Permittivity measurements using adjustable microscale electrode gaps between millimeter-sized spherical electrodes

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This paper presents a technique for measuring the electrical permittivity of liquids and gases using millimeter-sized spherical electrodes with adjustable microscale separation. This technique eliminates the need for wet calibration by using the precise adjustment of electrode separation to remove the inherent errors of parasitic capacitance and electrode polarization. The spherical electrode geometry also eliminates the need for precise parallel adjustment of electrode separation, and enables small-volume, small-electrode-gap measurements where the applied electric field is constrained in a region of well-defined geometry. By further leveraging the fact that spherical electrodes can be obtained with extremely high diametrical accuracy, absolute permittivity measurement accuracies within 1% of the established values has been demonstrated. Finally, the apparatus also enables the creation of nanometer electrode gaps between macroscopic electrodes with precisely controlled separation, which can be used to study the electrical properties of liquids in highly confined states. The electrode gaps created in this manner can be adjusted from 20 nm to 50 μm, in increments of 0.25 nm. © *2008 American Institute of Physics.*
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The measurement of electrical permittivity is a simple method for determining physicochemical properties of liquids and gases. For example, this technique has been used to measure solvent composition in solution chemistry,[1,2] soil moisture content in geological survey,[3] and liquid-gas fraction in chemical production.[4,5] Since permittivity is an intensive property, its determination requires the use of an impedance test cell to measure capacitance, which is then converted to permittivity using a geometrical conversion factor known as the cell constant. The accuracy of this conversion is a key source of error in permittivity measurements.

The relationship between capacitance and permittivity is described by $C = \varepsilon_r \varepsilon_0 / K_{\text{cell}} + C_0(\varepsilon_r, K_{\text{cell}})$, where ε_r is the relative permittivity of the sample, ε_0 is the permittivity of free space, K_{cell} is the cell constant derived from a geometrical model of the electrodes, and C_0 is the parasitic capacitance not described by the model of K_{cell}. Inaccuracy in the determination of ε_r is generally a result of uncertainty in C_0, which is dependent on both the relative permittivity and the geometry of the electrodes and lead wires. Techniques such as the use of guard electrodes can reduce the value of C_0, but cannot eliminate it completely. Other effects, such as electrode polarization,[6] surface absorption, and corrosion of the electrode surface, exacerbate the errors by altering the effective size of the impedance test cell.

Current measurement techniques typically address the uncertainty in C_0, as well as K_{cell}, by calibrating the impedance test cell using a standard liquid with established values of ε_r. The usefulness of this correction is limited since the value of C_0 is dependent on ε_r and K_{cell}. Furthermore, because of electrode polarization effects, the value of K_{cell} is also dependent on the bulk conductivity. The coupling of these properties means that calibration is valid only if the permittivity and conductivity of the sample liquid and the calibration liquid are approximately the same.[7] (In some highly tuned instruments for measuring the permittivity of liquids with very low conductivity, C_0 is exactly proportional to ε_r, and can thus be calibrated in vacuum.[1]) Furthermore, wet calibration is often undesirable because of the additional procedures involved, and because the calibration liquid may irreversibly contaminate the measurement electrodes.

Permittivity measurements without wet calibration generally involve impedance test cells in which the cell constant can be adjusted in a predictable manner in order to remove the effect of the parasitic capacitance. This approach is used to make extremely accurate permittivity and conductivity measurements for the purpose of creating standard tables of material properties.[8–10] Typically, the electrode separation or the overlap area between electrodes is adjusted. In either case, however, a measurement of this kind exhibits a fundamental trade-off between varying the cell constant over a sufficiently large range in order to make an accurate estimate of the permittivity, and minimizing the variation of the parasitic capacitance.

This paper presents a technique for measuring the electrical permittivity of liquids using an adjustable electrode separation to obviate the need for wet calibration by removing the errors caused by parasitic capacitance and electrode polarization. The key aspect of its design is to constrain the applied electric field between closely spaced spherical electrodes. The constrained electric field not only enables measurements of small volumes of liquid but also optimizes the aforementioned trade-off between varying the cell constant and minimizing the change to the parasitic capacitance since small modulations of the electrode separation greatly alter
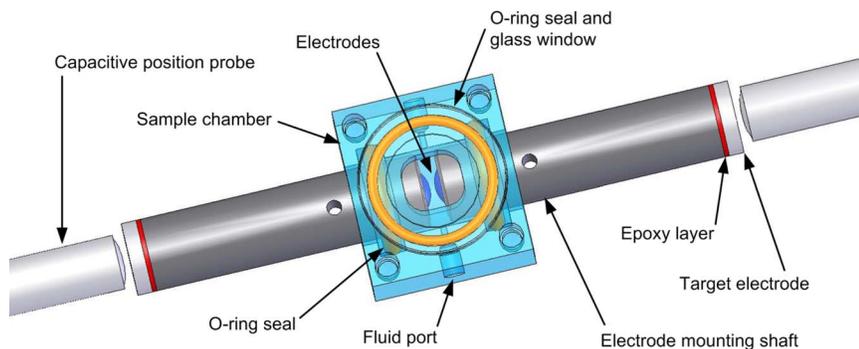
FIG. 1. (Color online) Model of the impedance cell designed to measure capacitance between closely spaced spherical electrodes.

the cell constant, but has little effect on the parasitic capacitance.

The standard approach of adjusting the separation between planar electrodes is problematic since it is mechanically very difficult to maintain electrode parallelism from one separation to the next. This type of variable mechanism has been explored by Wu and Stark.[11] However, without compensating for the electrode parallelism, uncalibrated conductivity measurements yielded errors as high as 80%; although, calibrated measurements were shown to be within 1% of established values. Our experience with creating adjustable gaps between planar electrodes using silicon microfabrication[12] also demonstrated that electrode parallelism errors can easily produce short circuits at small electrode separations. This led to the realization that the electrode parallelism problem can be avoided by using spherical electrodes, since the nearest points between two spheres, or between a sphere and a plane, are by definition tangent to one another independent of the path of approach.

Another key source of error in parallel-plate impedance cells is the tendency for the electric field to concentrate near the edges of the electrodes where the geometry is highly dependent on manufacturing variations. In contrast, spherical electrodes concentrate the electric field at the point of their nearest approach, while the parasitic electric field diminishes in a predictable way toward the equatorial region. Thus, using accurate spherical forms, which are readily obtained, highly repeatable measurements can be made.

For the measurements described in this paper, the electrodes are fabricated using a substrate of silicon-nitride spheres, which have a diameter of 9.5252 mm with a tolerance of ± 0.25 μm (Cerbec Saint Gobain Ceramics: Grade 5 Spheres). The electrode metal is electron-beam deposited on one hemisphere of the silicon-nitride spheres and consists of a 50 nm platinum layer above a 5 nm chromium adhesion layer. The electrodes are mounted in a cylindrical pocket bored into the tip of a stainless-steel shaft shown in Fig. 1. Each electrode sphere is constrained in the shaft using an externally threaded ring nut, which provides a preload force against the shaft and establishes electrical contact between the two bodies. The electrode separation is adjusted using a precision flexure that controls the electrode separation with a resolution of 0.25 nm and a range of 50 μm. The detailed design of the mechanism for adjusting the electrode separation is described elsewhere.[13,14]

The sample material is contained between the spherical electrodes by a stainless-steel chamber sealed using an O-ring around each shaft. The chamber is connected to ground and acts as a guard electrode for the impedance mea-

surement. The O-rings electrically isolate the shaft from the chamber, and act like elastic elements that flex, rather than slide to accommodate the micrometer displacements applied to the electrode shafts. The electrical impedance of the sample material is measured between the two spherical electrodes using an Agilent 8424A *LCR* meter. For measurements in liquid, the amplitude of the applied voltage is 100 mV rms, far below the Faradaic regime where electrolysis can occur.

The shafts containing the electrode spheres are rigidly clamped onto the flexure mechanism and are electrically isolated using an adhesive polyimide film. The relative positions of the electrodes are measured using capacitive displacement probes (Lion Precision) directed at the external face of each shaft, as shown in Fig. 1. The displacement of the electrode separation can be determined by combining measurements from these two sensors. The estimated uncertainty of this measurement is approximately 2 nm.

The capacitance between two spheres where the separation between spheres is significantly smaller than the sphere diameter can be approximated by

$$C = \pi R_e \varepsilon_r \varepsilon_0 \log\left(\frac{2R_e}{x - x_0}\right) + C_0, \tag{1}$$

from Boyer *et al.*,[15] where R_e is the radius of the electrode spheres and C_0 is a constant offset. The electrode separation is represented by $x - x_0$, where x is the measured coordinate from the displacement probes and x_0 is a constant offset. Equation (1) has the convenient property that the inverse of its spatial derivative is proportional to the absolute electrode separation such that

$$\frac{dx}{dC} = -\frac{x - x_0}{\pi R_e \varepsilon_r \varepsilon_0}, \tag{2}$$

where the differentiation has removed C_0. Since both x and C are measurable quantities, the value of ε_r can be determined from the slope of dx/dC as a function of x. Furthermore, the value of x_0 and hence the absolute electrode separation can be determined from the offset of this relation. Experimentally, the value of dx/dC can be approximated using $(x_{n+1} - x_n)/(C_{n+1} - C_n)$, where the location of dx/dC is assumed to be at the midpoint between measurements x_n and x_{n+1}. Substituting this expression for dx/dC into Eq. (2) gives the expression

$$- \pi R_e \varepsilon_0 \left(\frac{x_{n+1} - x_n}{C_{n+1} - C_n} \right) = \frac{(x_{n+1} + x_n)/2 - x_0}{\varepsilon_r}. \tag{3}$$

It is convenient to define the known expression on the left-hand side as y_n, such that the value of ε_r and x_0 can be determined by a linear least squares fit of the ordered pairs of (x_n, y_n) to equations

$$y_n = a + bx_n, \quad \varepsilon_r = \frac{1}{b}, \quad x_0 = \frac{x_{n+1} - x_n}{2} - a\varepsilon_r. \tag{4}$$

Equation (3) also serves to illustrate an important advantage of this technique for measuring permittivity. Since the absolute electrode separation $x - x_0$ is not required, the electrode separation needs only to be known precisely, but not accurately. Furthermore, since x terms appears on both sides of Eq. (3), scale factor errors in x also do not effect the measurement of ε_r. The only requirement is that the electrode separation can be adjusted in precise increments.

The fitting algorithm for determining ε_r and x_0 requires further attention since one of the underlying assumptions of least squares fitting is that the standard deviation of the variables is constant for all values. This assumption is not valid for y_n, since y_n is a function of the differential values of x_n and C_n. In particular, for a fixed change in electrode separation, ΔC is larger at small electrode separations than at large electrode separations. Thus, the standard deviations $\sigma_{\Delta C}$ and σ_y also vary inversely with electrode separation. The variable σ_y can be compensated using weighted least squares (WLS) fitting. In the standard application of this technique, the weight function w is defined as the reciprocal of the variance of the data such that

$$w = \frac{1}{\sigma_y^2}. \tag{5}$$

The uncertainty in ΔC is much greater than the uncertainty in x, which means that the expression for the weight function can be expanded as

$$w_n = \frac{1}{2\sigma_C^2} \left[\frac{\pi \varepsilon_0 R_e \ln\left(\frac{x_{n+1} - x_0}{x_n - x_0} \right)}{y_n} \right]^2. \tag{6}$$

The value of σ_C has been determined empirically to be 5×10^{-14} F for the given experimental conditions.

Since the value of x_0 is initially unknown, an initial guess for x_0 can be obtained using a simple least squares fit. Estimates for x_0 can then be improved using iterative application of the WLS fitting procedure. Three iterations are typically sufficient for x_0 to converge to within 1 nm. The value for ε_r can alternatively be extracted using direct non-linear fitting to Eq. (1). However, this procedure is less robust to noise than the WLS technique.

Measured values of x_n and y_n for isopropanol, methanol, and 0.1 mM potassium-chloride solution are shown in Fig. 2. The 0.1 mM potassium-chloride solution is used in place of pure water in order to obtain samples with a repeatable concentration of impurities. The measurements are made beginning at an electrode separation of 15 μm and decremented in steps of 0.5 μm until contact. The experimental uncertainty along the y axis, σ_y, can be estimated using Eqs. (5) and (6). These values are typically less than 50 nm, and therefore not shown as error bars in Fig. 2. The capacitance measurements
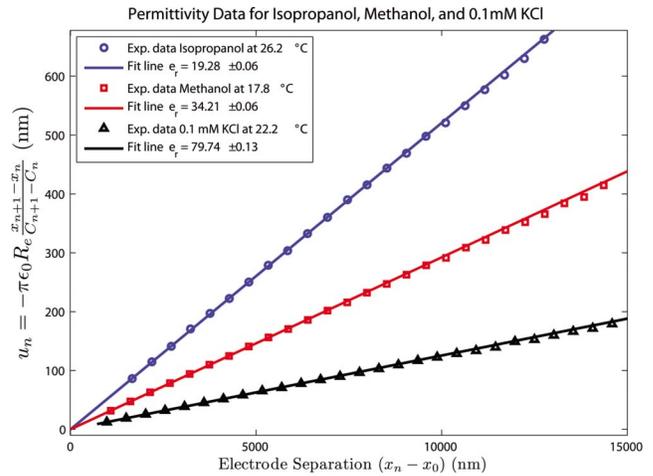

FIG. 2. (Color online) Calibration-free determination of the relative permittivity of isopropanol, methanol, and a 0.1 mM KCl solution.

are performed at 120 kHz, where the sample impedance is dominated by the bulk liquid, which can be considered to be a uniformly polarizable media. Electrode polarization, which is caused by the electrical double layer at the surface of the electrode, can be considered a constant parasitic that is removed with each ΔC measurement. Data points from below 1 μm are also not used in the fitting in order to avoid interactions between the double layers on each electrode, which are generally considered to be less than 100 nm thick.

The measured ε_r for isopropanol at 26.2 °C, methanol at 17.8 °C, and a 0.1 mM KCl solution at 22.2 °C are 19.28 ± 0.06, 34.21 ± 0.06, and 79.74 ± 0.13, respectively. The established ε_r values for these substances at the specified temperatures are 19.19, 34.06, and 79.26.[16] Thus, the technique described here achieves a measurement error of less than 1% without wet calibration. The measured results show permittivities that are consistently greater than the established values by approximately 0.5%. Additionally, the measured data points show a small, but noticeable droop from the fitted line at larger electrode separation. These errors are an artifact of the global geometrical shape of the electrodes, which not only include a sphere but also the cylindrical shaft and ring nut assembly shown in Fig. 1. This hypothesis is confirmed by modeling the measurement with an additional parallel-plate capacitor. The results show the expected error range and residue profile. These simulations and validation with experimental results are further detailed elsewhere.[13]

Repeated measurements of the relative permittivity of pure methanol at several different temperatures are shown in Fig. 3. Each data point is the mean of a set 10 to 20 repeated measurements. The error bars indicate the standard deviation of each data set. The measured results are well within $\pm 1\%$ of the established value at this temperature. In fact, the standard deviation of the measurement is approximately 0.1% of the mean. From this plot, it is clear that the measurements show a systematic offset, which is caused by the aforementioned global shape of the electrode.

A key capability of the apparatus shown in Fig. 1 is the ability to create small gaps between macroscopic electrodes with precisely adjustable separation. The minimum electrode separation is limited by the surface roughness of the elec-
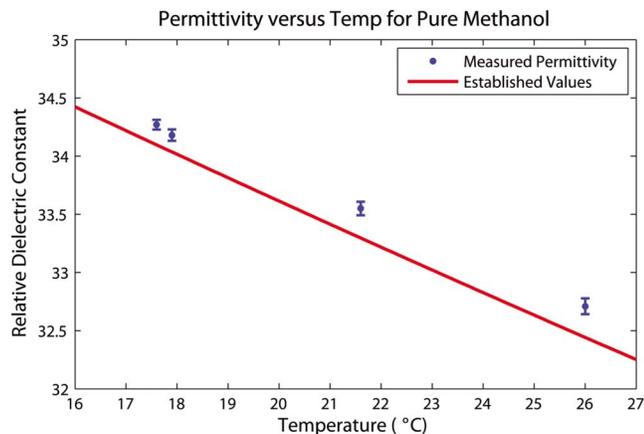
FIG. 3. (Color online) Repeated relative permittivity of pure methanol measured at several different temperatures.

trodes and the presence of dust particles adsorbed onto the electrode surfaces. Measurements of nanometer gaps in air have been achieved when the electrodes are assembled without the sample chamber, and cleaned using isopropanol and a nitrogen blast. The results from these studies are shown in Fig. 4, where the electrode separation is decremented in 1 nm steps. Above 30 nm separation, $y(x)$ follows the straight-line behavior observed at larger separations. Below 30 nm separation, the results begin to deviate from the straight-line model. This deviation can be explained using the surface roughness model developed by Boyer *et al.*[15] The surface model breaks down below 20 nm when the electrode separation is smaller than the peak-to-valley electrode roughness and the instantaneous $y(x)$ slope begins to decrease,
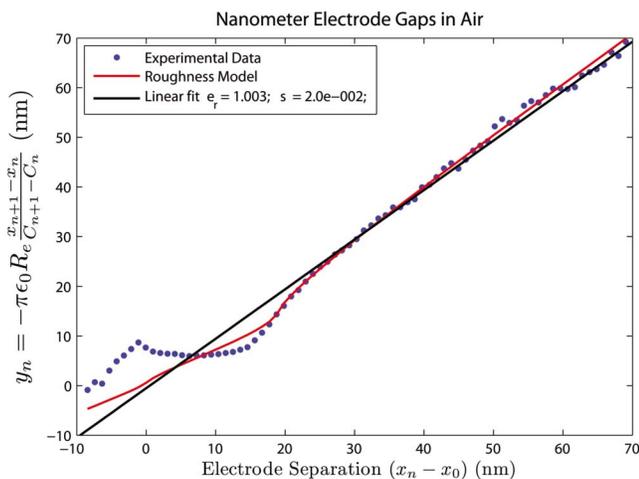

FIG. 4. (Color online) Transformed $C(x)$ data at small electrode gaps in air with overlayed surface roughness model.

signaling an increased electrical permittivity. This behavior is believed to be a result of bound water layers at the surface of the electrodes. At even smaller separations, the surface-bound water layer can be penetrated to create a direct conduction path. This measurement has been repeated using multiple excitation signals ranging from 100 mV to 1 V rms. No difference was observed between the results, confirming that this measurement is independent of electrostatic attraction between the electrodes.

In summary, a method for measuring electrical permittivity between spherical electrodes with adjustable separation is described. This technique enables accurate measurements of the electrical permittivity without calibration using a standard liquid. Initial permittivity measurements produced results within $\pm 1\%$ of established values. This technique can also be used to measure electrical conductivity with a similar degree of accuracy without wet calibration. The spherical electrode design also enables tens of nanometer electrode separation to be created without the parallelism errors that affected previous methods. The combination of accurate permittivity measurements and nanometer electrode separation could be used to study the property of liquids under high levels of geometric confinement.

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