_{\mathrm{LV}}} = \cos\theta^0 + \frac{C_1 V_1^2}{2\gamma_{\mathrm{LV}}} + \int_0^{V_{\mathrm{DL}}} \frac{\sigma_{\mathrm{DL}} \mathrm{d}V}{\gamma_{\mathrm{LV}}} - \frac{\Delta F_{\mathrm{conf.DL}}}{\gamma_{\mathrm{LV}}} \ . \tag{6}$$

To determine the exact dependence of the contact angle θ on the applied electric potential a model for the structure of the DL must be specified. In the simplest Helmholtz model the DL is modeled as a capacitor with a constant capacitance, $C_{\mathrm{DL}} = \varepsilon_0 \varepsilon_{\mathrm{r}}/\delta$, where ε_0 is the electric permeability of a vacuum, ε_{r} is the dielectric constant of the liquid and δ is the thickness of the DL. The integration of Eq. (6) for a Nernstian SL interface in this case gives

$$\begin{aligned}\cos\theta &= \cos\theta^0 + \frac{C_1 V_1^2}{2\gamma_{\mathrm{LV}}} + \frac{C_{\mathrm{DL}} V_{\mathrm{DL}}^2}{2\gamma_{\mathrm{LV}}} \\ &= \cos\theta^0 + \frac{C(V - V_{\max})^2}{2\gamma_{\mathrm{LV}}} \ , \end{aligned} \tag{7}$$

where the total potential $V - V_{\max} = V_1 + V_{\mathrm{DL}}$, $V_{\max}$ is the applied potential at the PZC (e.g. the potential at the electrocapillary maximum) and $C = \left(C_1^{-1} + C_{\mathrm{DL}}^{-1}\right)^{-1}$ is the total capacitance of the SL interface.

If the Gouy–Chapman model of the DL is used the surface charge on the SL interface becomes a function of the surface potential. In this case the capacitance of the DL and, consequently, the total capacitance of the interface is a function of the applied potential $C = f(V)$ or $C = f(V_{\mathrm{DL}})$. In order to calculate ΔF_{diel} and ΔF_{DL} one must first find the values of V_1 and V_{DL} as a function of V. The relation between V and V_{DL} is given by the following equation:

$$V - V_{\max} = V_1 + V_{\mathrm{DL}} = \frac{4n^0 zq}{C_1 \kappa} \sinh\left(\frac{zqV_{\mathrm{DL}}}{2kT}\right) + V_{\mathrm{DL}} \ , \tag{8}$$

where n^0 is the number concentration of the symmetric $z : z$ electrolyte, κ is the reciprocal DL thickness, q is the elementary charge and kT is the thermal energy. Solving Eq. (8) numerically, one can find the value of V_{DL} and, consequently,

$$\Delta F_{\mathrm{diel}} = -\frac{C_1 V_1^2}{2} = -\frac{\sigma_{\mathrm{DL}}(V_{\mathrm{DL}})}{2}(V - V_{\max} - V_{\mathrm{DL}}) \tag{9}$$

as a function of the applied potential. For Nernstian surfaces ΔF_{DL} is given by [10]

$$\Delta F_{\mathrm{DL}} = -\frac{8n^0 kT}{\kappa}\left[\cosh\left(\frac{zqV_{\mathrm{DL}}}{2kT}\right) - 1\right] \ . \tag{10}$$

This calculation can easily be modified to account for a structure consisting of multiple dielectric layers of capacitance C_i. In the case of the Helmholtz model, Eq. (7) will hold but the total capacitance, C, must be modified: $C = \left(\sum_i C_i^{-1} + C_{\mathrm{DL}}^{-1}\right)^{-1}$.

In the case of the Gouy–Chapman model, Eq. (8) must be modified:

$$\begin{aligned} V - V_{\max} &= \sum_i V_i + V_{\mathrm{DL}} = \frac{4n^0 zq}{\kappa} \sinh\left(\frac{zqV_{\mathrm{DL}}}{2kT}\right) \\ &\quad \times \sum_i \frac{1}{C_i} + V_{\mathrm{DL}} \ . \end{aligned} \tag{11}$$

Results and discussion

The theoretical models discussed previously are applied to calculate ΔF_{DL} and ΔF for a model system of a metal electrode coated with 10-μm parylene ($\varepsilon_{\mathrm{par.}} = 2.7$) and 100-nm AF1600 ($\varepsilon_{\mathrm{AF1600}} = 1.934$) layers. The spontaneous charging of the AF1600 is neglected (e.g. $V_{\max} = 0$). The applied potential is assumed to be 200 V or less. The effect of the electrolyte concentration on the surface free energy for an aqueous system ($\varepsilon_{\mathrm{water}} = 78.5$) is shown in Fig. 1. The electrolyte concentration strongly affects the value of ΔF_{DL}; however, the experimentally available concentration range is limited to at or above 10^{-6} M 1:1 electrolyte and the changes in C_{DL} and hence ΔF_{DL} are too small to cause any variation of ΔF as shown in the inset of Fig. 1. This is because the capacitance of the DL is much greater in comparison to the capacitance of the dielectric layers. The insensitivity of the contact angle to the electrolyte concentration in aqueous systems has already been observed experimentally for different EW systems [4, 8]. The Gouy–Chapman model predicts a general reduction of the free energy of the DL especially at low ionic strengths (Fig. 1) by increasing the value of the capacitance of the DL. Above 1×10^{-3} M , there is no difference between ΔF_{DL} values calculated by the two models. Because of the small value of ΔF_{DL} the effect does not cause any noticeable change in ΔF (see the inset of Fig. 1). The effect of the electrolyte concentration on the surface free energy for a nonaqueous system (CCl_4, $\varepsilon_{CCl_4} = 2.228$) is shown in Fig. 2. The Helmholtz model is not applicable in this case if the electrolyte concentration is 10^{-3} M or less because of the high values of the surface potential. It predicts a significant dependence of the EW effect on the electrolyte concentration at extremely low ionic strengths due to an overestimation of the value of V_{DL} (predicted to be of the order of several volts at the maximum applied potential). The more realistic Gouy–Chapman model predicts a value of V_{DL} of about 435 mV and an ΔF_{DL} value of about

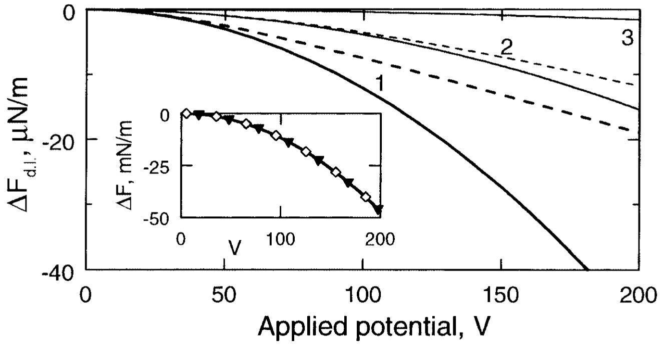

Fig. 1 Dependence of the free energy of the double layer, ΔF_{DL}, on the applied potential for an aqueous system at different electrolyte concentrations: *curves 1* 1×10^{-6} M; *curves 2* 1×10^{-5} M; *curves 3* 1×10^{-3} M. *Solid lines*: Helmholtz model; *dashed lines*: Gouy–Chapman model. Inset: dependence of ΔF on the applied potential at different electrolyte concentrations. *Solid line* 1×10^{-6} M, Helmholtz model; ◇ 1×10^{-6} M, Gouy–Chapman model; ▼ 1×10^{-3} M, Helmholtz model

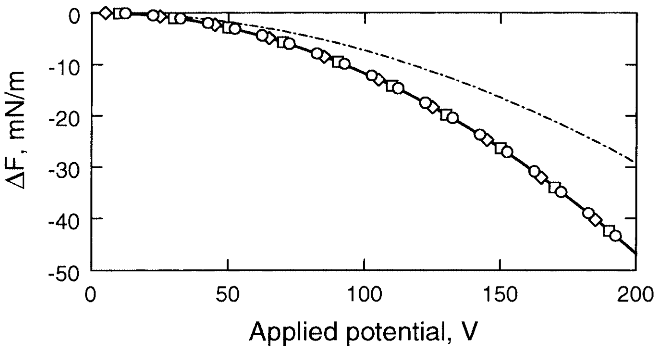

Fig. 2 Dependence of the total change of the free energy of the interface, ΔF, on the applied potential for a nonaqueous system at different electrolyte concentrations. Helmholtz model: 1×10^{-6} M (*solid line*); 1×10^{-10} M (*dash-dotted line*). Gouy–Chapman model: 1×10^{-6} M (◇); 1×10^{-10} M (□); 1×10^{-14} M (○)

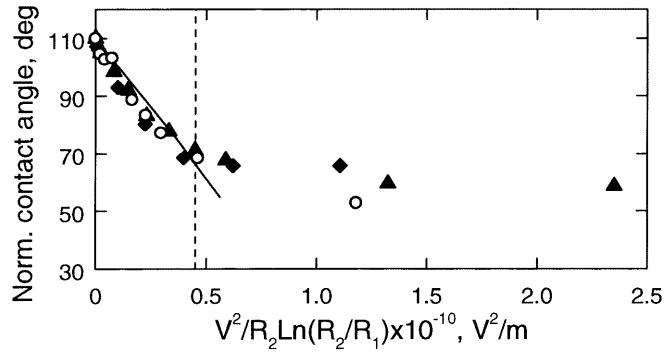

Fig. 3 Normalized contact angle versus $V^2/R_2 \ln(R_2/R_1)$, where $R_1 = 0.5$ mm is the radius of the rod and R_2 is the radius of the rod coated with a dielectric layer (the thickness of the fluoropolymer is neglected). Experimental data for a 30-μm dielectric layer (*triangles*), a 15-μm dielectric layer (*circles*), a 4-μm dielectric layer (*diamonds*) and the expected results from the theory (*solid line*). The *dashed line* represents the potential at which the solid–liquid surface energy becomes zero, which corresponds to the potential at which the experimental results deviate from the theory

−24 μN/m at the maximum applied potential in the case of an electrolyte concentration of 10^{-10} M. The amplitude of ΔF_{DL} is slightly increased in comparison to the maximum amplitude in aqueous solutions, where ΔF_{DL} is about −19 μN/m at the maximum applied potential and 10^{-6} M electrolyte. In the electrolyte concentration range 10^{-10}–10^{-6} M , only a slight reduction of the contribution of the DL is observed for the nonaqueous system. Even though the contribution of the DL increases in comparison to the aqueous systems it is still much smaller than the contribution of the dielectric layer. As a result, the contact angle is independent of the electrolyte concentration even for a nonaqueous system (Fig. 2). This effect has to be proven experimentally. The DL could be expected to influence ΔF at extremely low ionic strengths (much lower than 10^{-14} M electrolyte) and the influence will be noticeable as a decrease in the EW effect and as a deviation from the parabolic field strength dependence to a linear one.

Static advancing and receding contact angles were measured at 4 μm, 15 μm and 30 μm thicknesses of the parylene with a 100-nm overlayer of Teflon AF1600. The equilibrium contact angles were calculated from the experimental data and are shown in Fig. 3. The equilibrium contact-angle with no applied potential averaged for all samples was 110°, which is close to the values reported earlier [7]. The expected results from the preceding theory in the case of the Helmholtz model, modified to account for the cylindrical shape of the EW system used here is shown in Fig. 3 by the solid line. The contact angles are normalized for comparison, to an initial contact angle of 110°. The potentials are normalized such that rods with different dielectric thicknesses can be compared, and a single theoretical curve applied that is correct for each of the dielectric thicknesses. The experimental data for different thicknesses lay on a master curve. The EW effect increases up to 5×10^9 V^2/m in accordance with the theory. Above 5×10^9 V^2/m, the experimental data deviate from the theory and the EW effect saturates at high potentials as observed previously [4–8]. A total decrease of the contact angle of more than 60° is achieved. While the coincidence between the theoretical prediction and the experimental data suggests the theory accounts for the most essential features of the EW effect at low applied potentials the saturation of the EW effect at high potentials remains unexplained. This seems to be a general effect and is observed with all systems used for EW [4–8]. The contact-angle saturation has been attributed to charge buildup in the insulator [8], high electric field strengths in the three-phase zone [5], dielectric breakdown, adsorption of water molecules [7] or a combination of each, yet no single theory has been proven to be correct for a range of different EW systems. Here we propose a model that predicts a potential limit (V_{limit}) for which the previous EW theory is applicable. The model can be used to estimate the saturation contact-angle, although the experimental data show that the contact-angle may still decrease slightly for potentials greater than V_{limit}.

The EW effect works by reducing the SL surface energy as the potential is increased. Thus, at some potential, depending on the system, the SL surface energy will become zero. From Young's equation, if $\gamma_{\mathrm{SL}} \to 0$, the contact angle is dependent only on the solid–vapor (γ_{SV}) and liquid–vapor (γ_{LV}) surface energies:

$$\cos \theta_{\mathrm{limit}} = \frac{\gamma_{\mathrm{SV}} - 0}{\gamma_{\mathrm{LV}}} \quad . \tag{12}$$

This defines a contact-angle limit, θ_{limit}, fixed for a given system. Experimentally, the contact-angle may decrease below this angle slightly as this is only a thermodynamic analysis and does not take into account the kinetics of the wetting and the characteristics of the surface. It is thus more convenient to determine the potential at which $\gamma_{SL} = 0$, as this indicates the limit of EW theory, and potentials greater than this result in system instabilities and indeterminable effects occur. When $\gamma_{SL} = 0$, $\gamma^0_{SL} = -\Delta F. \gamma^0_{SL}$ can be determined from Young's equation if γ_{SV}, γ_{LV} and θ^0 are known. Knowing the thickness of the dielectric layers, the total capacitance of the system can be calculated and, in the case of the Helmholtz model, the potential at which $\gamma_{SL} = 0$ determined via

$$V_{\mathrm{limit}} = \sqrt{\frac{2\gamma^0_{SL}}{C}} \ . \tag{13}$$

For the system being investigated, V_{limit} equates to $4.5 \times 10^9\,\mathrm{V}^2/\mathrm{m}$ and is shown by the dashed line in Fig. 3. The potential at which the SL surface energy becomes zero, V_{limit}, corresponds well to the potential at which the experimental results deviate from the theory. Above V_{limit} the contact angle is almost constant as predicted by our model. In the classical Lippmann electrocapillary system (mercury/electrolyte), an interfacial tension of zero between the mercury and the aqueous electrolyte solution can result in the formation of an emulsion at the interface if electrolysis is avoided [11]. This is a result of the interface increasing its area to minimize its free energy. Apparently, this is not possible at the SL interface discussed here. Instead, at sufficiently high applied potentials (well above V_{limit}), system instabilities, such as a vibration in the system and even ejection of liquid from the three-phase zone, can be observed.

Conclusions

The theoretical treatment presented here shows that the EW effect is, in the most part, due to polarization of the dielectric as opposed to purely a rearrangement of the double layer and explains why there is no dependence of the EW effect on the electrolyte concentration. The theory is only applicable over a limited potential range and we have developed a model that predicts the potential at which this limit occurs. This is the potential at which the SL surface energy becomes zero. The model predicts the limiting potential to be dependent only on the bulk liquid and solid properties and is thus fixed for a given system. The limiting potential corresponds approximately to the onset of contact-angle saturation. The model predicts that for an EW device in which an aqueous droplet can be forced to completely wet a hydrophobic surface, a surface with basically the same surface energy as the liquid is required.

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