Electrical Deflection of Polar Liquid Streams: A Misunderstood Demonstration

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Photographs showing a polar-liquid droplet stream electrically deflected by a statically charged rod or balloon are a common feature of freshman chemistry texts. In current editions such images occur, for example, in texts by Atkins and Jones (1), Ebbing and Gammon (2), Kotz and Treichel (3), and Umland and Bellama (4). Typically, a water stream (readily deflected) is compared with a nonpolar liquid such as carbon tetrachloride, said to undergo zero deflection, although Atkins and Jones (1) and Umland and Bellama (4) show an intriguing demonstration in which they compare cis- and trans-dichloroethylene (the droplet stream of polar cis molecules is deflected, whereas the trans form is not). The authors' intent is to demonstrate visually a difference between polar and nonpolar molecules. However, the mechanism of this effect is usually not discussed in the figure captions. A casual interpretation of the figures could give some students the impression that the mere presence of molecular dipoles gives rise to a net force on the liquid droplets in an electric field, but of course in a uniform electric field dipoles experience only a torque, and no net force. Dipolar entities can only undergo deflection in a nonuniform electric field whose strength varies significantly on the length scale of the dipole. Intuition suggests that any nonuniformity in the electric field near a charged rod a few centimeters in diameter, or an electrified balloon, must be far too small to have any detectable effect on molecular dipoles.

In fact, the explanation for electrical deflection of a polar liquid droplet stream is that the polar liquid droplets carry an induced electrical charge. Electrical charging induced in water droplet streams by nearby charged objects has been known for well over two centuries, the first such observation being attributed by Benjamin (5) to Jean Théophile Desaguilers (1683–1744). (For a more recent review of static electrification phenomena, see Loeb [6].) The effect results from a charge separation in the water droplet as it forms, induced by the charge on the nearby deflection device. As the droplet separates, a fraction of the like charges repelled by the deflector statistically remain behind in the water reservoir so that the droplet acquires a net charge opposite to the charge on the deflector and is attracted to it. This was clearly stated in 1867 by Lord Kelvin (then Sir William Thomson) in describing his elegantly simple electrostatic generator based on this principle and known as the Kelvin water dropper: "If, owing to electrified bodies in the neighborhood, the potential in the air round the place where the stream breaks into drops is positive, the drops fall away negatively electrified; or vice versa" (7). Such an explanation, specifically addressing the now widespread chemistry demonstration, was repeated in this Journal in 1975 by Brindle and Tomlinson (8), but their paper and all previous literature seems largely to have been ignored by textbook

authors and in particular by Vemulapalli and Kukolich (9). These authors realized that an inhomogeneous field is needed to exert a force on a dipole. They calculated the force on a water molecule in a reasonably strong inhomogeneous field at the end of a wire 1 mm in diameter to be comparable to the gravitational force, but overlooked the fact that their experimental arrangement would induce significant charging of the falling liquid drops. Shakhashiri et al. (10) have also addressed this phenomenon. They were aware both of the need for an inhomogeneous field to exert a force on dipoles and also of the induced charge explanation of Brindle and Tomlinson. In contrast to Brindle and Tomlinson, Shakhashiri et al. suggested that deflection of a nonconducting liquid stream results from an effect known as *dielectrophoresis*, the lowering of potential energy when a dielectric material moves from a region of lower to higher electric field. They appear to argue that in conducting liquids a separation of mobile charges to opposite sides of the liquid stream again results in a net force in an inhomogeneous field, apparently rejecting the induced charge explanation of Brindle and Tomlinson (8), Kelvin (7), and many others.

In view of the widespread misconceptions about this phenomenon, evidenced by the growing penetration of the demonstration into general chemistry texts, the Shakhashiri discussion, and the Vemulapalli and Kukolich paper, it seemed worthwhile to explore some further demonstrations of the induced-charging model. To verify that water droplets issuing from a buret near a charged electrode are indeed charged, we have carried out deflection experiments in a uniform electric field, which cannot exert any force on dipolar but uncharged species. These deflection experiments in known field strengths allow a calculation of the droplet charge/mass ratio. We have further verified that a nearby charge is essential for droplet electrification and that water droplets formed in a field-free environment are not visibly deflected in a subsequent electric field, even a significantly inhomogeneous field comparable to that in the Vemulapalli and Kukolich experiment. Experiments with a variety of polar and nonpolar liquids have verified the generality of the induced-charge phenomenon. Finally, we were able to deflect a droplet stream of a nonpolar liquid (tetrachloroethylene), a phenomenon first reported by Brindle and Tomlinson.

Experimental Procedure

A deflector assembly capable of forming a uniform electric field was constructed by gluing together two aluminum plates ca. 17.5×13 cm, separated by Styrofoam spacers 2 cm thick. Within such parallel-plate deflectors, the electric field is quite uniform over the region extending to within about 1 gap width (2 cm) from the edge of the plates. For most experiments

the buret used to form the water stream was inserted into the gap between the plates so that the buret tip was 4-5 cm from the edge of the plates, assuring that droplets were formed and subsequently traveled in a region of uniform electric field. One plate was connected to ground. A copper wire was inserted into the buret to contact the liquid and was connected to the grounded deflector plate, assuring that the liquid within the buret was at ground potential. Some deflection experiments were carried out with the other deflector plate charged to a variable known potential up to 1,000 V using a power supply (Kepco ABC 1000M). For safety, higher potentials were obtained using an inflated balloon statically charged by friction, rather than a power supply. By comparison with the power supply measurements, it was estimated that potentials of several thousand volts could be produced on the balloon surface. It was found that when the charged balloon was brought to within a few centimeters of the exterior of the ungrounded metal plate a charge was induced on the plate, which often deflected the liquid stream sufficiently that it contacted the plate. Liquids investigated were distilled water, acetone, dichloromethane, trichloroethylene, and tetrachloroethylene.

CAUTION: Chlorinated hydrocarbons present hazards for inhalation and skin contact and should be handled in a fume hood. Skin contact should be avoided.

A modification of the Vemulapalli and Kukolich experiment was performed in which the point at which the water stream separated into droplets was electrically screened by an aluminum tube with an inner diameter of 7 mm pressed onto the buret tip and extending several centimeters beyond the droplet separation point. A wire deflector was formed from a 1-mm-diameter paper clip. The paper clip was pushed through a piece of Styrofoam for insulation and bent so that a 3-cm length was parallel to and 2–3 mm away from the liquid stream. A grounded aluminum foil counter-electrode was positioned behind the liquid stream ca. 1 cm distant from the wire deflector. This arrangement produces an inhomogeneous field comparable in field gradient to that in the Vemulapalli and Kukolich experiment, but acting over a significantly greater distance to maximize any effect on the droplets.

Results and Discussion

Experiments in the parallel-plate deflector assembly were carried out with water and dichloromethane streams. Figure 1 shows the deflection of a distilled water stream in the uniform field of the deflector assembly, induced by a nearby charged balloon (outside the field of view to the right). The observed deflection cannot be due to any dipole effect and is clear evidence that the water droplets are electrically charged.

In contrast, when the buret tip was within the deflector assembly, and *both* deflector plates and the water within the buret were connected to ground so that the buret tip was electrically shielded as droplets formed, it was not possible to observe any deflection of the water droplet stream issuing *below* the deflector, even with a vigorously charged balloon. This clearly demonstrates that there is *no* detectable deflection of *uncharged* water droplets and also confirms that the droplet electrification mechanism must involve charge induction in the separating water droplets induced by a nearby charged object. Similarly, water droplets issuing from the metal tube

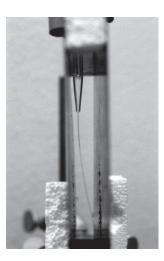


Figure 1. Electrical deflection of a distilled water droplet stream in a uniform electric field. The aluminum deflector plates were separated by 2-cm Styrofoam spacers (one is visible out of focus at the top of the image) and were insulated from the supporting clamp by other Styrofoam spacers visible at the bottom of the image. The plate on the left was grounded and a potential was induced on the right-hand plate by a statically electrified balloon (outside the field of view to the right).

screen in the electrically screened version of the Vemulapalli and Kukolich experiment were not detectably deflected with voltages (induced by a charged balloon on the 1-mm wire deflector) sufficient to strongly deflect unscreened droplet streams and, in this case, a strongly inhomogeneous field.

Why, if the Vemulapalli and Kukolich calculation is correct, is deflection of uncharged droplets not observed in a strongly inhomogeneous field? The answer appears to be that Vemulapalli and Kukolich calculated only the force on an isolated water molecule. Because this calculated force was comparable to the gravitational force, they assumed that the same would be true for the forces on a droplet; that is, that the total electrical force on a droplet would be the sum of the forces on individual free molecules, scaling in the same way as the gravitational force. This ignores the fact that owing to the large dielectric constant of water, the electrical force on molecules in the interior of the droplet is reduced by a factor of ca. 80 (and will be reduced still further if the applied field is further screened by the movement of free charges to the droplet surfaces).

Using the Kepco power supply, the deflection distance of water droplets at a point ca. 20 cm below the exit of the parallel deflector plates was measured as a function of the applied potential. Figure 2 shows that the amount of deflection was proportional to the square of the applied potential. This demonstrates that the average charge on the droplets increases linearly with the applied potential, as expected if charging is due to induction. The data of Figure 2 allow a calculation of the charge/mass ratio of the falling droplets. For an applied voltage of 700 V and an overall deflection of 16 mm, measured 20 cm below the bottom of the deflector, the charge/mass ratio was calculated to be ca. 3×10^{-5} C/kg. For a water droplet 1 mm in diameter, the corresponding charge would be ca. 1.5×10^{-11} C, or about 10⁸ electron (proton) charges. For these measurements the buret was fully open, and the calculated charge/mass ratio is a lower limit for two reasons. First, the calculation assumed that the droplets issued from the buret with zero velocity and did not account for the initial stream velocity, which could produce about a factor of 2 error in the calculation. A much larger effect results from the fact that the induced charge on the droplets is a function of the flow rate, as might be expected because charging requires a current flow as the droplets separate. Experiments with a charged balloon showed that if the flow was restricted to the lowest level that still produced a stream and not slowly forming droplets, the deflection for a given voltage (and thus the droplet charge) could increase by as much as an order of magnitude.

Notice that even potential differences of a fraction of a volt, which can result from contact potential differences, can induce on the order of 10^5-10^6 elementary charges on the droplets, depending on the flow rate. This why the Kelvin water dropper (7) begins to develop charge, even in the absence of an externally applied potential. Extremely careful experimental design would be necessary to eliminate all possibility of charging in order to search for the weak dipolar deflection effects that presumably do exist.

Two of the more intriguing textbook reports are those of Atkins and Jones (1) and later, Umland and Bellama (4), who show that droplet streams of polar organic (nominally insulating) liquids, specifically cis-dichloroethylene, are electrically deflected, whereas the nonpolar trans-dichloroethylene is undeflected. While it is easy to visualize charge separation in water due to its weak electrical conductivity, mobile protons, and possible ionic contaminants, it is harder to understand how charge separation can occur in insulating organic liquids. We did not carry out experiments with the dichloroethylenes, which were not readily available, but we did examine acetone and the compounds CH₂Cl₂, C₂HCl₃, and C₂Cl₄. In the absence of the metal plate deflector assembly (i.e., causing deflection directly with the charged balloon, which, with a radius of ca. 10 cm produces a nearly uniform field), the behavior of acetone and of CH₂Cl₂ was qualitatively similar to that of water, showing a strong deflection. A C₂HCl₃ stream was deflected more weakly. CAUTION: very fine droplets were often deflected so strongly that they contacted the charged balloon, with a crackling noise indicating that microscopic sparks were discharging the approaching droplets before they made contact. These sparks constitute a fire hazard for flammable liquids such as acetone and even more so for liquids such as benzene (9) and *n*-hexane (10).

There is a possibility that charging in the insulating liquids results somehow from frictional effects as the liquid exits the buret tip. To check this, attempts were made to deflect a dichloromethane stream originating within the grounded deflector assembly. As with water droplets, no deflection of the dichloromethane droplet stream exiting the deflector assembly was detectable under these circumstances, again demonstrating that an electric field must exist at the point of droplet separation to produce the charged droplet stream (and once again demonstrating that polar liquid streams are not deflected unless the droplets are charged).

The behavior of C_2Cl_4 was particularly interesting. With a vigorously electrified balloon it was just possible to detect a very weak deflection in a C_2Cl_4 stream even though this liquid is nonpolar. Brindle and Tomlinson reported that a strong

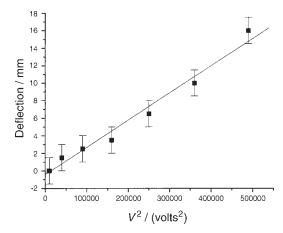


Figure 2. Water-droplet deflection distance vs the square of the applied potential. Error bars are estimated from the scatter in the droplet distribution.

deflection could be observed in a CCl₄ stream under conditions of low humidity (8); Vemulapalli and Kukolich (9) and Shakhashiri (10) observed deflection of benzene and n-hexane, respectively (attributed in ref 9 to forces on induced dipoles and in ref 10 to dielectrophoresis, the lowering of potential energy when a dielectric material moves from a region of lower to higher electric field). Given that the electric field near our charged balloon (ca. 10 cm radius) was only slightly inhomogeneous and that no deflection was observable in a strongly inhomogeneous field even for water in our re-creation of the Vemulapalli and Kukolich experiment when the droplets formed in an electrically screened region, induced charging, even of insulating liquids, seems to be the only general explanation for all of these observations. Harper suggested that the electrification of insulating liquids during splashing or bubbling is due to the presence of small amounts of dissolved ionic contaminants (11). He showed that this electrification effect (which arises from the disruption of a surface double layer, rather than induced charging) was undetectable for insulating liquids when they were purified. Harper, and later Brindle and Tomlinson (8), argued that the more polar the liquid, the greater the level of ionic contaminants it is likely to contain. Droplet electrification due to trace amounts of ionic contaminants or water appears to be the explanation for our observations and also for the observations of Atkins and Jones, and Umland and Bellama, with the dichloroethylenes: the more polar liquid accommodates significantly higher levels of polar contaminants, separation of which can be induced to produce charged droplets. The label analysis of our sample of dichloromethane gave as maximum limits an evaporation residue of 0.002% and water content 0.02%. For tetrachloroethylene an actual analysis was given, showing an evaporation residue of <0.00004%, chloride at 0.00002%, and water at 0.002%. Remarkably small amounts of contaminants thus seem to have a significant effect on electrification. The calculated charge on the water droplets corresponds to only ca. 3×10^{-10} mol of charge per liter of liquid, and deflection of the polar organic liquids was qualitatively similar to that of water, implying a similar amount of charge, so that separation of only a very small fraction of the listed contaminants would produce the observed

charging. While it is difficult to conceive of electrolyte dissociation in a nonpolar or weakly polar solvent that cannot adequately solvate the dissociated ions, it is possible that dissolved water in these materials facilitates dissociation. These effects probably tend to occur at surfaces, to which the polar impurities would segregate. If polar contaminants accumulate at the liquid–glass interface inside the buret and then at the droplet surface as it forms, the charges are ideally situated to be displaced as the droplet separates.

In summary, all the evidence in this work is consistent with electrical deflection of liquid streams being due to induced charges on the droplets. We have shown that deflection can be caused by homogeneous fields, which can exert no net force on molecular dipoles. We have further shown that when droplets of polar liquids form in an electrically screened fieldfree region, so that they are uncharged, no deflection is detectable in either homogeneous or inhomogeneous fields. The induced charge on the droplets depends on the electric field at the point of droplet separation, and even a very small potential difference (less than 1 V) can induce a significant droplet charge. Therefore it appears quite difficult to detect the relatively weak deflection expected because of the force on molecular dipoles, or dielectrophoresis effects, in an inhomogeneous field. All our observations are completely consistent with the report of Brindle and Tomlinson (8), which in turn reflected an understanding of induced-charge effects dating back well over a century (5, 7).

Regardless of this discussion and the one by Brindle and Tomlinson, should this demonstration be retained in general chemistry texts and lectures? In our opinion, a good demonstration should fulfill the following criteria:

- 1. It should be graphic and directly illustrate a core principle.
- 2. It should rest on science that the instructor comprehends.
- 3. It should be capable of being understood by the target audience with their current level of knowledge.

Droplet stream deflection is certainly graphic, but as shown here, the connection to any principle of molecular polarity is rather distant. Certainly comprehension of the science appears to have been generally lacking, but that can partly be corrected. However, the distinction between polar and nonpolar liquids, which is the intended result of the demonstration, is by no means absolute, as indicated by the ability to deflect nonpolar liquids; and the explanation of the latter effect descends into arcane issues of contamination, which even now are not fully understood. We recommend that use of this demonstration to illustrate the presence of molecular dipole moments be discontinued.

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