

# Static Electrification by Nonwetting Liquids. Contact Charging and Contact Angles

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A glass slide hydrophobized with dimethyldichlorosilane appears to be electrostatically charged when a nonwetting liquid recedes from its surface. The surface charge has negative polarity. The density of the charge which arises on retraction from water is  $10^{-4}$  C/m<sup>2</sup>. The half-life of the charge on the surface in air is 0.5 h. The charging effect is observed with different liquids and solutions for which contact angle and surface tension are high. A correlation of the value of the charge with the conductivity and double layer parameters is not pronounced. The electrification leads to a long range attraction between the plate and the liquid and influences the wetting of the substrate.

## Introduction

Contacting of a solid with a liquid can lead to static electrification. Mercury electrifies most of the surfaces.<sup>1</sup> The phenomenon known in the times of Galvani and Volta still lacks unambiguous interpretation. It has hardly ever been considered in wetting studies which deal with contact angles of liquids on solid substrates (see reviews in refs 2-4).

It was reported recently that a glass surface hydrophobed by dimethyldichlorosilane emerges charged on retraction from water.<sup>5</sup> The magnitude of the static charge decreases with decreasing contact angle on addition of ethanol. No other insight into the origin of the electrostatic phenomenon which clearly interferes with the wetting behavior was provided.

Wetting is a nonequilibrium phenomenon. Contact angle hysteresis is well-known and electrification is another example. Unlike other interactions considered by molecular theories of capillarity, electrostatic effects extend to macroscopic distances. Experimental data can be easily misinterpreted if charging phenomena are not recognized. Charging and wetting being interrelated are a general manifestation of molecular mechanisms involved in the dynamic interaction of the solid and the liquid phase.

Different mechanisms that give rise to static charging of the methylated glass can be envisaged. A spatial separation of charge occurs when a solid is in contact with a liquid. For water with its high dielectric constant, the Debye length (which gives the average distance between the plane of charges and the counterions) is large. It is between  $10^2$  and  $10^3$  Å (the exact value depends on the contaminant electrolyte). As the three-phase line slips when water recedes from a hydrophobic surface, neutralization of the ionized surface groups might be kineti-

cally prevented. Surface with bare charges would emerge out of the liquid (in which the excessive ions are trapped).

The argument can be disputed if charge neutralization on going from water to air is due to protons rather than to recombination with counterions within the double layer. As an alternative, the origin of the effect may be traced to the phenomenon of "triboelectricity". While spatial separation of charges in contact between two dissimilar solids hardly can exceed one atomic size (which is hundreds times less than within a double layer in water), charge transfer occurs on breaking the adhesive joint. The experiments described here were aimed to distinguish between the possible mechanisms that may be implicated in the charging.

## Theory of the Method

The force ( $F$ ) acting on a solid partly immersed into a liquid is a sum of the capillary force ( $F_c$ ) given by the vertical component of the surface tension ( $\gamma$ ) along the wetting line ( $L$ ) and the buoyancy force ( $F_b$ ). For a Wilhelmy plate or a cylinder

$$F/L = \gamma \cos \theta \quad (1)$$

(if the contact angle  $\theta$  is not uniform along the three-phase line, it is an effectively averaged quantity) and

$$F_b/S = \Delta \rho g Z \quad (2)$$

( $S$  is the horizontal cross section,  $\Delta \rho$  is the density of the liquid if the density of air is neglected, and  $Z$  is the depth of immersion).

The height ( $H$ ) of the capillary rise (the meniscus height) over an infinite wall follows the equation

$$\Delta \rho g H^2 / (2\gamma) = 1 - \sin \theta \quad (3)$$

(derivation given in ref 2; a limiting analytical expression exists also for a cylindrical geometry<sup>6</sup>). The plate (cylinder) when lowered touches the liquid at  $Z = 0$ . On rising the liquid bridge (meniscus) is stable up to a higher (positive)  $Z = H'$  as long as the receding ( $\theta_r$ ) angle is below  $90^\circ$ . Ideally  $H' = H(\theta=0)$  due to uncertainty of the angle at the edge. But in practice the bridge is destroyed at a lower value above  $H(\theta_r)$  because of imperfect geometry and alignment.

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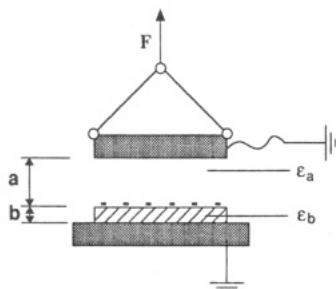
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**Figure 1.** The setup for measurement of the charge density (schematically). A glass plate (light gray) is placed on a grounded metal base (dark gray) and the force acting on the upper grounded metal plate is measured.

When the plate is charged an attractive electrostatic image force is superimposed. Because the range of the force is typically comparable to the size of the body, it does not simply scale with the perimeter. Nevertheless, the absolute charge density ( $\sigma$ ) can be easily determined without numerical simulations. This can be done by placing a uniformly charged plate between two earthed planes as shown schematically in Figure 1 and measuring the force. This charge image force is given by

$$F = \sigma AE \\ = \sigma^2 Ab / [\epsilon_0(\epsilon_a b + \epsilon_p a)] \quad (4)$$

Here  $A$  and  $b$  are the area and the thickness of the plate,  $a$  is the width of the air gap,  $\epsilon_0$  is the absolute permittivity of free space, and  $\epsilon_a$  and  $\epsilon_b$  are the relative permittivity of air and glass. The field ( $E$ ) is uniform in this case and the expression can be obtained using Maxwell's equations and Laplace's equation (see ref 7).

### Materials and Procedures

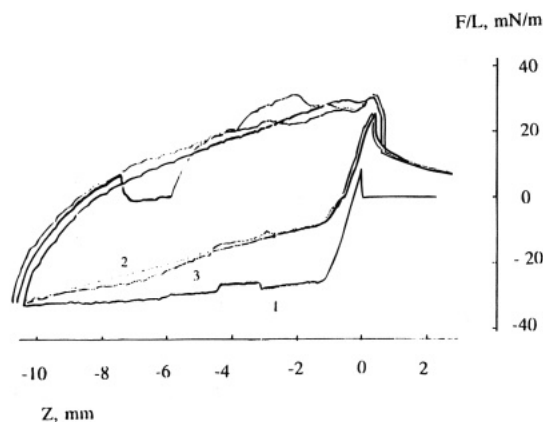
Glass substrates were microscope cover slips (22 mm  $\times$  45 mm  $\times$  130  $\mu$ m). Some experiments were repeated with Pyrex rods. The slides were first cleaned with hot chromic acid, rinsed in Millipore water, and dried in a jet of evaporated nitrogen. The silanation reaction was carried out by exposing the glass to saturated vapor of dichlorodimethylsilane (Ajax) over a period of 12 h. Finally the samples were rinsed in chloroform and distilled ethanol before being dried in nitrogen. Samples were stored in a vacuum dessicator. Chemicals used were of reagent grade without further purification.

Forces were measured using a feedback microbalance mounted on a microtranslation speed and position control stage. The samples were suspended from the balance through a small inlet in the cover into a glass cell. The experiments were carried out at ambient temperature (21–23  $^{\circ}$ C) with the vapor phase conveniently maintained (but not critical for the results) slightly undersaturated to minimize evaporation and prevent condensation. Videomicroscopy enabled simultaneous observation of the movement of the three-phase line and changes of the meniscus height. For absolute charge density measurements the plate after being fully immersed in the liquid and retracted was placed on an earthed plane and the other horizontal electrode was suspended from the balance on the microtranslator. A commercial piezoelectric charge neutralizer ("Zerostat", Sigma) allowed the removal of the charge by directing fluxes of positive or negative ions onto the plate and the determination of its sign.

### Results and Discussion

#### 1. General Features. Electrification with Water.

As an example illustrating some general features of electrostatic phenomena involved in the wetting, force vs depth of immersion curves for three subsequent cycles of immersion and retraction for a dimethyldichlorosilane-treated slide in water are shown in Figure 2. On the first



**Figure 2.** Force ( $F$ ) vs displacement ( $Z$ ) for methylated plate in water (while  $F/L$  is shown, it has to be kept in mind that force is not exactly scaled with the length when static charge is present). The data are for three subsequent runs. On the first approach the plate is uncharged and touches water at  $Z = 0$ . The three-phase line begins to move along the plate when its edge caves in the interface by 0.5 mm. Between positions  $-3$  and  $-5$  mm the speed was reduced from 1.8 to 0.18 mm/min; this can be noticed by an upward parallel shift of the receding path in the first run (the bottom line). Pronounced nonlinearity of the receding branch is the charging effect, as well as the attraction at positive  $Z$  after the meniscus being extended up by 0.6–0.7 mm, slides off the plate. On the second approach the meniscus forms 0.3–0.4 mm above the level because of the liquid jump caused by electrostatic attraction. The advancing branch is shifted upward because of the electrostatic attraction; the increased slope which resembles the receding slope results from charge neutralization. The advancing branches of the first and the second cycles finally converge after the previously retracted area is fully submerged and all the charge is neutralized. During the retraction the speed has been lowered to 0.18 mm/min and increased to 5 mm/min; the corresponding intervals are clearly marked by the cavern and the bulge accordingly. These intervals of a reduced and an increased charge density are responsible for the deviations of the advancing trace in the third cycle from that of the second cycle. Because of the long duration of the low speed interval (10 min) its track is more smeared by the natural decay of the charge.

approach there is no force acting on the plate until it touches the surface of the water. On the contact when the three-phase line is formed at the edge of the plate there is an instantaneous attraction ( $Z = 0$ ) due to an imperfect alignment (one of the corners of the plate touches the liquid which adheres to the bottom edge).

On subsequent immersion the force falls rapidly into the negative (repulsive) range. This is because the line stays fixed at the edge and the angle increases with the depth, according to eq 3 with  $H = Z$ , from the initial value of about  $90^{\circ}$  at  $Z = 0$  (for ideal geometry) to the critical advancing value  $\theta_a$ . The decrease of the force which becomes more repulsive when the meniscus becomes more concave proceeds according to eq 1 (on the background of this capillary effect the change of the buoyancy given by eq 2 is small in this short interval).

The line begins to slide over the vertical wall at a constant speed equal to the speed of the stage when the critical value of the advancing tension ( $\gamma \cos \theta_a$ ) at a given speed is reached. Under this condition the slope of the plot which is now small is due to the buoyancy alone.

The advancing tension increases (decreases in absolute value) with decreasing speed. This is clearly seen in the first cycle (bottom line, from  $-3$  to  $-5$  in  $Z$ ) where the speed was instantaneously reduced from 2 to 0.2 mm/min. The change is less than 10% on changing the speed by an order of magnitude. The weak speed dependence is in accordance with the long times (hours and more) over which the equilibrium tension is reached when the plate is at rest.<sup>5</sup>

(7) Crowley, J. M. *Fundamentals of Applied Electrostatics*; Wiley: New York 1986.

When the speed is reversed the line is pinned again (this time not at the edge but in the middle of the plate where it was stopped) and the contact angle decreases. The meniscus becomes convex and the capillary force becomes attractive. The subsequent receding (upper) part of the loop, unlike the advancing (bottom) one, is nonlinear over most of the range. Its slope, which decreases with the height, is larger than given by the buoyancy alone.

The receding branch is much more sensitive to speed variations. This can be clearly seen from the results of the second cycle in which the speed was varied. While the advancing slope is independent of the speed and stays at the buoyancy level (the results of the first cycle), the receding slope increases with increasing speed, with the buoyancy being the low speed limit.

The results clearly demand the inference of an additional factor beyond the constant tension and linear buoyancy effects. Its electrostatic origin is easily recognized by an attraction slowly decaying with distance which is seen after the plate has been detached from the liquid. If the plate is moved up and down without touching the liquid this interaction is reversible over a short period of time (up to several minutes). It drops noticeably over longer periods (typically an hour).

The attraction as it is seen when the plate is out of water clearly accounts for the peculiar shape of the receding branch. Charge generated on the retraction has a constant density if the speed is constant. The larger the retracted area is (the area which is charged), the larger the attraction. Because the range of the attraction is comparable to the length of the plate, the electrostatic component of the force changes nonlinearly with the depth.

The static charge changes the conditions of approach of the plate to the liquid. The stability is lost at a finite distance and the liquid jumps toward the plate. A convex (wetting type) meniscus is formed before the zero level is reached. A corresponding upward shift of the engagement coordinate (by a fraction of 1 mm) for the charged plate (second and third runs) compared to the contact at  $Z = 0$  for the uncharged plate (first run) is revealed by the plots. A "bulging" of the liquid under the plate before the jump is seen on the videorecords.

Several other curious phenomena accompany the process of entering of a strongly charged solid into the liquid. When the electrostatically attracted liquid jumps onto the plate, an electrical discharge occurs. Due to a partial charge neutralization, the attraction drops and the liquid can fall down again. The process can be repeated several times before the edge of the plate finally enters the liquid.

In experiments with a rod, a droplet that is a fraction of 1 mm in diameter typically remains at the bottom of the cylinder when it is detached from the liquid. On subsequent approach the droplet is ripped off the surface by the electrostatic forces and jumps into the liquid from a finite separation. A characteristic elongation of the droplet shortly before the jump can be noticed. The jump of the liquid onto the rod (which does not carry the liquid any more) occurs at a shorter separation.

As the plate is moved down while the three-phase line is pinned on the edge the charged area remains unchanged. This part of the plot resembles the corresponding part in the first run. It is shifted upward due to the electrostatic attraction. The attraction changes with height but as for the buoyancy the change is much smaller than the change of the meniscus force.

After the line starts to move the charged area decreases linearly with the depth because the charge on the immersed part of the plate is neutralized. Accordingly, the shape of the advancing branch resembles that for the retraction, but is displaced to a lower level by the value

of the constant difference between the receding and the advancing tension.

The advancing branches for the charged (second and third cycles) and uncharged (first cycle) plates converge as the immersion depth increases and the charged area decreases. When the depth to which the plate has been immersed in the previous run(s) is reached, all the charge is neutralized. If immersion is continued to a larger depth than in the previous cycles, the slope reduces to the constant buoyancy value. The advancing branch appears as a continuation of the advancing trace for the uncharged plate in the first cycle.

If the plate is continuously moved up and down at a constant speed with a constant amplitude, the force loops (except for the first cycle, when the plate was initially uncharged) coincide to a minor detail. These details can somewhat vary from plate to plate but otherwise the loops are similar with a reproducibility of a few mN/m.

The absolute magnitude of the charge collected on a plate withdrawn from water with a constant velocity of  $1.87 \pm 0.03$  mm/min is  $(6.2 \pm 0.9) 10^{-5}$  C/m<sup>2</sup>. This is deduced with eq 4 from force measurement in the parallel electrode geometry. The sign of the charge is negative and the half-life is 0.5 h. Note that the charge density measurements were recorded 15 min after the plate was retracted so that the initial (immediately after retraction) density of charge is somewhat higher, about  $10^{-4}$  C/m<sup>2</sup> (the exponential decay can be easily observed from the very beginning if the plate is left above the liquid after the retraction). A stream of negative ions directed onto the plate does not influence the charge, while positive ions lead to charge neutralization.

The force acting between the vertical plate and horizontal liquid surface is related to the charge density through a complicated boundary condition that cannot be resolved analytically. However, this force shows a similar magnitude and distance dependence as for the plane parallel geometry. Qualitatively it follows an inverse parabolic form with measurable forces at distances on the order of 1 cm.

A speed dependent slope of the receding branch shows that the density of the charge generated on the retraction is a function of the velocity. The lower curve of the third run confirms this. When the advancing three-phase line engulfs an area of higher charge (here the plate was moved at a higher speed on the retraction in the previous cycle), the slope of the line is greater. This is the result of the charge being neutralized at a greater rate with respect to distance over these areas.

Only at smallest velocities below 0.2 mm/min does the receding slope approach the theoretical buoyancy value and the electrostatic interactions become small on the background of the molecular wetting tension effects. Also for such velocities their product by the half-life of the charge becomes comparable and smaller than the effective range of the electrostatic interaction. Under this condition the natural decay of the charge becomes important.

At higher retraction speeds the dependence of the charge on the speed is more pronounced than could be explained by natural decay. A larger charge density is in fact generated at a higher velocity. The charge begins to interfere substantially with the wetting behavior. Both the wetting tension and the electrification depend on the rate at which the three-phase line is displaced. Electrostatic effects become dominating at higher speeds (we did not investigate a high speed limit). A maximum of several millimeters/minute in these experiments was used to ensure that dynamic effects are not invoked and the continuity of the three-phase line is maintained with no droplets ripped off the meniscus and transferred onto the plate).

Electrostatic attraction when superimposed should be taken into account together with the buoyancy in evaluating the wetting tension. While the advancing tension can be measured for an uncharged plate, the receding one can be measured directly only by continuous ionization of air. In the latter case the buoyancy slope appears also on the receding branch.

The estimated value of the charge of  $10^{-4}$  C/m<sup>2</sup> corresponds to an average charge to charge distance less than 500 Å. Because distances between the charges are not very large on the molecular scale, the electrostatic effects cannot be simply envisaged as an external macroscopic field superimposed on the capillary effects as is the case for the gravitational field. Deformations of an interface by gravity are accounted for simply by taking the sum of the hydrostatic pressure and the Laplace pressure. They do not influence the contact angle and thus do not enter into the Young equation.

At a strongly charged plate, the contact angle itself is also changed. The magnitude of electrostatic interactions at the shortest distances in the vicinity of the three-phase line is not negligible compared to molecular forces, even though the contact effects may be relatively small.

To what extent can the long range electrostatic and short range molecular effects be considered independently? To what extent might extrapolated angles be effected by static charges? To answer these questions the geometry of the meniscus down to the three-phase line has to be analyzed for capillary pressure and image charge interactions. For the moment we shall concentrate on further experiments with different liquids and solutions. These provide us with more insight into the origin of the static charge and the mechanisms of its generation.

**2. Conductivity and Double Layer. Electrification with Aqueous Electrolytes.** It has already been shown that the magnitude of the charging decreases with increasing wetting tension (decreasing contact angle and surface tension) as ethanol is added to water.<sup>5</sup> The result, reasonable in itself, cannot be unambiguously interpreted. (i) A denser and accordingly more conductive adsorbed film in equilibrium with the liquid phase is expected to favor an easier leakage of the charge from the solid-vapor interface into the liquid. (ii) The mode of slippage of the three-phase line can be changed. This might be a factor effecting the charge separation. (iii) A reduction of the surface tension and of the contact angle (as long as the latter is below 90°) corresponds to a virtual reduction of the normal stress at the three-phase line.

As a starting point we shall test the hypothesis which assumes a double layer origin for the surface charge. It has been repeatedly reported since the famous work of Kitchener<sup>8</sup> on the stability of aqueous films on methylated glass that a surface made hydrophobic by silane treatment retains the substantial surface charge of the initial silica substrate in water. This could be attributed to residual silanol groups left after silane treatment.

The layer formed by dimethyldichlorosilane in the presence of moisture is expected to contain dimethylsiloxane oligomers and polymers.<sup>9</sup> The end silanol groups if not grafted to the surface might be able to dissociate in water. The fact that the static charge which arises on the surface treated with dimethyldichlorosilane is negative is consistent with the idea of its possible relevance to the original charge which the surface had in water.

Given the hypothesis that the static charge results from a separation of the double layer, one might expect a

correlation with the Debye length and the surface charge. We shall look now into the factors which enable one to regulate electric properties of the solid-liquid interface without influencing the contact angle or the surface tension substantially.

An increase of ionic strength through addition of a neutral salt reduces the Debye length without changing the dissociation of surface groups. The total suppression of the double layer (the Debye length reduced to a molecular scale) occurs at concentrations of a 1:1 electrolyte on the order of  $10^{-1}$  M. At such concentrations the surface tension and contact angle effects are quite small (typical absolute values of  $d\gamma/dC$  of inorganic electrolytes are on the order of 1 mN/m per mol/l and less which means that the surface tension changes by less than 1%).

The magnitude of the attraction falls approximately 2 times for decimolar solutions of NaCl or KCl compared to pure water. While the charging decreases in the presence of these electrolytes, the background wetting tension remains apparently unchanged (for example, the advancing tension for uncharged plate is not affected to more than 1–2 mN/m). At low concentrations the effect is reversible and the initial high surface charge is restored if the experiments are repeated with pure water.

However, in concentrated solutions some irreversible changes gradually occur. After a long time the layer loses its ability to attain a charge on a retraction from water and appears more hydrophilic as shown by somewhat higher values of both the receding and the advancing tension. Such changes occur neither in pure water nor in organic solvents even after many days of immersion.

AFM profilometry has revealed that the layer which is initially uniform down to at least a nanometer scale attains a wavelike structure after long exposure to concentrated electrolyte. A penetration of the ions between the glass substrate and the siloxane layer which leads to its final detachment possibly occurs. A more detailed investigation of the instability is needed to arrive at more definite conclusions.

Dissociation of silanols increases with pH. At pH above 10 the surface of silica is fully dissociated and the charge is an order of magnitude larger than at normal pH. Nevertheless, the static charging slightly decreases rather than increases on going from water to  $10^{-3}$  M aqueous KOH. The result by itself does not yet rule out totally the double layer explanation. A rise of the surface charge due to dissociation of weak acidic sites (silanols) is accompanied by a decrease in the Debye length because of the increased ionic strength in alkaline solution compared to pure water.

At a pH below 2 dissociation of silanols is suppressed and the point of zero charge for silica is attained. The reduction of the static charge for HCl is slightly more pronounced than for neutral salts. The electrostatic attraction after retraction from  $10^{-3}$  to  $10^{-2}$  M HCl is several times weaker than after retraction from water but on the same order of magnitude. Again, the effect is reversible at low concentrations (down to pH 2 or 1), but a denaturation of the layer occurs at higher acidities.

The surface charge of silica in pure water can be fully neutralized without essentially changing the ionic strength by addition of a cationic surfactant. For example, the point of zero charge is achieved at a CTAB (cetyltrimethylammonium bromide) concentration of  $5 \times 10^{-5}$  M (for a detailed thermodynamic account of the wetting behavior of the silica glass in CTAB solutions, see ref 12). Such a low bulk concentration is comparable to the residual electrolyte content in pure water and the Debye length is not changed substantially. The surface tension effect at

(8) Kitchener, J. A. *Trans. Faraday Soc.* **1972**, *68*, 1435.

(9) Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 149.

(10) Yaminsky, V. V.; Ninham, B. W.; Stewart, A. M. *Langmuir*, submitted for publication.

(11) *Handbook of Chemistry and Physics*, 57th ed.; CRC Press: Cleveland, 1976–1977; pp F-30 and F-31.

(12) Yaminsky, V. V.; Yaminskaya, K. B. *Langmuir* **1995**, *11*, 936.

this concentration, which is 20 times lower than the cmc, is also quite negligible. Contrary to the neutral silica surface at a low pH which remains hydrophilic, charge neutralization by surfactants is accompanied by hydrophobization.

The effect of CTAB at this concentration is a reduction of the electrostatic attraction several times (up to an order of magnitude). This is even more pronounced than the corresponding effects of inorganic electrolytes at much higher concentrations. Nevertheless, in this case also the residual attraction is still substantial on the background of the wetting tension effects. No additional hydrophobization is observed besides the effects accounted for by the reduced electrostatic attraction.

The mechanism that leads to the reduction of static electrification by electrolytes is obviously different from that for water-ethanol mixtures. In the latter case the static charge drops in parallel with the contact angle, while the bulk conductivity is essentially unaffected. No electrification is observed with pure ethanol (contact angle about 25°). Electrification, though reduced, never totally disappears in electrolytes which do not influence the contact angle.

The main conclusion which can be drawn from the electrolyte experiments is that even if there is a correlation of the static charging with the Debye length and/or the surface charge at the solid-liquid interface, the relative changes of the static charge are smaller than for the corresponding double layer parameters.

Any interpretation which traces the effect to the double layer is also not supported by surface force measurements. The results considered in detail separately<sup>10</sup> show that in fact no interaction is seen down to a separation about 10 nm from which the surfaces jump into adhesive contact. Unlike bare hydrophilic silica, the methylated silica in pure water is apparently uncharged. Of course, a weak double layer repulsion not seen with the experimental accuracy may be present at long distances. Even very low surface charges (far below the level resolved by surface force experiments) would be enough to account for the magnitude of the static charge.

However, the important observation is that in  $5 \times 10^{-5}$  M CTAB, instead of an expected neutralization, a substantial surface charge appears. A DLVO type barrier with the Debye decay of about 300 Å and an  $F/R$  height of about 0.2 mN/m is clearly seen. The adlayer is undoubtedly formed not by the charge neutralization electrostatic but by the charge-generating hydrophobic mechanism. Adsorption of the surfactant ion as at the interface with air leads to a gradual build up of the charge (which is positive in the presence of the surfactant and at least several times larger in the absolute magnitude at this concentration than any charge which could arise in pure water).

A slight decrease of adhesion represents a slight hydrophilization expected for this type of adsorption. This indeed is opposite to what is observed in the case of the charge neutralization adsorption on bare silica. Because the adsorption at the methylated surface as at the water-air interface is low at this low concentration a corresponding decrease of the contact angle is not yet pronounced.

While adsorption is low compared to the condensed monolayer value (attained at much higher concentrations, comparable to the cmc), the surface concentration is orders of magnitude higher than the bulk concentration. Even in the rarefied monolayer the effective surface concentration (adsorption divided by the monolayer thickness) is in the molar rather than in the micromolar range (a condensed monolayer is essentially a pure surfactant). An increased surface conductivity in the layer formed by

fully ionized surfactant might be responsible for a weaker charge generation. Unlike surfactants, surface concentrations for inorganic electrolytes are not very different from the bulk.

In view of these results the effects of various electrolytes including salts, acids, bases, and surfactants on static charging may be viewed as related to an increased bulk and surface conductivity more than to the interfacial potential drop. The charging diminishes slightly with increasing bulk ionic strength and the surface activity (which leads to concentrating of ions at the interface).

**3. Surface Tension and Contact Angle. Electrification with Mercury.** The results of the previous section show that the presence of ionic species in the bulk and at the interface is not a critical factor in the generation of the charge. As long as the surface tension and contact angle are not changed significantly, the static charge density reduced in the presence of ionic species (as in the above experiments) retains the order of magnitude observed with pure water. It never falls to zero as it does for water-ethanol mixtures.

Different organic liquids with low surface tension and contact angles including purely dielectric ones such as alkanes do not charge the methylated glass. The contact angle and surface tension of the liquid clearly have a much more dramatic effect than bulk and surface conductivity.

Altogether, the charging effect is not restricted to aqueous media. It occurs similarly in nonaqueous liquids which have large surface tension and form high contact angles at hydrophobic surfaces. For example a charge which is only slightly (by about 50%) lower than in water is generated in formamide. The advancing tension for formamide is close to zero (advancing contact angle about 90°) compared to -20 mN/m ( $\theta_a$  over 105°) for water (surface tension is 58 mN/m for formamide compared to 72 mN/m for water). The charging behavior in formamide is similar to that in the water with 30% of ethanol. The wetting behavior in both cases is similar.

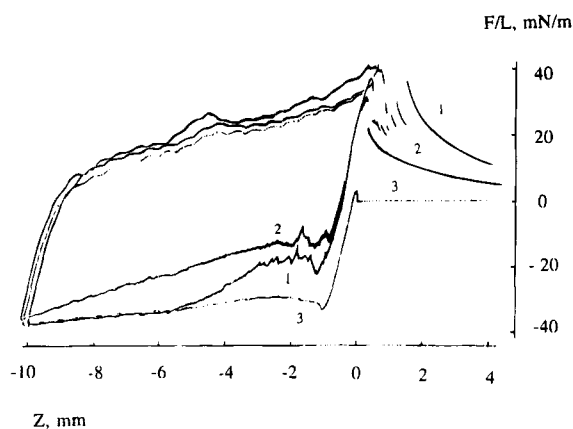
The dominating role of the capillary forces in determining the magnitude of the charge is clearly demonstrated by an experiment with mercury. The largest surface charge density was obtained by a retraction of the silane-coated plate from mercury. The results of the mercury experiment are quite indicative.

Mercury as a typical metal has a conductivity orders of magnitude higher than for aqueous electrolytes. Altogether its surface tension (400-500 mN/m<sup>11</sup>) is an order of magnitude larger than for other ordinary nonmetallic liquids at room temperature. Its contact angle on methylated glass (about 130° as estimated from a droplet profile) is larger than that for water.

Because of the large negative wetting tension and high density, the plate could not be forced into mercury within the range of the balance. The plate was simply dipped into mercury and the surface charge and the interaction with water were measured afterward (Figure 3). The electrostatic attraction is at least several times stronger than for charging in water. Electrical discharges begin at several times larger distances from the surface and continue during the approach until permanent contact with the liquid is established.

Immersion of the strongly charged plate into water reveals one more important feature which escaped our attention at lower charge densities. The receding branch reveals what one may take to be irreversible changes: sharp upward peaks at certain positions reproduced on subsequent immersions. However, after treatment of the plate with the ionic flux the normal wetting behavior is restored with no traces of the irregularities left.

The result suggests a self-consistent explanation for the whole set of the data. A displacement of the three-



**Figure 3.** Force ( $F$ ) vs displacement ( $Z$ ) after charging in mercury. Before measurement the methylated plate was dipped in mercury to the depth of 5–6 mm. Three subsequent immersions in water to a greater depth are shown. Electrostatic attraction before the first submersion is much stronger than after the retraction even though the area charged by water is more than twice the area initially charged by mercury (the limiting depth of the immersion into mercury can be clearly seen as the  $Z$  coordinate about  $-5$  mm below which the converging lines of the first and third immersions into water coincide). Electrical discharges on the first approach after charging in mercury which correspond to sudden drops of the force begin at large distances and continue over mostly a 1 mm path before the stable meniscus is finally formed at a shorter separation. The high charge density area, which extends to the position to which the plate was immersed in mercury, is clearly seen on the advancing branch of the first cycle. The increased slope results from charge neutralization. The line is modulated by sharp upward peaks indicative of locally increased attraction. The subsequent part of the branch is regular and the slope is the buoyancy part. The second cycle appears like an ordinary cycle in water. However, the peaks are still preserved at the same positions. After antistatic treatment before the third cycle the modulation disappears.

phase contact line causes a local rearrangement of the polydimethylsiloxane chains in the hydrophobic layer. The movement of the chains against the glass substrate can be viewed as a microfriction phenomenon. Hydrophilic silica glass and hydrophobic methylsiloxane polymer form a friction pair of dissimilar bodies which is generally expected to result in a separation of charges. Even though the rearrangement is mechanically reversible, the charges can be trapped within the dielectric layer.

Because of the hydrophobicity of the layer, some of the charges may be sparsely accessible to the electrically conductive aqueous environment. Altogether the layer is permeable to ions produced by an electrical discharge in air. It might be similarly permeable to wetting liquids such as ethanol which would also allow for an easier leakage of the charge.

The stress which leads to a local rearrangement of the layer may be determined by the normal component of the surface tension of the liquid. This component, "forgotten" in the Young equation, has to be counterbalanced by the elastic response of the substrate. The absolute magnitude of the stress is given by the ratio of the component to the effective thickness of the liquid–vapor interface and may be very high.

For contact angles around  $90^\circ$  the value of the component is close to the overall value of the liquid–vapor interfacial tension. For liquids away from the critical point, the effective thickness of the interface is on the order of the molecular diameter. This leads to absolute magnitudes of the local stress as high as the ideal strength of a condensed phase. Under such conditions rearrangement of interatomic bonds which results in the charge separation easily occurs. Because of the low thickness of

the layer, which is on the order of molecular sizes, and the high elasticity of polymer chains, deformations under such a critical stress are reversible.

On going from nonwetting liquids with high surface tension (such as water and especially mercury) to low surface tension wetting liquids (such as ethanol) the normal component of the interfacial stress falls by orders of magnitude. Also in the limit of low contact angles thick films are adsorbed at the solid–vapor interface. An enhanced surface conductivity would enable a leak of charges back into the liquid phase at the instant of their generation.

## Conclusion

A static charge is transferred onto a silica glass surface rendered hydrophobic by dimethyldichlorosilane when it emerges from water or some other nonwetting liquid. The density of the charge collected on the retraction at a fixed constant speed increases with an increase in the surface tension of the liquid and the contact angle. It ranges from zero (less than  $10^{-6}$  C/m<sup>2</sup>) for wetting organic liquids to high values (over  $10^{-4}$  C/m<sup>2</sup>) in the nonwetting limit.

For water and especially for mercury, for which the values of  $\gamma$  and  $\theta$  are the highest, the charge density is mostly as high as that produced on breaking ideal adhesive joints between dissimilar solids (over  $10^{-3}$  C/m<sup>2</sup><sup>13</sup>). Usually solid surfaces are not ideally smooth. The actual contact area of two real solids is much less than the apparent area, and ordinary frictional charges are typically smaller. While liquids form an ideal (over the entire area) contact with a solid (even when it is rough), the stress produced by the surface tension at the three-phase line can be as high as that due to adhesion forces between molecularly smooth solid surfaces. The mode of the slippage of the three-phase line may then be an important factor which controls the magnitude of the charge.

The results for formamide, water, and mercury show that given the values of  $\gamma$  and  $\theta$  the molecular nature of liquids which can be organic or inorganic, dielectric or metallic is not critical for the occurrence of the charging effect. Particularly, the bulk and interfacial conductivity due to dissolved and adsorbed ionic species appears to be only of secondary importance for the magnitude of the effect. No pronounced correlation with the parameters of the double layer at the solid–liquid interface has been found. The results indicate that the polymeric structure of the chemisorbed silane layer may be involved in the mechanism of the generation of the charge. The reduction of the magnitude of the effect with decreasing surface tension and contact angle corresponds to a reduction of the stress at the three-phase line.

The results demonstrate that the charging is implicated quite dramatically in the wetting behavior. Electrostatic forces can be easily comparable in magnitude to capillary forces, and the contact angles themselves may be affected by the presence of the charge.

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