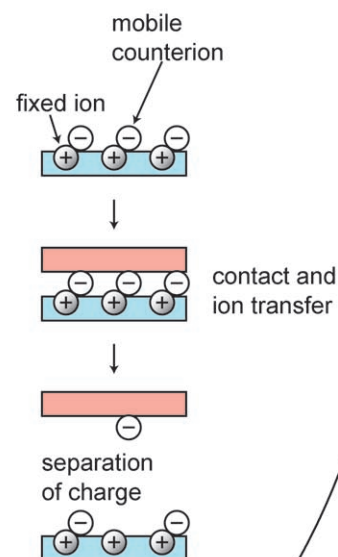
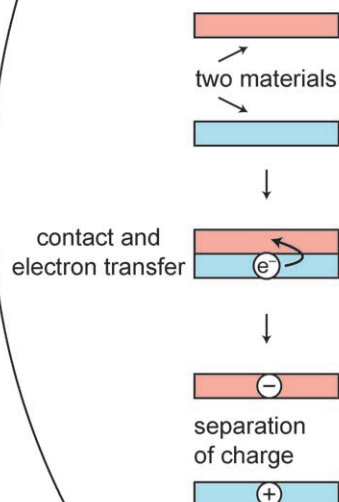
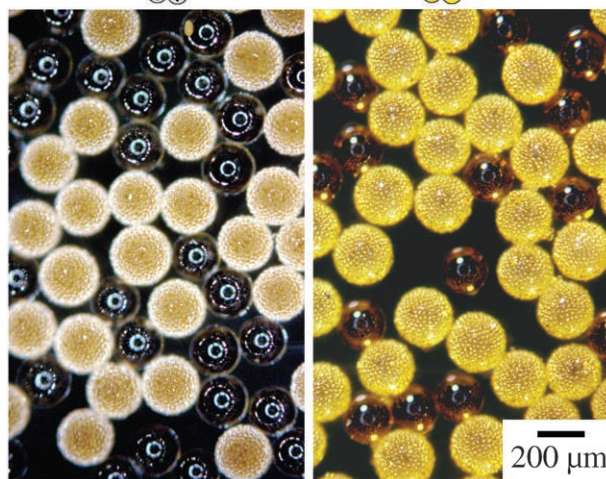
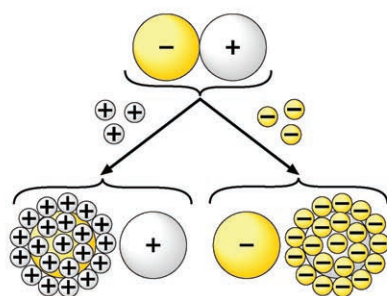


Electrostatic Charging Due to Separation of Ions at Interfaces: Contact Electrification of Ionic Electrets

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“Static Electricity”:
Electron transfer?
... or ion transfer?

This Review discusses ionic electrets: their preparation, their mechanisms of formation, tools for their characterization, and their applications. An electret is a material that has a permanent, macroscopic electric field at its surface; this field can arise from a net orientation of polar groups in the material, or from a net, macroscopic electrostatic charge on the material. An ionic electret is a material that has a net electrostatic charge due to a difference in the number of cationic and anionic charges in the material. Any material that has ions at its surface, or accessible in its interior, has the potential to become an ionic electret. When such a material is brought into contact with some other material, ions can transfer between them. If the anions and cations have different propensities to transfer, the unequal transfer of these ions can result in a net transfer of charge between the two materials. This Review focuses on the experimental evidence and theoretical models for the formation of ionic electrets through this ion-transfer mechanism, and proposes—as a still-unproved hypothesis—that this ion-transfer mechanism may also explain the ubiquitous contact electrification (“static electricity”) of materials, such as organic polymers, that do not explicitly have ions at their surface.

1. Introduction

An electret is a material that has a permanent, macroscopic electric field at its surface. There are two distinct classes of materials, both of which are called electrets: 1) dipolar electrets, which are overall electrically neutral, but have a macroscopic electric dipole moment, and 2) space-charge electrets, which have a net, macroscopic electrostatic charge. We define an ionic electret as a space-charge electret that has a net electrostatic charge due to a difference in the number of cationic and anionic charges in the material. For example, we discuss later the characteristics of polystyrene beads that contain a number of covalently bound sulfonate ions and a smaller number of sodium counterions. Although the difference in the number of charges is small (ca. 0.5 % of the ions at the surface of the beads), the electric fields that arise from this imbalance of charge can be substantial: they can exceed 30 kV cm^{-1} , the typical threshold for the dielectric breakdown of air. These ionic electrets defy the conventional assumption in chemistry that bulk matter is electrically neutral and that ionic materials must have an equal number of cationic and anionic charges.

This review provides a brief survey of the chemistry of ions at interfaces, and explains how the transfer of mobile ions, facilitated by adsorbed water, can yield macroscopically charged ionic electrets. We discuss applications of ionic electrets in Xerography (electrophotography) and self-assembly. Finally, we propose—as a still-unproved hypothesis—that the well-known phenomenon of contact electrification (the transfer of charge from one material to another upon contact) may, in many circumstances, be due to the unequal partitioning of aqueous ions (particularly H^+ and OH^-) between interfaces.

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2. Background

2.1. Properties and Uses of Electrets

The two-volume series *Electrets*, edited by Sessler and Gerhard-Multhaupt, provides a comprehensive treatment of the fabrication, properties, and applications of electrets from the vantage of engineering and condensed-matter physics;^[1] we offer only a brief introduction. The two basic types of electrets—dipolar electrets and space-charge electrets—are fabricated by quite different techniques. Slow cooling of a dielectric material from above its glass-transition temperature in the presence of a strong electric field (typically several hundred kV per cm) yields dipolar electrets: as the material solidifies, individual molecular dipoles become “frozen” with a net orientation in the direction dictated by the applied field. Classical wax electrets, known since the 19th century, are examples of dipolar electrets. (Oliver Heaviside coined the term “electret” in 1885 to describe a material that is an electrostatic analogue of a permanent magnet.^[2]) Today, many dipolar electrets are made from poly(vinylidene difluoride) (PVDF). This material contains the CF_2 moiety, a group with a high electric dipole moment, and has a structure in which these polar groups orient cooperatively within crystalline domains.^[3]

Space-charge electrets result from adding charge to the surface or the bulk of a material by bombarding it with an electron beam or ion beam, spraying it with ions from the corona discharge of a high-voltage electrode, contacting it directly with a charged electrode, or transferring ions to (or from) the material by other means (some of which we discuss herein). Electronic or ionic charges in space-charge electrets

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may reside on the surface or at sites deeper in the bulk of the material. Most insulating materials, especially organic materials, that are space-charge electrets probably contain ionic charges, regardless of the process by which they are charged: injection of an electron into an insulating organic material will result in its attachment to a functional group with a high electron affinity (e.g. C=O, C–Cl, or aromatic groups), or to impurities such as O₂ or CO₂. These electron-injection processes may also break bonds in the material.

Cellular polymer ferroelectrets share properties of both space-charge and dipolar electrets.^[4] These materials result from the application of a strong electric field to a cellular foamed polymer. The electric field causes dielectric breakdown (corona discharge) inside each polymer cell; this dielectric breakdown deposits equal and opposite electrical charges on opposite interior surfaces of the cell. Each cell in a cellular ferroelectret has space charges on its walls, but the ferroelectret overall is electrically neutral and acts like a dipolar electret with a large dipole moment.

Many applications of electrets involve coating an object with an electrically charged powder. Electrophotography uses a pattern of charge, formed by the selective discharge of the photoconductive surface of an imaging drum, to arrange oppositely charged toner particles on that drum;^[5] both the drum and the toner particles are electrets. Electrostatic powder coating and electrostatic spray painting, by giving particles of polymer or paint a net charge, can coat large objects with a uniform layer of these materials.^[6] Sessler discusses other applications of electrets, including electrostatic filters, electret microphones, and radiation dosimeters (which monitor the radiation-induced discharge of an electret).^[1] Electrostatic charging can also be undesirable: electrical discharges can destroy sensitive electronic equipment,^[7] and discharges between surfaces charged by friction, or by the flow of liquids, can result in sparks and explosions if flammable liquids or vapors are present.^[8]

Electrets need not be solids: any liquid that has a net electrostatic charge may be considered a liquid electret. The charged droplets formed during electrospray ionization are examples of liquid electrets. Most electrospray mass spectrometers produce charged droplets by direct contact between a metal electrode and the liquid analyte;^[9] a strong electric field can also cause a drop of liquid to break apart into small charged droplets.^[10]

2.2. Contact Electrification (Tribocharging)

When two solid surfaces are brought into contact and separated (with or without intentional rubbing or frictional contact), charge often transfers from one surface to the other; this process is known as contact electrification or tribocharging.^[11,12] Reports of contact electrification date back to ancient Greece; our word “electricity” is derived from the Greek word *ἤλεκτρον*, meaning amber—a material that develops a negative charge when rubbed with animal fur. The “triboelectric series” (Figure 1a) is a list of materials

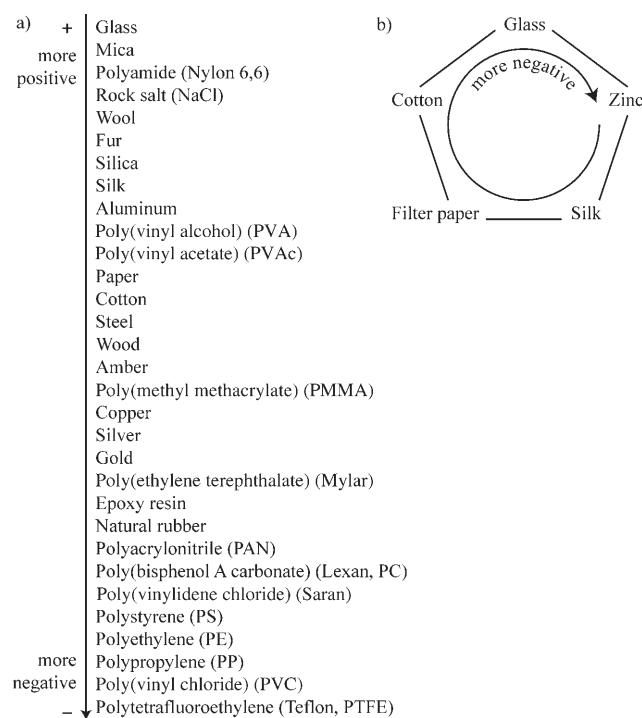


Figure 1. a) A triboelectric series that combines several different series from the literature. This series is excerpted from reference [13], which contains a more extensive list and highlights some of the inconsistencies between various series. For example, the positions of poly(methyl methacrylate), polystyrene, and poly(vinyl chloride) vary somewhat among different published series. b) An example of a set of five materials that form a cyclic triboelectric series (adapted from reference [11]).



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empirically ordered according to their tendency to acquire a positive or negative charge upon contact: the material closer to the top of the list will typically develop a positive charge, while the other material will develop a negative charge. Many triboelectric series have been published over the past 150 years, including many by amateur scientists and hobbyists; the series shown in Figure 1a is excerpted from a compilation by Diaz and Felix-Navarro of four published series.^[13] These published series generally agree with one another, despite inevitable differences in the composition of the materials, the preparation of the samples, and the environment of the laboratory. This list contains many curiosities, of which one of the most obvious is the tendency of materials that chemists commonly consider nonpolar (e.g. polyethylene or PTFE) to develop strong, negative charges upon tribocharging. “How,” one must ask, “is that possible?” A second, related feature of the list is the apparent correlation between polarity and charging, with polar materials becoming positive and nonpolar materials becoming negative.

If differences in a single physical property, such as the electron work function, were responsible for all instances of contact electrification, one could use the relative values of that property to arrange all materials into a single triboelectric series. There are some sets of materials, however, that form a *cyclic* triboelectric series (Figure 1b).^[11] The existence of such cyclic series suggests that a single physical property cannot explain all instances of contact electrification, and indicates that contact electrification probably involves more than one mechanism.

Most quantitative measurements of contact electrification have studied the contact between an insulating material and a metal probe. One must control the details of contact (e.g., area of contact, sliding, rolling, amount of normal force) to achieve reproducible results. We developed a simple tool that yields reproducible measurements of contact electrification between metals and polymers (Figure 2a).^[14] A rotating bar magnet causes a magnetic steel sphere to roll in a circular path on the surface of a polymer; contact between the sphere and the polymer results in contact electrification. The charged sphere passes periodically over a metal electrode connected to an electrometer, which measures the charge on the sphere by induction. This induced charge is recorded as a “spike” on the electrometer; Figure 2b shows that the device gives both the kinetics of contact electrification and the steady-state charge on the sphere.

We also recently developed a device that measures the contact electrification of microspheres made of nonconductive materials, such as polystyrene or glass (Figure 3a).^[15] The device consists of a polyethylene tube threaded through two concentric aluminum cylinders. One end of the tube is connected to house vacuum, which causes a steady flow of air (or other gas) through the tube. We charge a batch of microspheres by contact with various materials (metals, polymers, or glass) and use the flow of air to draw a single sphere through the polyethylene tube (contact between the sphere and the polyethylene tube can also lead to further contact electrification and complicate measurement and interpretation). As a charged sphere passes through the

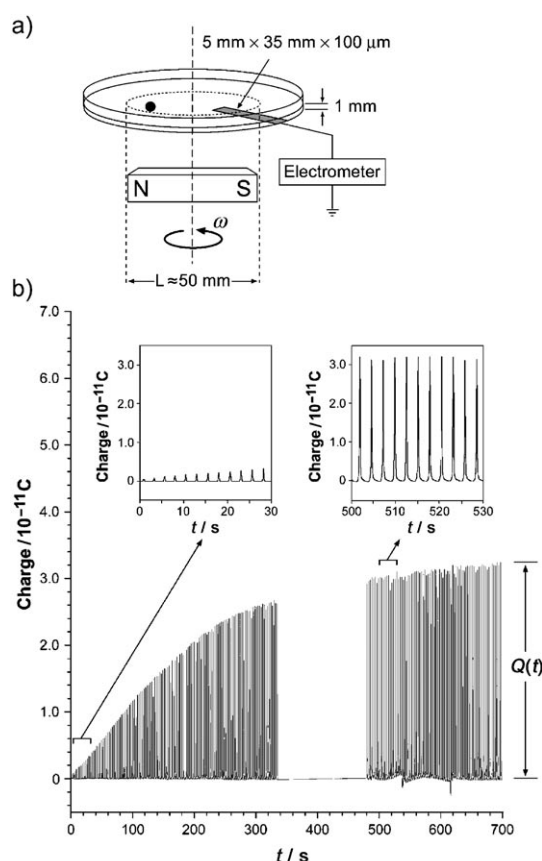


Figure 2. a) A schematic representation of a tool that measures the contact electrification between a rolling metal bead and a polymer. b) An example of the output from the electrometer from a single experiment. Each “spike” indicates the charge of the bead as it passes over the metal electrode. (The gap in the data between 340 and 480 s is due to consolidation and transfer of data by the electrometer because of limited storage capacity.) (From reference [14], reprinted by permission.)

device, its charge induces an opposite charge on the inner cylinder and an equal charge on the outer cylinder. An electrometer records the total flow of charge (the integrated current) between the two concentric cylinders. The passage of each bead yields a single peak on the electrometer, and the height of the peak is equal to the charge on the bead. Figure 3b shows the electrometer output resulting from the passage of 41 positively charged beads through the device. Each bead yielded a single peak, and the height of each peak is roughly the same for each bead. (One peak, marked with an asterisk, was unusually small, for reasons explained in the original reference.^[15] That reference also discusses the variation in the widths of the peaks, and the drift in the baseline.)

Using the understanding of contact electrification gained by measurements of the sort sketched in Figure 2, we designed systems in which contact electrification guided the self-assembly of millimeter-sized spheres into ordered structures. Polymer spheres, charged by contact electrification against a gold substrate (Figure 4a), self-assembled into two-dimensional Coulombic crystals (Figure 4b);^[16] astonishingly, some of these crystals exhibited an overall net electrostatic

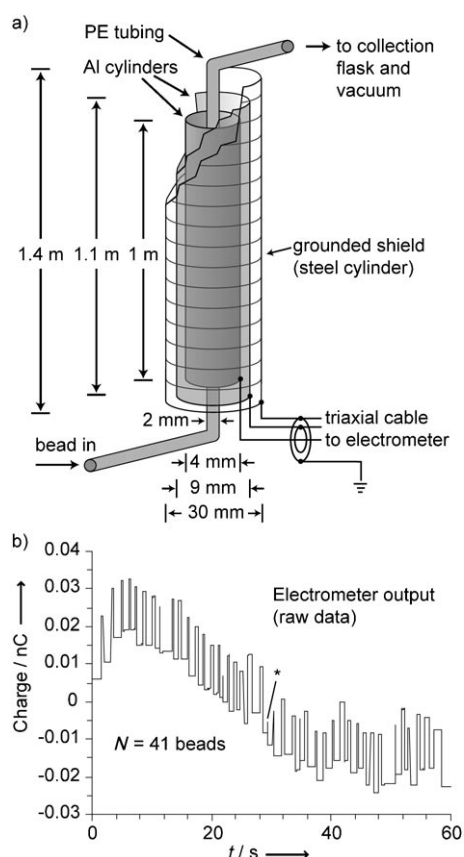


Figure 3. a) Apparatus used for measuring the charge on individual microspheres. b) The electrometer output from the measurement of 41 positively charged 200- μm -diameter beads. The peak indicated with an asterisk (*) was excluded from the data to be analyzed for reasons explained in the text. (From reference [15], reprinted by permission.)

charge (Figure 4c). The interplay between magnetic and electrostatic forces on steel spheres charged by contact with a polystyrene surface resulted in the dynamic self-assembly of ordered rings of spheres (Figure 4d,e).^[17] These self-assembled structures result from the rotating (dynamic) magnetic force on the beads, the electrostatic attraction of the beads for an oppositely charged “track” on the polystyrene surface, and the electrostatic repulsion between the like-charged beads.

2.3. Mechanisms of Contact Electrification: Electron Transfer versus Ion Transfer

Despite the technological significance of contact electrification, there is little consensus on how charge transfers from one material to another upon contact. The elementary charge-transfer step could involve the transfer of either an electron or an ion (Figure 5); the transfer of bulk material is also possible, but is relevant only to the extent that it transfers charge. Contact electrification between different metals almost certainly involves the transfer of electrons from one metal to another (reflecting the different electron work functions of the metals).^[11,18] The observed correlation between work function and contact electrification for metal–metal contact supports this mechanism.^[11]

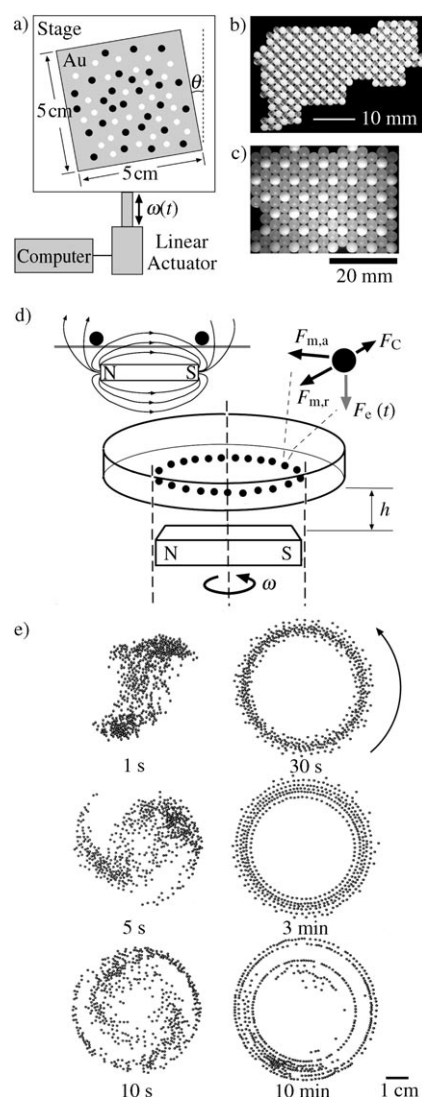


Figure 4. a) Apparatus used for electrostatic self-assembly of two-dimensional Coulomb lattices by contact electrification. b) An example of a self-assembled lattice formed by contact electrification of positively charged PMMA spheres (transparent) and negatively charged PTFE spheres (white) in a 1:1 ratio. c) An example of a self-assembled lattice formed by contact electrification of positively charged nylon spheres (gray) and negatively charged PTFE spheres (white) in a 2:1 ratio. Since the magnitude of charge on each sphere in this lattice is roughly the same, the entire lattice has a net positive charge. (From reference [16], reprinted by permission.) d) A schematic of the apparatus used for dynamic self-assembly of metal spheres on a polystyrene surface. The forces on a single sphere are: the angular magnetic force ($F_{m,a}$), the radial magnetic force ($F_{m,r}$), the centrifugal force (F_c), and the time-dependent electrostatic attraction ($F_e(t)$) between the sphere and the charged “track” formed by contact electrification with the polystyrene. e) A time-series of images showing the dynamic self-assembly of stainless steel beads charged by contact electrification. (From reference [17], reprinted by permission.)

Most researchers have assumed that the contact electrification of insulators also involves the transfer of electrons,^[18,19] but experimental observations appear to contradict this view. The contact electrification of insulators does not correlate with bulk electronic properties, such as the dielectric

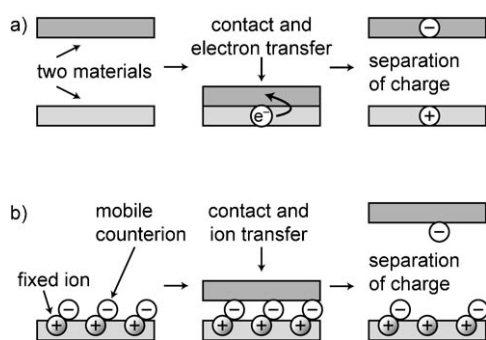


Figure 5. Possible mechanisms of charge transfer. a) Transfer of an electron. b) Transfer of an ion.

constant, or atomic properties, such as ionization energy, electron affinity, or electronegativity.^[14] Theoretical considerations also argue against a mechanism involving electron transfer.^[20] Consider, for example, contact electrification between nylon and polyethylene: according to the triboelectric series, nylon will acquire a positive charge, while polyethylene will acquire a negative charge. Electron transfer between these materials would require removal of an electron from nylon (costing several eV), separation of charge across the interface (a cost of < 1 eV, depending on the distance), and addition of an electron to polyethylene. The final step, for these materials, also costs energy: adding an electron to an alkane (or to solid polyethylene) is an endothermic process, as shown by both experimental and theoretical results.^[21] (Presumably, electron transfer to polyethylene might involve, in practice, a polar site, such as an adventitious Na^+ ion, a carbonyl group, or a hydroperoxide group.) The overall process of electron transfer would be endothermic by about 5–10 eV; this value is much larger than the thermal energy ($kT \approx 0.026$ eV at room temperature). In general, transfer of an electron from a filled orbital (or valence band) of one insulating material to an unfilled orbital (or conduction band) of another insulating material will be endothermic by an amount roughly equal to the typical HOMO–LUMO gap (or band gap) for these materials—on the order of several eV. The electron-transfer model is energetically plausible only for materials with no band gap (metals) or small band gaps (semiconductors).

Electron transfer between neutral organic molecules usually occurs only for molecules with well-matched donor and acceptor orbitals. Although there are many important examples of organic charge-transfer complexes, these complexes all involve donors with electron-rich functional groups (e.g. perylenes, tetrathiofulvalenes) and acceptors with electron-poor functional groups (e.g. tetracyanoethylenes, quinones).^[22] The functional groups in most organic polymers, by contrast, do not exhibit exceptional ability to donate or accept electrons. Just as one would not expect electron transfer between ϵ -caprolactam and hexane, one should not expect electron transfer between nylon and polyethylene. Furthermore, doping organic polymers with electron-rich molecules (perylenes) does not affect the contact electrification of these polymers.^[20]

Although contact electrification of insulators does not correlate with bulk electronic properties, several researchers have noticed that it does correlate with the acidity or basicity of insulating materials. In 1902, Knoblauch observed that solid organic acids tended to become negatively charged and solid organic bases tended to become positively charged when these powders were shaken from a piece of filter paper;^[23] he proposed a proton-transfer mechanism for contact electrification. Medley made similar observations with acidic and basic ion-exchange resins in 1953,^[24] and Diaz proposed that a proton-transfer mechanism could explain the contact electrification of a wide range of insulating materials.^[13] Proton-transfer is, of course, a specific example of the more-general mechanism of ion transfer. In general, the propensity for proton transfer or ion transfer does not correlate with the propensity for electron transfer: it is not the case that all acids are oxidants or that all bases are reductants. Thus, these observations that the acidic or basic properties of materials correlate with their contact electrification are difficult to reconcile with a mechanism that involves electron transfer.

Two independent groups of researchers have observed a correlation between the Lewis acidity and/or basicity of an insulating surface and its behavior upon contact electrification, but have interpreted this correlation as evidence for an electron-transfer mechanism.^[25–27] Both groups observed that solid surfaces with significant Lewis basicity (as determined from contact-angle measurements or inverse gas chromatography) tended to become positively charged upon contact electrification, whereas surfaces with significant Lewis acidity tended to become negatively charged. According to these researchers, since Lewis bases are “electron donors” and Lewis acids are “electron acceptors,” this correlation supports a mechanism in which electrons transfer from a Lewis basic site on one material to a Lewis acidic site on the other. It appears, however, that they have confused the Lewis acid–base concept, in which an electron pair from a Lewis base is shared with a Lewis acid, with the concept of electron transfer (or oxidation–reduction), in which an electron is transferred from an electron donor (reductant) to an electron acceptor (oxidant). These concepts are quite distinct: Lewis bases, for example, are not necessarily good electron donors. Water is a strong Lewis base but a poor reductant; the Cr^{2+} ion is a powerful reductant but is not a Lewis base (it is, instead, a Lewis acid). As Diaz observed, the oxidation–reduction (electron transfer) properties of various organic dopants do not correlate with the contact electrification of materials containing these dopants.^[20] Indeed, the observed correlation between Lewis acid/base behavior and contact electrification suggests a mechanism in which various ions (protons, hydroxide ions, alkali metal cations, halide anions, etc.) transfer from Lewis acid/base sites on one surface to Lewis acid/base sites on another surface. For example, the metal oxides investigated by Veregin and co-workers certainly have protons, hydroxide ions, and metal cations at their surface.

In his monograph on contact electrification, Harper considers the evidence for the electron-transfer mechanism, and concludes: “I am of the opinion that a definite answer can now be given which is that the carriers [of charge] are *never* electrons—when the material being charged is strictly an

insulator.”^[11] His arguments against the electron-transfer mechanism are persuasive, although his mechanistic rationalization of the alternative (the ion-transfer mechanism) is less so. In particular, he never explains convincingly the origin of mobile ions (which would be required for a mechanism involving ion transfer) on the surface of nonionic insulating polymers. Although glass, for example, has mobile protons and alkali metal cations on its surface, the source of ions on the surface of an organic polymer such as polyethylene is not obvious. Harper suggests that ions could be adsorbed from the environment, but the consistency between the triboelectric series determined by different experimenters under various conditions suggests that these postulated ions cannot arise merely from random contamination of the surface of a polymer (unless the contaminant is one that is ubiquitous, such as H₂O, CO₂, or O₂; we return to this point later).^[13] Harper's 1967 book (reprinted in 1998) did not persuade other researchers that the contact electrification of insulators involves the transfer of ions and not electrons: the influential 1980 review article by Lowell and Rose-Innes reached the opposite conclusion,^[18] despite extensive citation of Harper's work. Forty years after the publication of Harper's monograph, the question of ion versus electron transfer for nonionic insulating materials remains unanswered. We will consider the more straightforward case of ion-containing materials first, and return to the question of contact electrification of nonionic insulating materials towards the end of this review.

3. The Contact Electrification of Materials Containing Mobile Ions

3.1. Experimental Evidence for the Transfer of Mobile Ions upon Contact

The electrophotographic process generally uses two different techniques for creating charged materials: 1) a plasma or corona discharge typically charges the photoconductive imaging drum, and 2) contact electrification charges the imaging powder (toner): the toner is mixed with carrier beads or rolled between a cylindrical roller and a blade.^[5] Toners are typically made by melt-blending polymers with pigments and other additives. The search for toners that would charge reliably led to the empirical discovery of numerous “charge-control agents” that could be added to the toner.^[28] Certain additives caused the toner to acquire a negative charge, whereas others caused it to acquire a positive charge upon contact electrification. Interestingly, typical electron donors or acceptors such as electron-rich aromatic compounds or electron-poor quinones are not effective charge-control agents; this observation suggests that the contact electrification of toners is not due to electron transfer. Many successful charge-control agents are ionic organic dyes. A glance at a list of these charge-control agents reveals an obvious correlation pointed out by Diaz:^[20] dyes that contain a large organic cation and a small inorganic anion (e.g. crystal violet) yield a positively charged toner, whereas dyes that contain a large organic anion and a small inorganic cation

(e.g. sulfonated azo dyes) yield a negatively charged toner. Nonionic organic dyes, such as perylenes, do not affect the contact electrification of toners. A comparison of the oxidation potential of these dyes with their effect on contact electrification shows no correlation; this observation again suggests that electron transfer is not involved. The simplest explanation for these observations is that the toners are charged by ion transfer: small counterions from the organic dyes transfer preferentially from the toner upon contact in a process similar to that shown in Figure 5b. Although the large organic ions are not covalently bound to the toner, they appear to be less likely to transfer upon contact; Diaz suggested that the large organic ions may be less mobile than the small counterions.^[20]

Several experimental studies support this ion-transfer mechanism. Mizes et al. studied the contact electrification of polystyrene doped with deuterium-labeled cetylpyridinium bromide.^[29] The doped polymer acquired a positive charge upon contact with indium, in accord with the hypothesis that bromide transfers more readily than the large cetylpyridinium ion. Secondary-ion mass spectrometry (SIMS) showed approximately 20 bromide ions for every cetylpyridinium ion on the indium surface, after correction for surface contamination and artifacts of ionization. Although oxidation of the indium surface complicates the interpretation of these results, the greater transfer of bromide is consistent with the observed charge. Law et al. studied the contact electrification of poly(styrene-*co*-butadiene) doped with cesium 3,5-di-*tert*-butylsalicylate;^[30] this polymer acquired a negative charge, as expected for an ion-transfer mechanism, upon contact with metal carrier beads coated with a mixture of PVDF and PMMA. Both X-ray photoelectron spectroscopy (XPS) and SIMS showed the cesium cation but not the organic anion on the carrier beads following contact. Law et al. also found a linear relationship between the amount of charge transfer and the amount of cesium on the carrier beads.

The best evidence for the transfer of mobile ions upon contact comes from the study of polymers that contain covalently bound ions and mobile counterions. With these polymers, one need not postulate a difference in ionic mobility between cations and anions, since one type of ion is covalently anchored to the polymer and must be immobile. Figure 5b shows the proposed mechanism of contact electrification for these materials: the cations in this illustration are bound covalently to the polymer, whereas the anions are mobile and transfer to another surface upon contact. Medley was the first to observe a correlation between the sign of the covalently bound ion and the charge acquired through contact electrification in his study of the contact electrification of ion-exchange resins.^[24] Diaz and co-workers made detailed studies of the contact electrification of ion-containing polymers.^[31] The sign of charge that these materials acquired through contact electrification was always the same as the sign of the covalently bound ion. They found that increasing the concentration of ions in the polymer led to increased charging, and they used XPS to demonstrate transfer of the mobile ion but not the covalently bound ion.^[32] Although, as we shall discuss, the dielectric breakdown of air (or other surrounding gas) imposes an ultimate limit on the amount of

charge that can accumulate on an electret, the charges observed by Diaz were below that limit.

We recently showed that the predictions of the ion-transfer model hold for materials with various covalently bound ions and mobile counterions, that the amount of charge on these materials is directly proportional to their surface area, and that the patterning of ionic functional groups on a surface leads to a pattern of electrostatic charge.^[15] Figure 6 shows the charges acquired by functionalized polystyrene or glass microspheres upon contact with an aluminum surface. (We measured the charges on these spheres using the tool shown in Figure 3 a.)

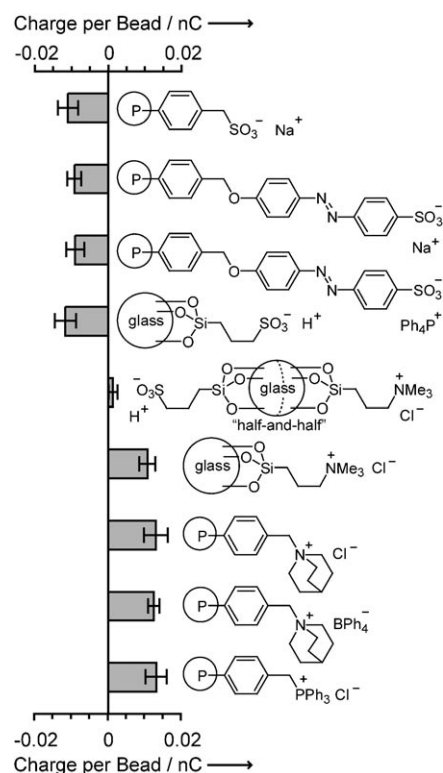


Figure 6. Charges observed on 200- μ m-diameter functionalized polystyrene or glass microspheres after contact electrification with aluminum. In every case, the bead had the same charge as the covalently bound ion. The “half-and-half” glass microspheres had one hemisphere functionalized with bound cations and the other hemisphere functionalized with bound anions; these beads exhibited nearly zero net charge. Values of contact electrification are from reference [15]. As discussed in that reference, the magnitude of the total charge (ca. 0.010–0.015 nC per bead) is probably set by the dielectric breakdown of air; beads with charges above that level will spontaneously discharge to some adventitious ground.

3.2. The Ion-Transfer Mechanism of Contact Electrification

Figure 7a (adapted from Harper)^[11] shows a schematic representation of the mechanism of ion-transfer. We assume that the potential energy of a mobile anion (or cation) between two surfaces at different electrical potentials is given by the sum of three terms: two short-range interactions (one for each surface, with potential-energy curves shaped like a

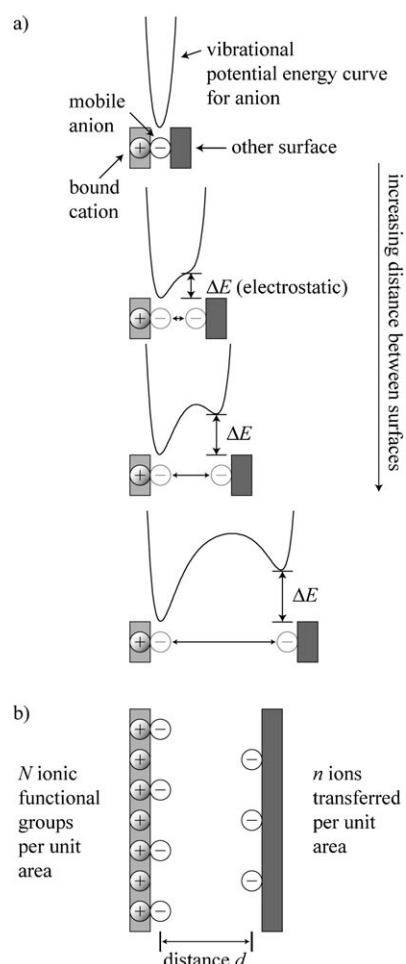


Figure 7. a) A schematic representation of the mechanism of ion transfer (adapted from reference [11]). b) The model used to estimate the amount of charge separation that can arise from the transfer of ions.

Lennard–Jones potential or Morse potential) plus a long-range Coulombic interaction. In the hypothetical geometry in which the two surfaces are in van der Waals contact, an ion between the surfaces experiences a single potential well. As the two materials separate, the potential-energy surface evolves into an asymmetric double-well potential. The energy of the mobile ion is generally lower when it is close to its covalently bound counterion because of the favorable Coulombic interaction in that location.

Consider the behavior of a single anion during the separation of the two materials. When the two surfaces are in contact, the ion will move within its single potential well. When the surfaces are a small distance apart, and the double-well potential has a sufficiently small barrier, the ion can move freely between the two surfaces. (The ion must surmount this barrier by thermal activation, as tunneling is highly unlikely for any ion more massive than H^+ .) At this intermediate distance, if the ion is in thermal equilibrium between the two surfaces, the Boltzmann distribution gives the relative probability of finding the ion on each surface. (In the figure, we ascribe the energy difference ΔE to the electrostatic interaction alone; in reality, local interactions

between the ion and the proximal interface will also contribute.) At some distance, the potential barrier becomes sufficiently high that it traps the ion kinetically on one surface or the other. The charge distribution at this instant is typically preserved as the two surfaces are separated further, although several processes, which we will discuss later, can cause partial discharge of one or both surfaces. Note that the final charge distribution attained through contact electrification is not an equilibrium distribution of charge. As two charged surfaces are separated to a large distance, the electrostatic energy ΔE becomes orders of magnitude larger than the thermal energy kT ; if the ions could move freely between the two surfaces, virtually all of them would reside at equilibrium on the surface with their bound counterions, and no separation of charge would result. The energy required to separate the surfaces, and increase the electrostatic potential between them, is supplied by the mechanical work used to separate the surfaces: one must not forget that contact electrification involves both contact and macroscopic separation of two materials. (Contact between the two materials need not be conformal, as long as their surfaces are close enough to allow charge to transfer between them.)

We can estimate the magnitude of charge transfer (charge per unit area) that could arise from this ion-transfer mechanism with a simple calculation. Consider a planar surface containing N ionic functional groups per unit area separated by a distance d from an unfunctionalized planar surface (Figure 7b). If n of the mobile anions are transferred per unit area from the left surface to the right surface, the charge densities on the surfaces are $+ne$ and $-ne$, respectively, where e is the magnitude of charge on a single ion. Under these conditions, the electrostatic work required to transfer an anion from the left surface to the right surface is nde^2/ϵ_0 (this expression assumes a uniform distribution of charge on each surface; ϵ_0 is the permittivity of the vacuum, which is close to that of air). At equilibrium, the ratio between the number of anions per unit area on the two surfaces is given by the Boltzmann distribution [Eq. (1)].

$$\frac{n}{N-n} = \exp\left(-\frac{nde^2}{\epsilon_0 kT}\right) \quad (1)$$

Given some reasonable assumptions about the number of ionic functional groups per unit area (N) and the distance at which ion-transfer becomes kinetically prohibited (d), we can solve this equation numerically for n , the number of ions that will be transferred at equilibrium, and hence predict the approximate charge density that can be attained by this mechanism. This equilibrium distribution represents a balance between two opposing tendencies: electrostatics, which tends to keep all anions close to their cations (which we assume to be immobilized on one surface), and entropy, which tends to equalize the concentration of anions on the two surfaces. For a rough estimate, we consider a temperature of 298 K and take N to be equal to one univalent ionic functional group per 10 nm^2 of surface. This calculation is not particularly sensitive to the distance d at which the ions become kinetically trapped and can no longer move freely between the surfaces; we estimate that d is on the order of 2 nm, but

any choice between 1 and 5 nm yields similar results. Using these parameters, we calculate that approximately 3 % of the ions will reside on the unfunctionalized surface at equilibrium. The resulting charge density (ca. 3000 elementary charges per square micrometer) is greater than the typical charge densities observed in contact electrification (ca. 300 elementary charges per square micrometer, according to Harper;^[11] we observe ca. 500 charges per square micron^[15]). Thus, a simple model of entropically driven separation of charge can account for the typical magnitude of charging observed in contact electrification. As we will discuss later, the dielectric breakdown of air or the surrounding medium ultimately limits the final stable charge density of these materials. Although these simple calculations suggest that the magnitude of charging would be less at low temperatures, we have found no studies of contact electrification of ion-containing materials at low temperatures. Such studies could help to confirm the ion-transfer mechanism, since changes in temperature would not affect the tunneling of electrons that is proposed in the electron-transfer mechanism^[18,19] (although electron-transfer could also be thermally activated).

3.3. Limitations on the Charge Density of Ionic Electrets

Whereas the ion-transfer mechanism leads to charge separation, other competing processes lead to charge recombination, or electrical discharge, of ionic electrets. These processes include tunneling of electrons, field emission of electrons, and dielectric breakdown of the surrounding gas.^[1,11] The final charge on an ionic electret following contact and macroscopic separation depends on both charging and discharging processes. These discharging processes can discharge any charged object; they are not specific to ionic electrets. They usually involve electron transfer—even for the discharge of an ionic electret—and although there is little specific information on the processes of electron generation, tunneling or plasma formation, and electron capture, we can sketch the general character of these processes.

Consider the process of separating two flat, parallel surfaces, one bearing a positive charge and the other bearing an equal and opposite negative charge. (Recall that an external agent must supply the work to separate these surfaces.) In the absence of any processes of charge relaxation, the charge density on these surfaces will remain constant: there will be a constant electric field E , proportional to the charge density, in the gap between the surfaces. This constant electric field will be $E = \Delta V/\Delta x$, where ΔV is the electrostatic potential difference and Δx is the distance between the surfaces; since the electric field is constant, $\Delta V/\Delta x$ must remain constant. Thus, as the separation Δx increases, the electrical potential difference ΔV will increase proportionally.

Figure 8a shows a schematic illustration of electrons tunneling through an idealized potential barrier between the two surfaces, in the case of electric fields less than approximately 10^4 kV cm^{-1} . Although a classical particle could not penetrate this barrier, quantum-mechanical tunneling allows an electron to traverse the barrier when the

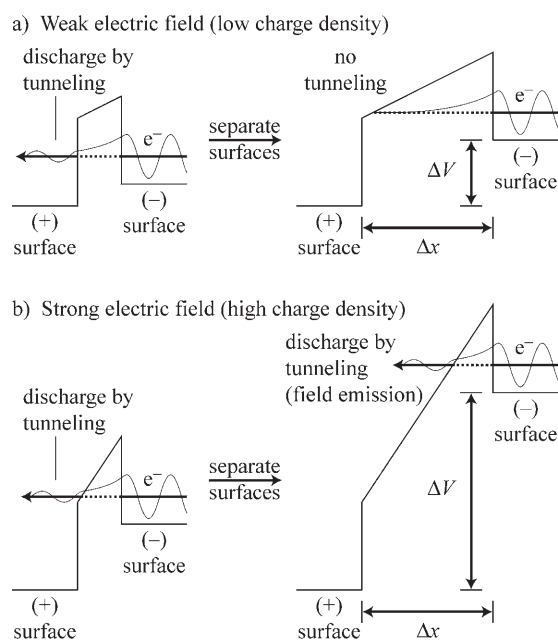


Figure 8. a) Tunneling of electrons between two oppositely charged surfaces in the case of a relatively weak electric field (less than ca. 10^4 kVcm $^{-1}$). Once the surfaces are separated beyond a few nanometers, tunneling becomes highly improbable. b) Tunneling of electrons between two oppositely charged surfaces in the case of a strong electric field (greater than ca. 10^4 kVcm $^{-1}$). The strong field (large potential gradient) allows electrons to escape from the negatively charged surface by field emission, even if the distance between the surfaces is large.

surfaces are close together (Δx is less than a few nanometers). Once the separation exceeds this value, however, tunneling becomes vanishingly improbable. For a typical electron binding energy of around 5 eV, the probability that an individual electron will tunnel across a 2-nm gap is approximately 1 in 10^{20} .^[11] This tunneling probability corresponds to an electrical resistance of around 10^{24} Ω , so the tunneling current will be essentially zero, despite the electrical bias across the gap. Thus, discharge by electron tunneling and charge separation by ion transfer probably occur simultaneously when the surfaces are in close proximity, but cease when the surfaces are separated by more than a few nanometers.

When the electric field is sufficiently large (greater than around 10^4 kVcm $^{-1}$), electrons can escape from the negatively charged surface into vacuum regardless of the distance between the surfaces; this process is known as field emission. As shown in Figure 8b, a large electric field corresponds to a steeply sloped potential gradient ($\Delta V/\Delta x$). Assuming an electron binding energy of around 5 eV, an electric field of 5×10^9 Vm $^{-1}$ (5×10^4 kVcm $^{-1}$) would yield a barrier with a width of only approximately 1 nm, through which an electron could tunnel readily. An electric field of this magnitude would be created by a surface charge density of roughly one elementary charge per 4 nm 2 . Although the specific ion-transfer mechanism discussed above is not likely to yield such high charge densities, it is possible that other mechanisms, such as crystal fracture, could do so: consider, as an extreme

example, the cleavage of a crystal of NaCl between the planes of Na $^+$ and Cl $^-$ ions. The separation of charge upon crystal fracture, followed by electrical discharge, can cause triboluminescence;^[33] a well-known example is the light emitted upon crushing wintergreen-flavored LifeSavers candy.^[34] In this case, the methyl salicylate (wintergreen flavor) enhances the natural pale-blue fluorescence of ionized molecules of nitrogen gas. The molecular details of triboluminescence are not known, but the energy released upon fracture is sufficient to initiate gas-phase reactions.^[35]

Under most conditions, the dielectric breakdown of the surrounding gas determines the ultimate limit on the stable surface charge density of an electret. Dielectric breakdown begins when an electric field accelerates an adventitious gaseous electron or ion, and that charged species collides with a neutral gas molecule with energy sufficient to ionize that molecule. A rapid cascade of collisions and ionizations creates enough charged species to yield a conductive path through the gas.^[36] Although charged gaseous species are rare (cosmic rays produce about 2 ion pairs per cm 3 s $^{-1}$ in the ambient atmosphere),^[11] an ion created in the vicinity of a charged object can be drawn to that object by the electric field. The threshold for dielectric breakdown of air in a uniform electric field is approximately 30 kVcm $^{-1}$; such a field would be generated by a uniform planar surface charge density of approximately 300 elementary charges per square micrometer, the typical limit for charging of a planar surface. For comparison, this density of surface charge corresponds to one elementary charge per 10^4 functional groups having the projected area of a methyl group on the surface. According to Harper, the threshold for dielectric breakdown increases if the strong electric field is confined to a small region in space, as in the case of a small charged sphere.^[11] Note that the strength of the electric field, not the amount of charge, determines whether dielectric breakdown occurs. For a uniformly charged sphere, the electric field at the surface is proportional to the total charge enclosed, according to Gauss's Law, so the dielectric constant of an isolated, uniformly charged sphere will not affect the threshold for dielectric breakdown. For nonuniform charge distributions, or in other geometries, the dielectric constant of the substrate may have a significant effect. Consider, for example, a localized region of charge on a planar dielectric substrate. The electric field near this region of charge will be reduced if the substrate has a high dielectric constant, because induced dipoles in the dielectric substrate will partially cancel the electric field of the surface charge. Thus, a substrate with a high dielectric constant can generally support a greater density of surface charge than a substrate with a low dielectric constant.

We recently studied the contact electrification of polymer microspheres functionalized with bound ions and mobile counterions, and found that Harper's estimate of the dielectric breakdown of air accurately described the limiting charge those spheres acquired.^[15] Figure 9 shows a graph of the charges we observed on functionalized polystyrene microspheres of various diameters; the dashed line shows the limiting charge calculated by Harper. We also observed directly the electrical discharge of single spheres. Micro-

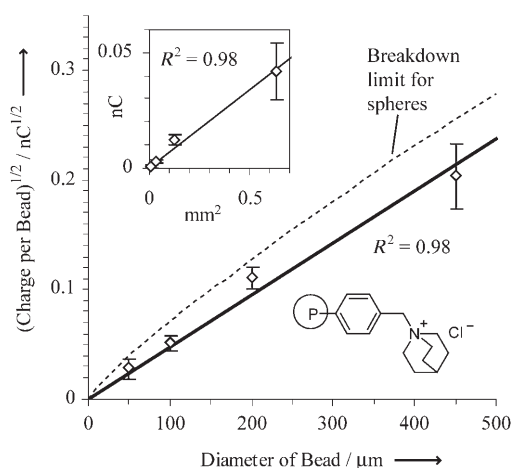


Figure 9. The relationship between the size and the amount of electrostatic charge on single microspheres. The inset shows the linear correlation between the charge on a single microsphere and the surface area of the bead; the main graph shows the linear correlation between the square root of the bead charge and the diameter of the bead. (All beads had covalently bound tetraalkylammonium cations, as shown, and were charged by contact with aluminum having a native surface film of aluminum oxide.) The dashed line indicates the predicted limit imposed by the dielectric breakdown of dry air. (From reference [15], reprinted by permission.)

spheres had less charge (relative to their charge in air) when they were charged in a gas with a low threshold for dielectric breakdown (Ar), and more charge when they were charged in a gas with a high threshold for dielectric breakdown (SF_6).^[36] These observations support our hypothesis that contact electrification of these ionic electrets yields initial charge densities above the limit for dielectric breakdown, and that subsequent breakdown reduces their charge to an amount below that limit.^[15]

Matsuyama and Yamamoto found that dielectric breakdown also limits the magnitude of charge attained by contact electrification of nonionic insulating materials against a metal surface.^[37,38] In those experiments, induced charges in the metal contributed to the strength of the electric field between the charged particle and the metal surface. The authors found reasonable agreement between the observed charges and the limiting charges predicted by a model that contained no adjustable parameters.

It is well-known that humidity plays a role in the discharge of electrets; the hazards of “static electricity” are generally reduced when the atmospheric humidity is very high. The presence of water vapor in the atmosphere actually *increases* the threshold for dielectric breakdown of air: the dielectric strength of air at room temperature is about 2% greater at 95% relative humidity (RH) than at 40% RH.^[36] The surface conductivity of insulating materials increases greatly with increased humidity, however, as conductive layers of water form on solid surfaces.^[11] Under humid conditions, charge on an electret can flow along the surface and discharge to another material and ultimately to ground.

Horn, Smith, and Grabbe observed dielectric breakdown between two charged insulating surfaces as they were separated following contact electrification.^[39] They contacted

a bare silica surface with a silica surface functionalized with an amine-terminated silane. Contact electrification between these surfaces yielded a negative charge on the bare silica and a positive charge on the amine-coated surface, presumably as a result of proton transfer. They separated the surfaces while measuring the electrostatic force between the surfaces by using a surface-force apparatus. They observed several abrupt, discontinuous decreases in the electrostatic force at distances between 1 and 3 μm ; they attributed these decreases to electrostatic discharges that partially neutralized the charged surfaces. (The final surface charge densities reported in that paper are probably incorrect: they are about two orders of magnitude higher than would be expected on the basis of dielectric breakdown. The authors did not account for the lateral spreading of charge on the surfaces following contact electrification,^[11] so the initial area of contact—0.01 mm^2 —was probably much smaller than the final area over which the charge was spread.)

3.4. Applications of Ionic Electrets

We consider an ionic electret to be any material with a net electrostatic charge that results from an imbalance between the number of cationic and anionic charges in the material. According to the ion-transfer mechanism, contact electrification of materials that contain mobile ions and bound counterions will generate ionic electrets. Although other methods of charging, such as corona discharge or bombardment with an electron beam, probably ultimately yield ionic charges by capture of electrons on atoms or functional groups,^[1] we limit our definition to those materials that explicitly contain mobile ions and are charged by contact electrification. Examples of ionic electrets include polymers with covalently bound ions and mobile counterions, polymers doped with organic salts (charge-control agents), and inorganic materials such as glass that have mobile ions at their surface. The ion-transfer model explains the sign of charge that these materials acquire upon contact electrification. This method of charging is predictable and reproducible: it offers a simple, inexpensive alternative to other methods of charging electrets. Since the stable charge on an electret is ultimately limited by the dielectric breakdown of air, the charge densities achieved by physical transfer of ions from one interface to another (several hundred elementary charges per square micrometer) are comparable to those achieved by other methods of charging.^[1] The electrophotographic industry depends on the reliable contact electrification of toner particles, which are typically ionic electrets.^[20] Although some methods for electrostatic powder coating and electrostatic spray painting involve contact electrification, the use of ionic charge-control agents in these applications is presently limited.^[40] Typically, a metal grid maintained at a high electrostatic potential charges the powder or paint particles through a combination of direct electron transfer and corona charging (presumably followed by electron capture in the paint or polymeric medium).^[6]

We recently began to explore some other possible uses for ionic electrets: one plausible application is in systems that self-assemble. We synthesized polystyrene microspheres that

contained mobile ions and covalently bound cations (see Figure 6). These materials developed positive or negative charges as predicted by the ion-transfer mechanism. Contact electrification of these microspheres with diameters of 5–50 μm guided the electrostatic self-assembly of these charged spheres onto larger, oppositely charged spheres in greater than 99.9% yield. These microstructures formed as a result of the electrostatic attraction between oppositely charged spheres; repulsion of like-charged spheres prevented adhesion (Figure 10).^[41] We also used the ion-transfer model of contact electrification to design materials that exhibited a micrometer-scale pattern of charge; these patterns of charge can direct the electrostatic self-assembly of charged micro-

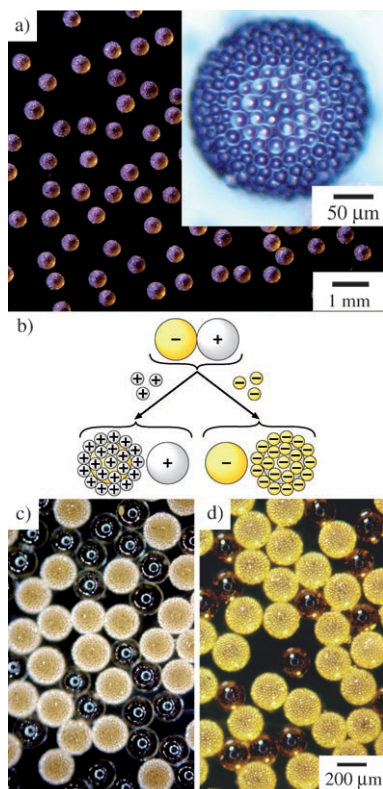


Figure 10. Self-assembly of polystyrene microspheres that contain covalently bound ions and mobile counterions (see Figure 6). a) Optical micrographs of the structures resulting from a combination of 200- μm -diameter negatively charged yellow spheres with 20- μm -diameter positively charged colorless spheres. b) A schematic representation of the electrostatic self-assembly of functionalized polystyrene microspheres charged by contact electrification. This experiment demonstrates both the attraction between oppositely charged spheres and the repulsion between like-charged spheres. c) An optical micrograph of the assemblies resulting from a mixture of 200- μm -diameter positively charged colorless spheres, 200- μm -diameter negatively charged yellow spheres, and 20- μm -diameter positively charged colorless spheres. Note that the yellow spheres are completely covered with a monolayer of small spheres, whereas the colorless spheres remain uncovered. d) An optical micrograph (on the same scale) of the assemblies resulting from a mixture of 200- μm -diameter positively charged colorless spheres, 200- μm -diameter negatively charged yellow spheres, and 20- μm -diameter negatively charged yellow spheres. Note that the large yellow spheres remain completely uncovered, whereas the colorless spheres are covered with a monolayer of small yellow spheres. (From reference [41], reprinted by permission.)

particles (Figure 11).^[15] The contact electrification of glass microspheres that had one hemisphere functionalized with mobile cations and the other functionalized with mobile anions yielded spheres with almost no net charge (the “half-and-half” spheres illustrated in Figure 6).^[15] This approach could yield materials that develop no net charge upon contact electrification.

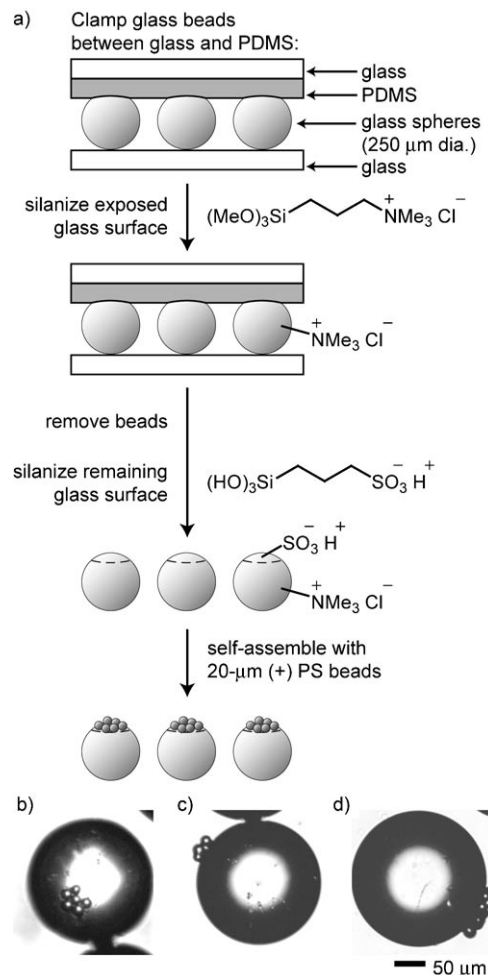


Figure 11. a) Procedure for patterning ionically functionalized silanes on the surface of 250- μm -diameter glass beads. The PDMS blocks the tetraalkylammonium-containing silane from reacting with a region around the “north pole” of each bead. The resulting pattern of covalently bound ions generates a pattern of charge that directs the self-assembly of positively charged 20- μm microspheres. b–d) Optical micrographs (all on the same scale) of three different self-assembled structures. The selective adhesion of the small positively charged beads to a small region on each large bead shows that the negative charge on the surface of each large bead is confined to that region. (From reference [15], reprinted by permission.)

4. The Role of Water in Contact Electrification

Many recent studies of contact electrification used clean, well-characterized surfaces in vacuum or in an inert atmosphere such as nitrogen.^[11,18] As Harper so gracefully explained in the preface to his monograph, however, “it must not be forgotten that the technologist may be more

interested, in the field of static charging, with the behavior of dog food, for example, than with that of super-pure germanium.”^[11] Atmospheric moisture deposits a thin film of water on nearly all surfaces. Even hydrophobic surfaces such as fluorocarbons adsorb water from the air, as shown by gravimetric measurements on PTFE (around 2 monolayers of water are claimed to adsorb at 80% RH)^[42] and infrared absorbance measurements on poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) (ca. 1.5 monolayers of water at 80% RH).^[43] Although the water on these hydrophobic substrates is probably localized in islands and does not form a continuous film, the presence of water does affect surface conductivity,^[42] and is likely to affect contact electrification under ambient conditions.

4.1. Ions at the Solid/Water Interface: The Electrical Double Layer

Electrostatic interactions in water are quite unlike electrostatic interactions in air or in vacuum. Water has three important electrical properties: First, it has a high bulk dielectric constant ($\epsilon = 78$ at 298 K), which reduces the strength of all electrostatic interactions by that factor. (The dielectric constant of water at an interface may be substantially lower, however.)^[44] Second, aqueous solutions contain mobile ions (H^+ , OH^- , and other electrolyte ions) that additionally screen electrostatic charges. Third, the dielectric constant of water is strongly dependent on temperature; this temperature dependence reflects the importance of the entropy of solvation of ions.^[45] (In fact, in water, the attraction of unlike charges, and the repulsion of like charges, appears to be largely an entropic—rather than enthalpic—effect.^[45]) Figure 12a shows a schematic representation of the interface between the charged surface of a solid and an aqueous solution; this interface is conventionally known as the “electrical double layer,” although it is often subdivided into more than two layers. In this illustration, we assume that the solid has a positive electrostatic charge arising from covalently bound cations at its surface. Some of the counterions (anions) accumulate in an immobile layer (the Stern layer) close to the surface of the solid. The remaining anions, along with other electrolyte ions, form a diffuse “ion atmosphere”—the Gouy–Chapman layer—that extends into the electrolyte solution. The total interfacial region (the positively-charged surface plus the counterions and electrolyte ions in the Stern and Gouy–Chapman layers) is electrically neutral.

The classic text by Adamson offers an excellent treatment of the electrical double layer;^[46] we provide here a brief overview. At equilibrium, the electrochemical potential $\bar{\mu}_i$ of each ionic species must be the same everywhere [Eq. (2)].

$$\bar{\mu}_i = \bar{\mu}_i^0 + RT \ln c_i + z_i F \psi \quad (2)$$

In this equation, c_i is the local concentration of the ionic species i , z_i is the (signed) valence of that species, F is the Faraday constant, and ψ is the average local electrical potential. This equation combines the two thermodynamic

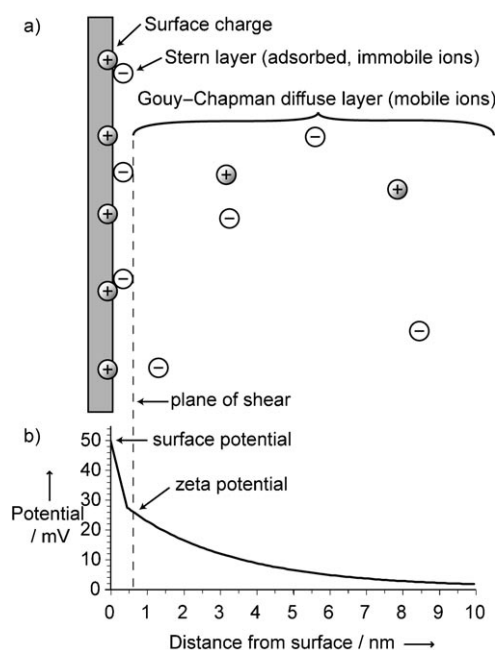


Figure 12. a) The interface between a charged solid and an aqueous electrolyte solution. b) The calculated average electrostatic potential corresponding to the model shown in (a). The discontinuity in the derivative of the potential at the Stern layer is not physically realistic: it is an artifact of treating the ions in the Stern layer as immobile point charges all located in a single plane. The plane of shear is expected to lie just outside of this discontinuity, as the plane of shear lies at the outer edge of the immobile layer of ions.

influences on an electrolyte ion: the electrostatic energy, represented by the term $z_i F \psi$, and the entropy of dilution, represented by $RT \ln c_i$. (Since the ions are treated as point charges in a continuous dielectric medium, the entropy of dilution is the only entropy considered at this level of approximation.) Given that $\bar{\mu}_i$ must be the same everywhere, if we represent the local concentration of cations as c_+ , the concentration of anions as c_- , and the bulk electrolyte concentration at infinity as c (where $\psi = 0$, by definition), we can derive the Boltzmann distributions for both ions in a symmetrical electrolyte of (unsigned) valence z [Eq. (3); note that $F/R = e/k$].

$$\frac{c_+}{c} = \exp\left(-\frac{z e \psi}{k T}\right), \quad \frac{c_-}{c} = \exp\left(\frac{z e \psi}{k T}\right) \quad (3)$$

The Poisson equation of classical electrostatics relates the Laplacian of the electrical potential ψ to the local charge density, which is equal to $z e(c_+ - c_-)$, and the dielectric constant ϵ [Eq. (4)].

$$\nabla^2 \psi = -\frac{z e(c_+ - c_-)}{\epsilon_0 \epsilon} \quad (4)$$

Combining Equations (3) and (4) gives the Poisson–Boltzmann equation [Eq. (5)].

$$\nabla^2 \psi = \frac{2 c z e}{\epsilon_0 \epsilon} \sinh \frac{z e \psi}{k T} \quad (5)$$

With this equation, the equilibrium electrical potential can be calculated at any point in an electrolyte solution; the electrical potential determines the ion concentrations according to Equation (3). The Poisson–Boltzmann equation provides an approximate quantitative treatment of the ion concentrations in the diffuse Gouy–Chapman layer. In particular, we can estimate the size of this diffuse ion atmosphere. If $ze\psi/kT \ll 1$, we can use the linear approximation $\sinh x \approx x$ to obtain the Debye–Hückel equation [Eq. (6)], in which we introduce the Debye parameter κ , with dimensions of inverse length.

$$\nabla^2 \psi = \frac{2c z^2 e^2 \psi}{\epsilon_0 \epsilon k T} = \kappa^2 \psi \quad (6)$$

For a charged planar surface with a potential ψ_0 at the surface, the solution to the Debye–Hückel equation is given by Equation (7), in which x is the distance from the surface.

$$\psi = \psi_0 e^{-\kappa x} \quad (7)$$

The Debye length $1/\kappa$ is the distance at which the potential is reduced to $1/e$ of its value at the surface; for a univalent 0.01M electrolyte at 25°C, the Debye length is 3 nm. If the linear approximation of Debye is not valid, then the potential falls off even more rapidly with distance.

Electrostatic forces and specific interactions with the surface affect the ions in the Stern layer. Stern treated these ions using a Langmuir adsorption isotherm with an additional term for the electrostatic interactions;^[46] this quantitative treatment of adsorption in the Stern layer is beyond the scope of this review.

Figure 12b shows the results of a calculation of the electrostatic potential for a typical solid–aqueous interface. We chose parameters that match the schematic illustration in Figure 12a, which is drawn roughly to scale. For the purpose of illustration, we assume that there is one surface-bound cation per 10 nm², the anions in the Stern layer neutralize 3/5 of these cations, the bulk electrolyte concentration is 0.01M, and the temperature is 298 K. The Debye length under these conditions is about 3 nm.

There is an important distinction between the ions in the Gouy–Chapman layer and the ions that are covalently bound or adsorbed in the Stern layer. If an external force causes the aqueous solution to flow with respect to the solid interface, the ions in the Gouy–Chapman layer will move with the liquid, whereas the ions in the Stern layer will remain immobile (along with the first, adsorbed layer of solvent molecules). The hypothetical plane that divides the immobile Stern layer from the mobile Gouy–Chapman layer is known as the plane of shear, as indicated in Figure 12; the zeta potential, by definition, is the electrical potential at the plane of shear. This distinction between mobile and immobile ions leads to several phenomena known collectively as electrokinetic phenomena: electrophoresis, electroosmosis, streaming potential, streaming current, sedimentation potential, and sedimentation current.^[44,47] In conjunction with appropriate theoretical models, one can use these experimental phenomena to determine the zeta potential at the interface between a

charged solid and an aqueous electrolyte solution. The sign of the zeta potential is of particular importance: it indicates the net charge of the immobile ions at the surface of a solid.

4.2. The Role of Water in Contact Electrification of Materials With Mobile Ions

Adsorbed water from the atmosphere plays a complicated role in the contact electrification of solids. One effect of adsorbed water is to increase the surface (ionic) conductivity of insulating solids.^[11] This increase in conductivity allows local regions of charge on a surface to spread and ultimately to discharge to ground. One does not ordinarily observe electrostatic phenomena when the atmospheric humidity is high, because any accumulated charge dissipates rapidly through the lateral movement of ions across surfaces.

In a study of the effect of humidity on contact electrification of polymers containing bound ions and mobile counterions,^[48] Diaz and co-workers observed almost no contact electrification at 0% RH, maximum contact electrification around 30% RH, and a decrease in contact electrification above 40% RH. They also observed that the thickness of the adsorbed water layer (measured by ellipsometry) on these ion-containing polymers increased nearly linearly with relative humidity; the average thickness of the water layer at 90% RH was around 0.4 nm, corresponding to about 1.5 monolayers of water. The decrease in contact electrification at high humidity is not surprising and probably involves increased surface conductivity as mentioned above. The decrease in contact electrification to nearly zero at 0% RH suggests that water is necessary for the transfer of ions during contact electrification.

Diaz proposed that the contact of two surfaces, each having an adsorbed film of water, yields a “water bridge” between the surfaces. Figure 13 shows a schematic representation of the ion-transfer mechanism of contact electrification, modified to include this role of water. Once the water bridge forms, mobile ions can diffuse within this thin region. If the water bridge has a thickness of approximately 1–2 nm, then the entire water bridge is thinner than the Debye length in a typical aqueous solution. Over this short distance, the entropic (diffusional spreading) tendencies of the ions are comparable to the electrostatic forces, so the mobile ions will distribute themselves across the entire thickness of the water bridge. The high dielectric constant of water reduces the electrostatic cost of separating the mobile ions from their counterions. The final separation of charge occurs when the water bridge splits into individual adsorbed layers of water. As with the ion-transfer mechanism discussed earlier, once the gap between the two layers of water is sufficiently large, ions become trapped kinetically on one surface or the other. This mechanism for contact electrification probably requires thin layers of water. (If a layer of water is greater than about 2 nm thick, the central part of the layer will have the properties of bulk water.)^[49] If thick layers of water were present, ionic conductivity within this water layer could discharge the materials as they are separated: the ion-transfer mechanism requires that the ions be kinetically trapped on

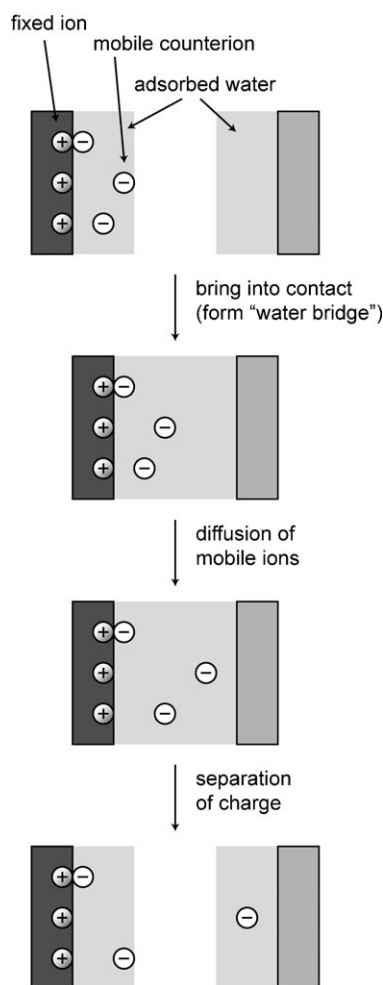


Figure 13. The role of water in the ion-transfer mechanism of contact electrification for polymers that contain covalently bound ions and mobile counterions. (This illustration is not drawn to scale; a single monolayer of water would be ca. 0.3 nm thick.) The mobile ions could be counterions from the polymer, or other aqueous ions such as H^+ or OH^- . As in the case of the Gouy–Chapman double layer, electrostatic forces tend to concentrate the mobile ions at the charged interface, whereas entropy tends to cause diffusion of those ions; the ambient temperature (kT) sets the balance between electrostatics and entropy.

the surfaces. As an extreme example, the separation of two oppositely charged colloids in an aqueous solution will not result in macroscopic charge separation, as each charged colloid will maintain an equilibrium ion atmosphere of equal and opposite charge.

On the basis of the ion-transfer model of contact electrification, one would expect a direct relationship between the zeta potential of an ion-containing material and the contact electrification of that material. A material with covalently bound cations and mobile anions will have a positive zeta potential and will develop a positive charge upon contact electrification; a material with covalently bound anions and mobile cations will yield the opposite charges. Electrokinetic phenomena and contact electrification distinguish between immobile ions and mobile ions: in the former,

the mobile ions move with the solvent and the immobile ions remain on the surface; in the latter, the mobile ions transfer to the other surface and the immobile ions remain in place. In addition to the obvious correlation between zeta potential and contact electrification for polymers that contain bound ions and mobile counterions, Forssberg and co-workers observed a correlation between the zeta potentials of several inorganic minerals and the contact electrification of these minerals.^[50] The zeta potentials of inorganic solids are related to the presence of dissociable ionic functional groups (often oxides) at their surface;^[47] the ion-transfer model predicts that contact electrification of these solids is likewise related to mobile ions at their surface.^[11]

Baur and co-workers noted a similar correlation between electrokinetic behavior and contact electrification for polymers doped with organic salts (charge-control agents).^[51] Many of these organic salts are surfactants (e.g. cetylpyridinium bromide, used by Mizes and co-workers);^[29] the large organic ion accumulates at the water/air or water/solid interface, while the small inorganic counterion remains in the bulk solution. These salts also tend to be hygroscopic, so they facilitate the adsorption of water on the surface of otherwise hydrophobic organic polymers. The preferential adsorption of hydrophobic organic ions in the Stern layer yields a zeta potential with the same sign as that of the organic ion.^[47] This adsorption of organic ions in the Stern layer can also explain the observation that the small counterions (which are less likely to be adsorbed in the Stern layer) transfer preferentially upon contact electrification of polymers doped with organic salts. This explanation of the different propensities of ion transfer for small versus large ions is superior to the usual explanation that small ions are simply more mobile than large ions. Although large ions (e.g. tetraalkylammonium ions) are generally slightly less mobile than small ions (e.g. halide ions), as shown by their diffusion coefficients in water,^[52] the slightly slower diffusion of a large ion versus a small ion across a gap of a few nanometers (a process taking approximately 10^{-9} s) cannot account for the observed effect that these ionic additives have on contact electrification.

In a revealing study, Law and co-workers found that the amount of charge acquired through contact electrification of poly(styrene-*co*-butadiene) doped with various alkali-metal di-*tert*-butylsalicylates increases in the order $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$.^[53] This observation supports the hypothesis that the adsorption of ions in the Stern layer is more important than ionic mobility in determining contact electrification. Cesium is the least hydrated cation of these alkali metals, so it is the most likely to adsorb in the Stern layer; lithium is so strongly hydrated that it has virtually no tendency to adsorb in the Stern layer.^[47] The co-adsorption of Cs^+ cations along with the organic anions in the Stern layer would lead to less transfer of these cations (relative to Li^+) and less contact electrification, in agreement with Law's observations. The usual argument based on differences in the mobility of the ions would predict the opposite result: in water, cesium is the most mobile cation, whereas lithium is the least mobile,^[52] so differences in ionic mobility would tend to promote the transfer of cesium.

4.3. The Role of Water in Contact Electrification of Nonionic Materials

The relationship between electrokinetic phenomena (e.g. the zeta potential) and contact electrification may help to clarify the mechanism or mechanisms of contact electrification of nonionic materials under ambient conditions. A glance at the triboelectric series (Figure 1a) shows that many common polymers, such as PMMA, polyethylene, polystyrene, and PTFE, all exhibit contact electrification, even though these polymers do not contain mobile ions. Despite the significant advances made by Diaz, Law, and Mizes in explaining the contact electrification of ion-containing materials, the familiar phenomenon of contact electrification between nonionic organic polymers remains unexplained. We return to the question that bedeviled Harper: if the contact electrification of insulating polymers results from the transfer or asymmetric partitioning of ions between two surfaces, what is the nature and source of these ions?

An examination of the zeta potentials of organic polymers suggests a possible explanation. Figure 14 shows a correlation

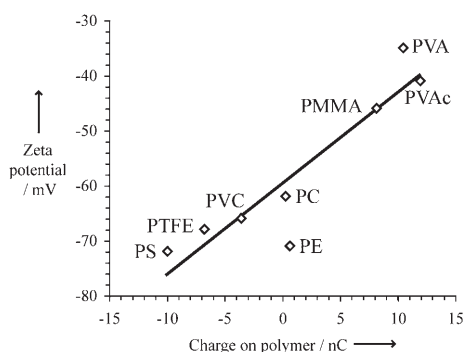


Figure 14. Correlation ($R = 0.92$) between contact electrification and zeta potential for eight polymers. (Abbreviations for polymers are those used in Figure 1.) The two notable outliers are polyethylene (PE) and poly(vinyl alcohol) (PVA). Contact electrification data are from reference [14]; zeta potentials are from reference [54]. The point labeled PVAc (poly(vinyl acetate)) represents the contact electrification of poly(vinyl acetate) but the zeta potential of the related polymer cellulose acetate, which exhibits contact electrification similar to poly(vinyl acetate), according to reference [13].

between the zeta potential of several organic polymers and the charges acquired by these polymers upon contact with a gold-coated metal sphere. The values of the zeta potentials are from a single study by Jacobasch and co-workers;^[54] zeta potentials determined by different researchers under different conditions often vary widely.^[55] Likewise, the contact electrification data are from our recent paper.^[14] We included every polymer that was studied in both papers. Each of these sets of data should be internally consistent, but the polymer samples used for the zeta-potential measurements were obviously not the same as those used for contact electrification. There are two notable outliers: polyethylene and poly(vinyl alcohol). Commercial polyethylene films often contain plasticizers, and polyethylene is susceptible to autoxidation; indeed, the conventional triboelectric series (Fig-

ure 1a) suggests that polyethylene and polystyrene should charge similarly; this suggestion would be consistent with the zeta-potential data. Poly(vinyl alcohol) is hydrophilic, and the level of ambient humidity may affect its contact electrification (the measurements of contact electrification were made at 20–24 % RH, whereas the zeta-potential measurements were made in water). PVA also tends to adsorb adventitious cations (e.g. the K^+ cations used in the buffer for the zeta-potential measurements); perhaps the measured zeta potential is more positive than it would be in the absence of such adsorption of cations. Measurements of both the zeta potential and the contact electrification for a single set of polymer films under comparable conditions would be valuable in testing the relationship suggested by Figure 14.

One might expect that a neutral organic polymer—one containing no ionic functional groups—would have no surface charge and a zeta potential of zero. All of the polymers had negative zeta potentials; this observation suggests that anions from the aqueous phase preferentially accumulate in the immobile Stern layer. Jacobasch measured zeta potentials in aqueous KCl, so the anions in the Stern layer could be either chloride or hydroxide. Zeta-potential measurements by Werner and co-workers showed that there is a strong preference for hydroxide adsorption at a water/fluoropolymer interface, even in the presence of significant concentrations of chloride.^[56] The negative zeta potentials of these organic polymers appear to arise from the presence of hydroxide ions in the Stern layer.

This segregation of hydroxide at the interface between water and an organic polymer appears to be a specific example of a more general phenomenon: anions in general, and hydroxide ions in particular, appear to accumulate at the water/solid or water/air interface.^[56–63] To understand this phenomenon, we must briefly review the general behavior of ions at aqueous interfaces.

For most of the 20th century, chemists believed that the surface of an aqueous electrolyte solution was devoid of ions. The observation that the surface tension of an electrolyte solution is greater than that of pure water supported this model. According to Gibbs, solutes that accumulate at the surface of a liquid (e.g. surfactants) lower its surface tension, whereas solutes that are depleted in the surface region of a liquid increase its surface tension.^[46] Onsager and Samaras proposed that ions in a medium of high dielectric constant (water) would be repelled from an interface with a medium of low dielectric constant (air) on the basis of electrostatic arguments alone.^[64] This repulsion is easily understood qualitatively: an ion immersed entirely in a high-dielectric medium (water) will have all of its electric “field lines” in the high-dielectric medium, whereas an ion near the interface will have some field lines that extend into the low-dielectric medium (air). The energy of an electric field is lower if that field is in a high-dielectric medium relative to a low-dielectric medium, so the electrostatic energy of an ion will be minimized if the ion is completely immersed in the high-dielectric medium. (The electrostatic force on an ion near the boundary between two dielectric media can be calculated exactly using the method of images.)^[65] This classical model prevailed for many years, primarily because surface-tension

measurements were the only tool for probing the *equilibrium* structure of the surface of ionic solutions. Electrokinetic measurements of aqueous interfaces, however, appeared to contradict this model of an ion-free aqueous surface. Experiments in the early 20th century showed that the water/air interface had a negative zeta potential; recent experiments have confirmed these observations.^[57,58] The strong pH dependence of the zeta potential of gas bubbles suggests that hydroxide ions accumulate preferentially at the water/air interface. The similar interface between water and hydrophobic liquids or solids also exhibits a negative, pH-dependent zeta potential.^[56,59] Indeed, this apparent segregation of hydroxide ions in the Stern layer is not limited to hydrophobic interfaces. A hydrophilic oligo(ethylene glycol)-terminated self-assembled monolayer exhibited similar electrokinetic behavior,^[66] and even the ice/water interface shows adsorption of hydroxide: the zeta potential of D₂O ice (which freezes at 3.8 °C) in H₂O liquid water at 3.5 °C was negative, and the pH dependence of its zeta potential was remarkably similar to that of hexadecane droplets in water.^[67]

Both the ion-free model and the hydroxide-enriched model of the water surface coexisted uneasily for most of the last century, in part because the researchers who studied electrokinetic phenomena were somewhat isolated from the mainstream academic community of physical chemists. In the past decade, advances in computational modeling and surface-specific nonlinear spectroscopic techniques such as vibrational sum-frequency generation (VSFG) and second harmonic generation (SHG) have clarified the interfacial structure of aqueous electrolyte solutions.^[60] These results demonstrate that *polarizable* anions such as chloride, iodide, and thiocyanate accumulate at the surface of water in concentrations that exceed their bulk concentrations. (These experiments have not been able to probe the concentrations of hydroxide ion at the aqueous surface.) Unfortunately, a schism remains between these researchers (spectroscopists and theoreticians) and those who study electrokinetic phenomena: the recent single-topic issue of *Chemical Reviews* on aqueous interfaces appears to ignore the entire literature on electrokinetic phenomena.^[61] The molecular-dynamics simulations that predict enhanced concentrations of polarizable anions at the aqueous surface also predict that the concentration of the nonpolarizable hydroxide ion is depleted at the surface.^[68] In contrast, electrokinetic experiments suggest that hydroxide adsorbs at a water/fluoropolymer interface in preference to chloride (by a factor greater than 10⁶).^[56]

A recent experiment by Beattie and Djerdjev demonstrated that the *equilibrium* interface between water and hydrophobic organic liquids accumulates hydroxide ions.^[62] They prepared surfactant-free emulsions of various hydrophobic organic liquids in water and passed these emulsions repeatedly through a homogenizer, which breaks the oils into smaller and smaller droplets. To maintain a constant pH in the aqueous phase, they had to add hydroxide to the emulsion after each step of homogenization. Apparently, the increased surface area of the organic phase adsorbs a measurable amount of hydroxide from solution. These results show that the accumulation of hydroxide at an aqueous interface is not merely an artifact of the electrokinetic tools used to study

such interfaces: it is an equilibrium property of the surface of water. Unfortunately, molecular-dynamics simulations have been unable to reproduce this phenomenon, with the sole exception of a recent paper by Zangi and Engberts.^[69] Those authors proposed that the dipolar hydroxide ion interacts with oriented water dipoles at the interface between water and a hydrophobic organic solid, whereas ions with a spherical charge distribution show no such interaction. More recent experimental results by Beattie and co-workers, however, contradict this model: they found no preference for adsorption of dipolar anions (thiocyanate, iodate, or acetate) versus spherical anions (halides).^[70] They speculated that the specific adsorption of hydroxide must be due to some unique role of hydroxide in the hydrogen-bonding structure of interfacial water. Without an atomic-level picture of this interface, however, a detailed understanding of hydroxide adsorption remains elusive. In any event, the negative zeta potentials observed for nearly all organic polymers most likely result from this adsorption of hydroxide.

Different polymers have different zeta potentials (Figure 14). Some polymers evidently adsorb more hydroxide than others do, for reasons that remain unclear. This observation, combined with the water bridge model proposed by Diaz, suggests a possible mechanism for the contact electrification of nonionic polymers under ambient conditions (Figure 15). In the thin film of water on the surface of each polymer, hydroxide accumulates in the Stern layer, whereas hydronium remains solvated. This interfacial structure is consistent with the observed negative zeta potential of all polymers. Contact between the two polymers results in rapid equilibration of hydroxide and hydronium ions within the water bridge; in particular, the polymer with a greater affinity for hydroxide accumulates a greater concentration of hydroxide in the Stern layer near its surface. Finally, splitting of the water bridge into two separate films of water leads to the separation of charge: the polymer with more hydroxide in its Stern layer acquires a net negative charge. This proposed role of hydroxide in the contact electrification of nonionic polymers can explain the puzzling tendency of polyethylene and polypropylene, which have no affinity for electrons, to acquire a negative charge upon tribocharging. Under ordinary conditions, of course, surface contaminants will contribute other ions to the surface of these materials. Carbon dioxide, for example, will react with water and hydroxide to yield carbonate or hydrogen carbonate ions, which may play a role in contact electrification; carbonate (like nitrate) would be expected to be highly anisotropic in its polarizability and hydrophobicity.^[71]

This model of hydroxide adsorption may also help to explain some results obtained recently in our research group.^[72] We studied the kinetics of contact electrification of polystyrene with gold or stainless steel as a function of relative humidity and found that the rate of charging increased as the humidity increased. This trend is consistent with Diaz's observation that the presence of water facilitates contact electrification, as well as with our proposed role of adsorbed water in the contact electrification of nonionic polymers. Although we did not investigate contact electrification at 0 % RH, extrapolation of our data suggests that little

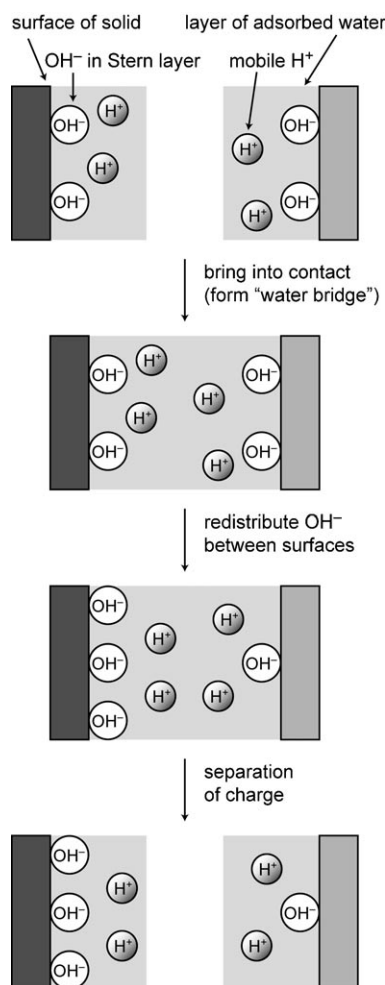


Figure 15. Proposed hydroxide-adsorption model of contact electrification for nonionic polymers. (The hydration of H^+ and OH^- ions is not shown.)

or no contact electrification would occur in the absence of moisture. We also saturated the chamber used for contact electrification with vapors of 1M aqueous ammonia or 1M acetic acid and found that the rate of charging of polystyrene (which acquired a negative charge, as expected) increased in a basic environment, and decreased in an acidic environment. This observation supports the hydroxide-adsorption model of contact electrification: more hydroxide would adsorb on polystyrene under basic conditions than under acidic conditions. In addition, our puzzling observation of a weak correlation between refractive index and contact electrification^[14]—polymers with a greater index of refraction tended to become negatively charged—is consistent with the suggestion by Jacobasch^[54] and others that polymers capable of stronger interactions by dispersion forces tend to adsorb more hydroxide.

More experiments are required before we can properly evaluate the role of hydroxide ions in contact electrification. We need better measurements of the relationship between zeta potential and contact electrification for a wide variety of materials, and further studies of the influence of environmental acidity or basicity. Studies at low temperature could be

enlightening, as the ion-transfer mechanism depends on thermal activation. In addition, although this hydroxide-adsorption model of contact electrification may address Harper's concern about the source of ions on nonionic polymer surfaces, it does not answer the more fundamental question: why does hydroxide segregate at such interfaces in the first place? We suspect that a complete answer to that basic question will require a significant increase in our understanding of the remarkable structure and properties of liquid water.

5. Summary and Outlook

Materials that contain covalently bound ions and mobile counterions develop a net electrostatic charge upon contact with other materials. Substantial evidence suggests that this charge is due to the transfer of mobile ions to the surface in contact with the ionic material. With an understanding of this ion-transfer model of contact electrification, one has a rational approach to the design of ionic electrets—materials that bear a net electrostatic charge as a result of an imbalance between the number of cationic and anionic charges in the material. In addition to their use in self-assembly and electrophotography, ionic electrets could, in some applications, replace polymer electrets that are charged by poling or by direct injection of electrons.

We suggest, as a hypothesis to guide further research, that the familiar phenomenon of contact electrification of nonionic low-polarity solids may be due to the segregation of hydroxide ions at the interface between the solid and a thin layer of adsorbed water. The known accumulation of hydroxide at water–solid interfaces, combined with a correlation between zeta potential and contact electrification for several common polymers, provides some support for this conjecture.

If this model is correct, there are at least three different mechanisms for contact electrification under ambient conditions: 1) electron-transfer for contact between metals or semiconductors; 2) ion-transfer for contact involving materials that contain mobile ions; and 3) asymmetric partitioning of hydroxide ions between adsorbed layers of water for contact involving nonionic, insulating materials. Discharge of these charged materials can involve tunneling of electrons, field emission, dielectric breakdown of the surrounding gas, or surface (ionic) conductivity facilitated by adsorbed water.

Despite some real advances in our understanding of contact electrification, many questions remain unanswered. The fundamental mechanism of contact electrification between insulating materials still eludes us, although the proposed hydroxide-adsorption mechanism makes several testable predictions. A combination of classical techniques (electrokinetic phenomena, temperature effects, isotope effects), new surface-specific spectroscopic techniques that can be used under ambient conditions, and increasingly sophisticated computer simulations may be able to test this hypothesis. The preparation of ionic electrets also poses a fundamental question for chemists: what is the chemistry of materials that bear a net electrostatic charge? One of the basic assumptions of chemical thermodynamics is that bulk

matter is electrically neutral; abandoning that assumption allows us to contemplate, for example, the free energy of transferring a single ion from one phase to another.

There are also a number of important technological questions. One is whether we can use our emerging understanding of contact electrification to create materials that will not become charged upon contact. The many hazards of unwanted contact electrification—fires, explosions, damaged electronic equipment—still pose a serious challenge. A second question is whether, now that we can create materials that have a net electrostatic charge by design, we can find new classes of applications for these materials. Electrostatic forces can be quite strong, although the amount of stable charge that can accumulate on an electret is ultimately limited by the dielectric breakdown of air or the surrounding medium. One might seek to use permanent electrets in place of permanent magnets in electromechanical devices—motors, generators, actuators, relays—particularly as these devices are further miniaturized to the micro- and nanoscale.

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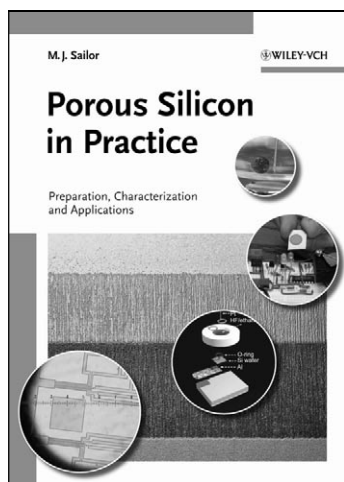
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- [1] *Electrets*, 3rd ed. (Eds.: G. M. Sessler, R. Gerhard-Multhaupt), Laplacian, Morgan Hill, **1998**.
- [2] O. Heaviside, *Electrician* **1885**, *14*, 230.
- [3] V. V. Kochervinskii, *J. Polym. Sci. Part B* **2003**, *45*, 326.
- [4] S. Bauer, R. Gerhard-Multhaupt, G. M. Sessler, *Phys. Today* **2004**, *57*, 37.
- [5] D. M. Pai, B. E. Springett, *Rev. Mod. Phys.* **1993**, *65*, 163.
- [6] D. S. Richart in *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 6, 4th ed. (Eds.: J. I. Kroschwitz, M. Howe-Grant), Wiley, New York, **1992**, pp. 635–661.
- [7] W. D. Greason, *IEEE Trans. Ind. Appl.* **1987**, *23*, 205.
- [8] N. Gibson, *J. Electrostat.* **1997**, *40–41*, 21.
- [9] R. B. Cole, *Electrospray Ionization Mass Spectrometry: Fundamentals, Instrumentation, and Applications*, Wiley, New York, **1997**.
- [10] R. L. Grimm, J. L. Beauchamp, *J. Phys. Chem. B* **2003**, *107*, 14161.
- [11] W. R. Harper, *Contact and Frictional Electrification*, Laplacian, Morgan Hill, **1998**.
- [12] A. D. Moore, *Electrostatics: Exploring, Controlling, and Using Static Electricity, Including the Dirod Manual*, Laplacian, Morgan Hill, **1997**.
- [13] A. F. Diaz, R. M. Felix-Navarro, *J. Electrostat.* **2004**, *62*, 277.
- [14] J. A. Wiles, B. A. Grzybowski, A. Winkleman, G. M. Whitesides, *Anal. Chem.* **2003**, *75*, 4859.
- [15] L. S. McCarty, A. Winkleman, G. M. Whitesides, *J. Am. Chem. Soc.* **2007**, *129*, 4075.
- [16] B. A. Grzybowski, A. Winkleman, J. A. Wiles, Y. Brumer, G. M. Whitesides, *Nat. Mater.* **2003**, *2*, 241.
- [17] B. A. Grzybowski, J. A. Wiles, G. M. Whitesides, *Phys. Rev. Lett.* **2003**, *90*, 083903.
- [18] J. Lowell, A. C. Rose-Innes, *Adv. Phys.* **1980**, *29*, 947.
- [19] B. A. Grzybowski, M. Fialkowski, J. A. Wiles, *J. Phys. Chem. B* **2005**, *109*, 20511.
- [20] A. F. Diaz, J. Guay, *IBM J. Res. Dev.* **1993**, *37*, 249.
- [21] M. Meunier, N. Quirke, *J. Chem. Phys.* **2000**, *113*, 369.
- [22] H. S. Nalwa, *Handbook of Organic Conductive Molecules and Polymers*, Wiley, New York, **1997**.
- [23] O. Knoblauch, *Z. Phys. Chem.* **1902**, *39*, 225.
- [24] J. A. Medley, *Nature* **1953**, *171*, 1077.
- [25] J. H. Clint, T. S. Dunstan, *Europhys. Lett.* **2001**, *54*, 320.
- [26] R. P. N. Veregin, M. N. V. McDougall, M. S. Hawkins, C. Vong, V. Skorokhod, H. P. Schreiber, *J. Imaging Sci. Technol.* **2006**, *50*, 282.
- [27] R. P. N. Veregin, M. N. V. McDougall, M. S. Hawkins, C. Vong, V. Skorokhod, H. P. Schreiber, *J. Imaging Sci. Technol.* **2006**, *50*, 288.
- [28] H. T. Macholdt, A. Sieber, *J. Imaging Technol.* **1988**, *14*, 89.
- [29] H. A. Mizes, E. M. Conwell, D. P. Salamida, *Appl. Phys. Lett.* **1990**, *56*, 1597.
- [30] K. Y. Law, I. W. Tarnawskyj, D. Salamida, T. Debies, *Chem. Mater.* **1995**, *7*, 2090.
- [31] A. F. Diaz, *J. Adhes.* **1998**, *67*, 111.
- [32] A. F. Diaz, D. Wollmann, D. Dreblow, *Chem. Mater.* **1991**, *3*, 997.
- [33] J. I. Zink, *Acc. Chem. Res.* **1978**, *11*, 289.
- [34] P. B. O'Hara, C. Engelson, W. St Peter, *J. Chem. Educ.* **2005**, *82*, 49.
- [35] N. C. Eddingsaas, K. S. Suslick, *J. Am. Chem. Soc.* **2007**, *129*, 6718.
- [36] J. M. Meek, J. D. Craggs, *Electrical Breakdown of Gases*, Clarendon, Oxford, **1953**.
- [37] T. Matsuyama, H. Yamamoto, *J. Phys. D* **1995**, *28*, 2418.
- [38] T. Matsuyama, H. Yamamoto, *J. Phys. D* **1997**, *30*, 2170.
- [39] R. G. Horn, D. T. Smith, A. Grabbe, *Nature* **1993**, *366*, 442.
- [40] A. G. Bailey, *J. Electrostat.* **1998**, *45*, 85.
- [41] L. S. McCarty, A. Winkleman, G. M. Whitesides, *Angew. Chem.* **2007**, *119*, 210; *Angew. Chem. Int. Ed.* **2007**, *46*, 206.
- [42] Y. Awakuni, J. H. Calderwood, *J. Phys. D* **1972**, *5*, 1038.
- [43] A. L. Sumner, E. J. Menke, Y. Dubowski, J. T. Newberg, R. M. Penner, J. C. Hemminger, L. M. Wingen, T. Brauers, B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.* **2004**, *6*, 604.
- [44] R. D. Vold, M. J. Vold, *Colloid and Interface Chemistry*, Addison-Wesley, Reading, **1983**.
- [45] I. Gitlin, J. D. Carbeck, G. M. Whitesides, *Angew. Chem.* **2006**, *118*, 3090; *Angew. Chem. Int. Ed.* **2006**, *45*, 3022.
- [46] A. W. Adamson, A. P. Gast, *Physical Chemistry of Surfaces*, 6th ed., Wiley, New York, **1997**.
- [47] R. J. Hunter, *Zeta Potential in Colloid Science*, Academic Press, New York, **1981**.
- [48] S. Pence, V. J. Novotny, A. F. Diaz, *Langmuir* **1994**, *10*, 592.
- [49] I.-F. W. Kuo, C. J. Mundy, *Science* **2004**, *303*, 658.
- [50] H. R. Manouchehri, K. H. Rao, K. S. E. Forssberg, *Part. Sci. Technol.* **2001**, *19*, 23.
- [51] R. Baur, H. T. Macholdt, E. Michel, *Electrostatics 1999, Institute of Physics Conference Series, Vol. 163*, **1999**, pp. 285–288.
- [52] *CRC Handbook of Chemistry and Physics* (Ed.: D. R. Lide), Taylor and Francis, Boca Raton, **2006**.
- [53] K. Y. Law, I. W. Tarnawskyj, D. Salamida, T. Debies, *J. Imaging Sci. Technol.* **1997**, *41*, 618.
- [54] N. Kühn, H.-J. Jacobasch, K. Lunkenheimer, *Acta Polym.* **1986**, *37*, 394.
- [55] B. J. Kirby, E. F. Hasselbrink, *Electrophoresis* **2004**, *25*, 203.
- [56] R. Zimmermann, S. Dukhin, C. Werner, *J. Phys. Chem. B* **2001**, *105*, 8544.
- [57] A. Graciaa, G. Morel, P. Saulner, J. Lachaise, R. S. Schechter, *J. Colloid Interface Sci.* **1995**, *172*, 131.
- [58] M. Takahashi, *J. Phys. Chem. B* **2005**, *109*, 21858.
- [59] K. G. Marinova, R. G. Alargova, N. D. Denkov, O. D. Velez, D. N. Petsev, I. B. Ivanov, R. P. Borwankar, *Langmuir* **1996**, *12*, 2045.
- [60] P. B. Petersen, R. J. Saykally, *Annu. Rev. Phys. Chem.* **2006**, *57*, 333.

- [61] *Chem. Rev.* **2006**, *106*, 1137 (single-topic issue on aqueous interfaces).
- [62] J. K. Beattie, A. M. Djerdjev, *Angew. Chem.* **2004**, *116*, 3652; *Angew. Chem. Int. Ed.* **2004**, *43*, 3568.
- [63] J. K. Beattie, *Lab Chip* **2006**, *6*, 1409.
- [64] L. Onsager, N. N. T. Samaras, *J. Chem. Phys.* **1934**, *2*, 528.
- [65] D. J. Griffiths, *Introduction to Electrodynamics*, 3rd ed., Prentice Hall, Upper Saddle River, **1999**.
- [66] Y. H. M. Chan, R. Schweiss, C. Werner, M. Grunze, *Langmuir* **2003**, *19*, 7380.
- [67] J. Drzymala, Z. Sadowski, L. Holysz, E. Chibowski, *J. Colloid Interface Sci.* **1999**, *220*, 229.
- [68] M. Mucha, T. Frigato, L. M. Levering, H. C. Allen, D. J. Tobias, L. X. Dang, P. Jungwirth, *J. Phys. Chem. B* **2005**, *109*, 7617.
- [69] R. Zangi, J. Engberts, *J. Am. Chem. Soc.* **2005**, *127*, 2272.
- [70] J. K. Beattie, A. M. Djerdjev, G. V. Franks, G. G. Warr, *J. Phys. Chem. B* **2005**, *109*, 15675.
- [71] W. Kunz, L. Belloni, O. Bernard, B. W. Ninham, *J. Phys. Chem. B* **2004**, *108*, 2398.
- [72] J. A. Wiles, M. Fialkowski, M. R. Radowski, G. M. Whitesides, B. A. Grzybowski, *J. Phys. Chem. B* **2004**, *108*, 20296.

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