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A MILLI-FLUIDIC DEVICE FOR ELECTRICAL IMPEDANCE SPECTROSCOPY OF COMPLEX LIQUIDS

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ABSTRACT

Rapid characterization of complex liquids such as solutions, mixtures, dispersions, and emulsions is useful in a variety of industrial applications ranging from cosmetics, pharmaceuticals, to petroleum production. An electrical impedance spectroscopy (EIS) based technique for rapidly determining the characteristics of liquid-liquid mixtures is presented in this study. A milli-fluidic liquid film impedance measurement cell is developed employing 3D printing technology. The cell is tested using glycerol-water mixtures followed by castor oil in water emulsion samples. Frequency response analysis and equivalent circuit modeling are performed on each sample to quantify the emulsion properties in the form of equivalent capacitance and resistance. The developed technique provides an inexpensive and disposable, yet robust experimental platform for applying EIS to investigation and rapid estimation of different properties of oil-water emulsions.

INTRODUCTION

Complex liquids such as liquid-liquid-mixtures, colloidal dispersions, and emulsions are encountered in a variety of industrial applications including petroleum production, food processing, biomedical processes, cosmetics and pharmaceuticals, to name a few. Rapid assessment of the stability of such multicomponent and multiphase liquids is an important issue faced in these applications. For instance, rapid sensing of stability and degree of emulsification is crucial for optimization of emulsification and de-emulsification processes, as well as monitoring the phase behavior of emulsions [1–3]. Phenomena such as flocculation, coalescence and Ostwald ripening can affect the electrical response of these liquids in different ways depending on the colloidal properties of these systems [4–6]. The effective electrical properties of colloidal systems are manifestations of the electrical properties of the components, as well as the shapes of individual dispersed elements and the topological structure of the dispersed phase in the host medium [5, 6]. Changes in the volume fraction of the components and the structure of the dispersed phase may be captured through variations of capacitance and resistance. This makes electrical impedance scpectroscopy (EIS) not only a means for studying the physics of emulsions but also a technique which can be used in designing diagnostic tools for rapid sensing of complex systems [7].

Studying dielectric properties of emulsions started in early 20th century with works of Maxwell, Garnett and Wagner [8, 9] who proposed models for dielectric properties of homogenous mixtures. The model, known as the “effective medium theory”, is valid for very low concentrations of the disperse phase (below %2). Later, Bruggeman [10], Hanai [11], and Boyle [12] proposed models for dielectric properties of homogenous composite systems with higher concentrations of the disperse phase. However, those models fail when the colloidal system phase behavior deviates from the homogeneity assumption. In a more recent work, Skodvin and Sjoblom [6] developed models for dielectric properties of water-in-oil (W/O) emulsions assuming that dispersed drops coalesce to form larger spheres or flocculate to form spheroids. They studied the effect of shape factor of the spheroids on dielectric properties.

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Experimentally, Sjoblom et. al. [4] used shear as a means to disintegrate the flocculated droplets of water-in-oil emulsions, and studied the effect of the changed colloidal structure on the EIS response of the system. DC electric fields and temperature can also affect the electrical properties of the complex system components as well as the colloidal structure [13, 14]. Numerical simulation of dielectric behavior of composite media has also been attempted by several researchers [15, 16] who investigated the frequency-dependent dielectric response of dispersions containing evenly distributed inclusions in composite dielectrics. Dielectric spectroscopy of emulsions has been mostly performed on water-in-oil (W/O) emulsions to avoid the effects of large electrode surface polarization caused by ionic emulsifying agents [5]. However, Hanai et. al. [11] showed that permittivity and conductivity of oil-in-water (O/W) emulsions with ionic surfactants is a weak function of frequency above approximately 10 kHz.

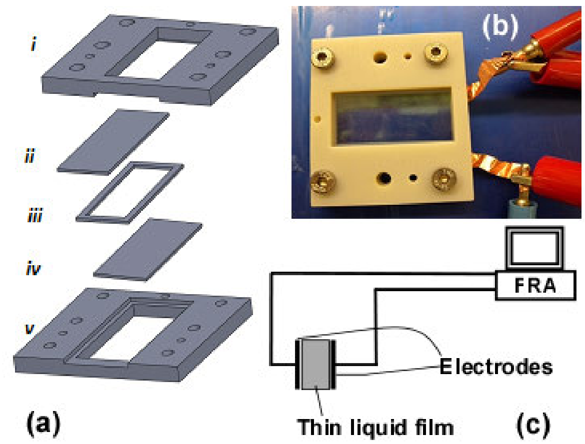

FIGURE 1. (a) Drawing of the sample holders: *i*-top cover, *ii*-top electrode (ITO coated glass), *iii*-spacer (PDMS or Teflon), *iv*-bottom electrode (ITO coated glass), *v*-bottom cover. (b) Photograph of the test cell. (c) Schematic of the experimental setup.

The high sensitivity of EIS imposes serious demands on the experimental setups used for impedance measurements. Impedance cells have to be carefully designed and calibrated to ensure good contact of the sample with electrodes, reproducible wetting of the electrodes with samples, low interference with the samples, extremely clean surfaces of the cell, and no contamination of the electrodes. These limitations have traditionally restricted EIS to laboratory environments, and prevented its rapid proliferation into industrial diagnostics of liquids. Large-scale impedance measurement requires cells that are expensive to fabricate, are prone to fouling by the fluids, require cleaning and maintenance, all of which adversely influence its reliability [17]. On the other hand, our earlier studies [18] showed that implementing impedance measurement at a microfluidic length scale, though highly sensitive, requires extreme care in fabricating and handling the devices. The microfluidic devices are expensive to fabricate, and foul readily when subjected to industrially relevant fluids. In this article, we present a milli-fluidic (as opposed to micro-fluidic) device for impedance spectroscopy of oil-in-water emulsions. The core impedance cell, being made using 3D printing technology, is inexpensive and disposable, thus avoiding its scope of being fouled by other contaminants during repeated use. Our study shows that miniaturization of impedance measurement cells is possible, and valuable information about the sample properties (such as oil/water content) is attainable using a simple parallel-plate configuration, using disposable measurement modules. We report the performance of the cell as an EIS cell using glycerol-water mixtures followed by castor oil-in-water emulsions as model complex liquids. The results are compared to existing theoretical models describing the electrical behavior of composite systems.

MATERIALS AND METHODS

Experimental setup

Figures 1-a to 1-c show the experimental setup. The sample holders were designed with SolidWorks and fabricated with Objet Eden350/350V 3D printer. In the reported experiments, two indium-tin oxide (ITO) coated glass chips (Prazisions Glass & Optik) were used as electrodes, since we intended to set up a transparent cell to observe the liquid film using a microscope. The electrodes can be made from other materials as well. The ITO coated surfaces of the glass were conductive. The electrodes enclose a 500 μm film in a 45 mm × 20 mm parallel-plate capacitor configuration. The electrodes were connected to the frequency response analyzer, FRA (Solartron 1260) for two-electrode electrical impedance spectroscopy using copper strips. A sinusoidal electric signal with an amplitude of 25mV was applied to the cell, and frequency was swept between 10 MHz to 1 Hz. The typical semi-circular Nyquist plot representing the relaxation behavior of emulsions was observed in this range. The accuracy of the impedance measurement at each single frequency was %0.1 (according to Solartron 1260 gain phase analyzer specifications), and the effect of possible relaxation-related errors in the frequency range of the measurements is reflected in the error bars of the plots.

Equivalent circuit modeling

The frequency response of the emulsions were fitted to a simplified Randles circuit [19] ($R_s - R|C$) including a resistor (R_s) in series with a parallel RC circuit. The resistance of the leads and electrodes (R_s) was constant (20 Ω) in all experiments. Complex Nonlinear Least Square (CNLS) fitting scheme [17] (embedded in frequency response analysis (FRA) software, ZPlot) was used for fitting the experimental data to the model circuit.

Sample preparation

The glycerol-water mixtures were obtained by vigorous stirring of different volume fractions of glycerol (Sigma Aldrich) in 10^{-4} M solutions of KCl in water. Glycerol and water form clear, well mixed and homogenous mixtures. The O/W emulsions were prepared by homogenizing different volume fractions (%0.1, %0.5, %1, %5, %10) of castor oil (Sigma-Aldrich) in 10^{-4} M KCl solutions using IKA T25 Digital Ultra-Turrax homogenizer. Emulsion samples were homogenized at 1300 rpm for 20 minutes with the tip of the homogenizer placed 2 cm above the bottom of 1000 mL beakers (600 mL of the emulsions were prepared in the beakers). Experiments were performed while the emulsions were fresh and no observable phase separation occurred within the first 30 - 45 minutes. The experiments done with emulsions are intended to study the impedance behavior in oil-in-water emulsions rather than water-in-oil emulsions. Hence, the oil content is kept below 10%. Electrode polarization in low frequencies make EIS of conductive media difficult [5] and as mentioned in the introduction section, with higher oil content, particularly when stable water in oil emulsions are formed, the measurement technique produces more reliable and reproducible results, since the oil continuous system impedance is resolved by the impedance spectroscopy technique with greater reliability. Our study shows that the developed device can be used for characterization of O/W emulsions in the frequency range of interest and produce results in reasonable agreement with theoretical values.The oil content below 10% also allows preparation of relatively stable emulsions by means of homogenization and without using surfactants. Higher oil content would need surfactants to stabilize the emulsions. We deliberately conducted the study with pure two-component emulsions, to enable facile comparison of the experimental results with theoretical models, so that we could assess the accuracy and reliability of the technique.

Droplet size measurement

For oil-in-water emulsion samples, the size distribution of the oil droplets dispersed in water was acquired by light scattering measurements using the Mastersizer 2000 (Malvern Instruments).

RESULTS AND DISCUSSION

Figure 2 shows the frequency response (Nyquist plot) of the glycerol-water samples obtained using the developed impedance cell. The circles show the experimental data, whereas the lines depict the equivalent circuit Nyquist curves fitted to the measurements. It is observed in Figure 2 that the equivalent $R-R|C$

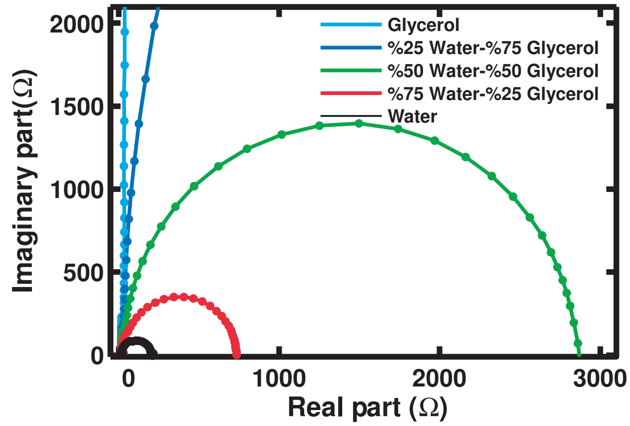

FIGURE 2. Nyquist plot of glycerol-water samples. The circles represent the measurements, whereas the lines depict the equivalent circuit Nyquist curves fitted to the experimental data.

circuit represents a good model for the experimental data. As the Glycerol percentage is increased in the mixture, the frequency response behavior becomes increasingly capacitive.

Figure 3-a depicts the capacitance of glycerol-water samples with different volume fractions of glycerol. The results are compared to the capacitance obtained from the effective medium permittivity expression proposed by Maxwell, Wagner and Garnett ([8,9])

$$\epsilon_{eff} = \epsilon_{medium}\left(1+\phi\frac{3(\epsilon_{disperse}-\epsilon_{medium})}{\epsilon_{effective}(1-\phi)+\epsilon_{medium}(2+\phi)}\right) \quad (1)$$

where ϕ is the glycerol volume fraction in the mixture. As expected for a well-mixed homogenous system, the Maxwell-Garnett model predicts the dielectric behavior of the system very well and the experimental results from the developed device show good agreement with the model. The resistive behavior of glycerol-water samples are shown in figure 3-b. The results are compared to the data provided by Glycerine Producers' Association [20] for conductivity of glycerol-water solutions showing a good agreement between the two sets of experimental data. In figures 3-a and -b, it is demonstrated that the developed device provides correct estimates for the electrical properties of the homogeneous system of water and glycerol mixtures.

The next set of experiments were conducted on castor oil in water emulsions. Figure 4-a illustrates the capacitance of the emulsions of castor oil in aqueous 10^{-4} M KCl solutions. It is observed that adding oil to water results in a decrease in the effective dielectric constant and capacitance of the samples. In figure 4-a, the experimental capacitance obtained by fitting the measurements to the $R_s-R|C$ circuit is compared to the capacitance

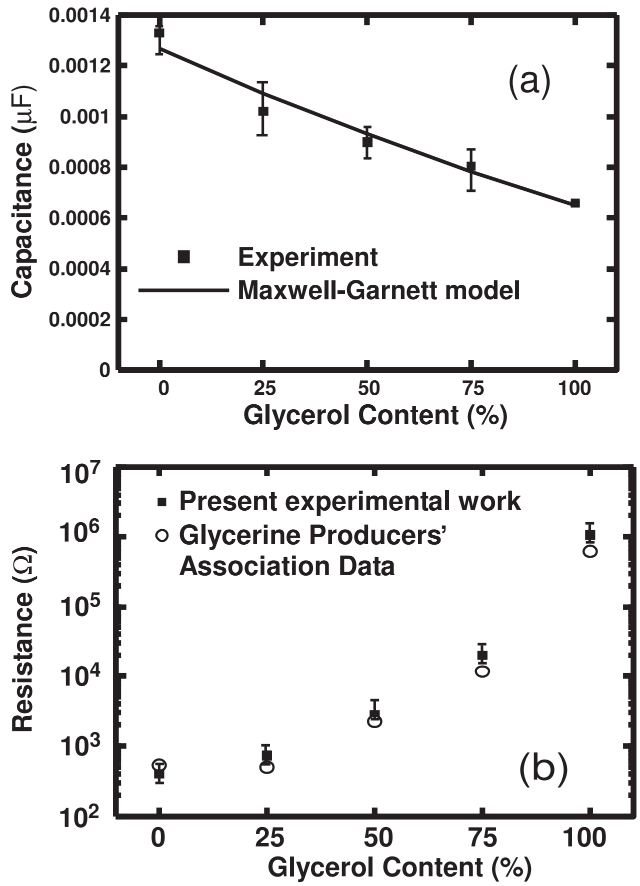

FIGURE 3. (a) Capacitance of glycerol-water mixtures with different volume fractions of glycerol. The squares show the measurements fitted to the equivalent circuit model and the solid line depicts Maxwell-Garnett's model. (b) Resistance of glycerol-water mixtures. The squares show the measurements fitted to the equivalent circuit model in the present work and the open circles depict the results from reference [20].

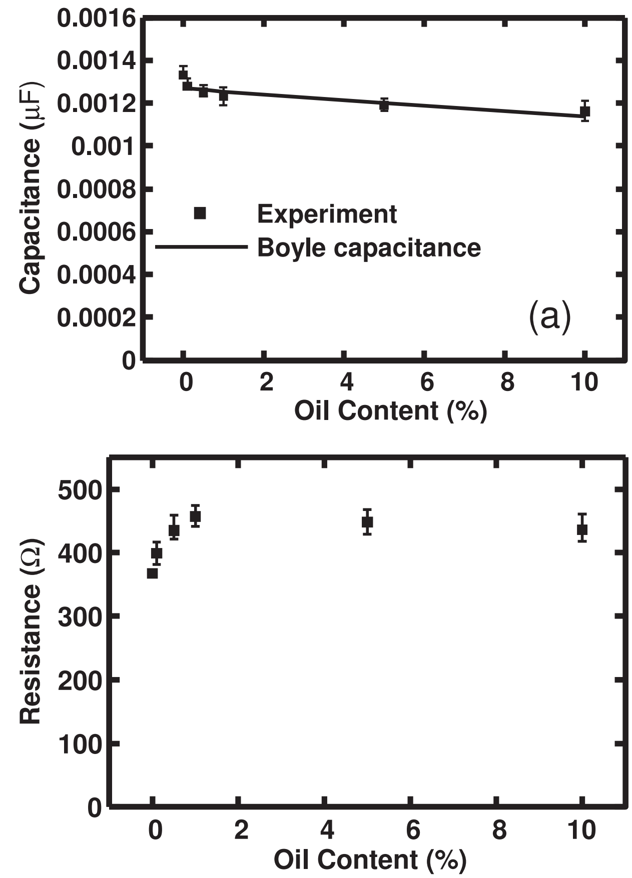

FIGURE 4. (a) Capacitance of castor oil in KCl-water emulsions with different volume fractions of castor oil. The squares show the capacitance values obtained from the experimental measurements fitted to the equivalent circuit model and the solid line depicts Boyle Capacitance model predictions (eq. 2). (b) Resistance of castor oil in KCl-water emulsions. The maximum resistance is observed at about 1% castor oil.

of the emulsions obtained from Boyle effective dielectric:

$$1-\phi = \frac{\epsilon_{eff}-\epsilon_{disperse}}{\epsilon_{medium}-\epsilon_{disperse}}\left(\frac{\epsilon_{medium}}{\epsilon_{eff}}\right)^{A_a} \qquad (2)$$

where ϕ is the oil volume fraction, and the exponent A_a is the depolarization factor of spheroidal flocs which is considered 0.1 for a typical spheroid with axial ratio between 0.2 and 0.5 [6].

The effective permittivity is obtained by Newton-Raphson iterative solution of equation 2. Since the emulsions are fresh and homogenous, the measurements are expected to be in agreement with Boyle's model. Figure 4-a demonstrates that the experiments show acceptable agreement with the model. By comparing figures 3 and 4, it is observed that the dielectric behavior of the clean system (glycerol-water) is different from that of the two-phase heterogenous system (O/W emulsions) with dispersed droplets in the host medium. The difference can be attributed to the fact that in a heterogenous system, the electric field is distorted in the boundaries of the two phases. Therefore, the dielectric properties can be affected not only by the oil/water ratio, but also by the size of the oil drops (the size distribution of the oil drops is shown in figure 5 which shows a 10 μm peak for all emulsions prepared). On the other hand, in a clean system, there is no heterogeneity and the dielectric behavior of the system is only defined by the glycerol/water ratio. Figure 4-b shows the resistance of the samples obtained from the experiments. As shown in the figure, a maximum resistance is observed around %1 castor oil volume fraction. While electrode polarization is

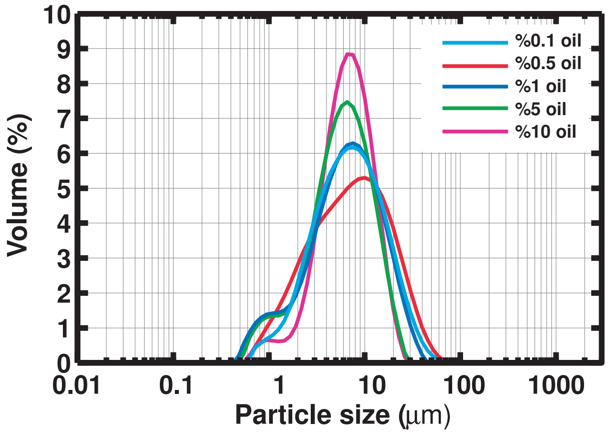

FIGURE 5. Size distribution of the oil droplets of castor oil dispersed in water, for different oil/water ratios.

a barrier in EIS of oil-in-water emulsions [5] (specially in low frequencies), the above-mentioned results show that the developed device can be used for characterization of O/W emulsions in the frequency range of interest and produce results in accordance with theoretical models for both homogeneous (glycerol-water) and heterogeneous (emulsified two-phase) liquid systems.

The variations of resistance and capacitance of the tested samples indicate the ability of the impedance measurement system to provide a facile interface for characterization of these complex fluid systems. The entire system can be packaged and calibrated for efficient quality control of different types of mixtures and emulsions. The key feature of the experimental system is that the manufacturing process employed ensures that the impedance of the cells manufactured using the 3D printing processes practically remained constant over the different cells fabricated and tested. The sample loading in the cell was quite straightforward, involving injecting liquids using a syringe into the cell. The only care needed is that the trapped gas bubbles are not present. The sample loading process can be further improved using automated sample loaders.

Concluding Remarks

In this article, a milli-fluidic impedance measurement cell fabricated employing 3D printing technology is used for electrical impedance spectroscopy of complex liquids. The device provides a simple yet robust experimental platform for rapid EIS of the samples. The technique was applied to glycerol-water mixtures as well as castor oil-in-water emulsions. The capacitance and resistance of the samples were quantified by fitting the experimental data to an equivalent circuit by means of complex nonlinear least squares (CNLS) fitting. The measurements show acceptable agreement with the existing models of dielectric properties of complex liquids and homogeneous mixtures showing that the reported device can be used for further characterization of physics of emulsions including stability and phase change dynamics.

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