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Dielectric behavior of oil-water emulsions during phase separation probed by electrical impedance spectroscopy

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Abstract

Electrical impedance spectroscopy (EIS) is applied to studying the stability and phase behavior of oil-water emulsions. The method involves EIS on 500-micron-thick samples of emulsions in a parallel-plate capacitor test cell. The frequency response data is fitted to an equivalent circuit model to estimate the electrical impedance of the samples. The technique is used for investigating the capacitance and resistance of emulsions during phase separation. A theoretical explanation based on the capacitance of the emulsion layer is provided to understand the reason behind the variation in the dielectric constant of the samples during phase separation. It is observed that creaming and sedimentation can be captured as a permittivity decay, so permittivity measurements can be utilized to sense phase separation. The technique is shown to be more effective for oil-in-water emulsions rather than water-in-oil ones.

Keywords: phase separation monitoring, liquid system sensing, emulsion, electrical impedance spectroscopy, equivalent circuit, milli-fluidic

1. Introduction

Characterization of emulsions and sensing emulsion stability are crucial for a variety of industries ranging from cosmetics\cite{1} and pharmaceutical\cite{2}, to the petroleum industry\cite{3,4}. The structure of the dispersed phase affects electrical properties of emulsions\cite{5,6,7,8,9}. Therefore, variations in electrical properties of emulsions in different frequency ranges can be used for detecting changes in the structure and arrangement of the dispersed phase. This makes electrical (electrochemical) impedance spectroscopy (EIS) a sensing technique and a powerful experimental tool for investigating emulsion physics as well as characterization and stability sensing of emulsions\cite{10,11,9}.

Dielectric spectroscopy has been applied to investigation of the structure of emulsions. Sjoblom et. al. \cite{5} investigated the effect of flocculation on dielectric properties in water-in-oil emulsions by means of shear-driven droplet floc disintegration. They also studied the effect of water fraction and salt concentration on static and high-frequency permittivity of water-in-oil (W/O) emulsions. The effect of temperature and high DC electric fields on percolation of W/O microemulsions has also been studied\cite{6}. More recently, measurement of dielectric properties has been applied to water-in-crude-oil emulsions\cite{12,4} and multiple emulsion production \cite{3}. Theoretical explanation of dielectric properties of heterogenous media has been attempted by researchers in different areas such as colloidal science, solid electronics and material science\cite{13,11,14,15}. The initial models are based on Maxwell-Garnett’s\cite{16} effective medium theory for homogenous distribution of the dispersed phase and are valid for low concentrations (below 2%). Bruggeman\cite{17}, Hanai\cite{18}, and Boyle\cite{8} proposed models for higher concentrations of the dispersed phase in homogenous emulsions. Their studies show that coagulation effects may cause drastic deviations from the homogeneity assumption. Skodvin

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and Sjoblom [11] modified homogenous mixture dielectric models by taking into account flocculation of drops to bigger dispersed micro-scale spherical drops or spheroidal flocs in W/O emulsions. However, electrical response resulting from flocculation that not only results in floc formation, but also in phase separation (creaming/sedimentation), has not been analytically formulated. More recently, critical micelle concentration (CMC) [19] measurement [20], micro-scale phase inversion [21], and mobilization of ions [22] have been experimentally studied with EIS. However, larger scale phase separation in the form of creaming/sedimentation has not been experimentally probed. In this work, the developed EIS test fixture, along with the droplet size of the prepared samples, allows studying macro-scale phase separation of emulsions. The phenomenon is also analytically investigated and a decay function is proposed for modeling the separation rate.

In this paper, capacitance and resistance of oil-water emulsions are experimentally and analytically investigated during phase separation. Different dosages of emulsifier agents as well as stirring and homogenization (i.e. high-frequency stirring) are used to make the oil-water emulsions stable for approximately 10 hours before phase separation (checked by visual observation of the bulk samples). The effect of emulsification degree and stability on the impedance of the samples over time is studied. EIS and equivalent circuit modeling [23] is performed on each sample to find the effective resistance (dielectric loss) and capacitance (dielectric constant). Ripening of the oil-water emulsions results in topological change and permittivity variation in the samples during phase separation, which is modeled by equivalent circuit analogy.

2. Materials and Methods

The experiments are performed using a test fixture fabricated according to the procedure explained in the authors’ previous works [24, 25]. In the test setup [24, 25], the samples are enclosed between two rectangular electrodes to form a 45mm × 20mm parallel-plate capacitor configuration with a 500µm-thick film between the two electrodes. The sample thickness is chosen based on the observation made of the droplet size in the prepared oil-water samples. The electrodes are connected to the frequency response analyzer, FRA (Solartron 1260), and a sinusoidal electric signal with a 25mV amplitude is applied to them with frequency swept from 10MHz to 1Hz (the 10MHz-1kHz subset is used for equivalent circuit modeling as electrode polarization occurred at \(~1kHz\)). A simplified Randles [26] circuit (\(R_s\)−\(R|C\)) corrected for the resistance of the leads and electrodes is fitted to the frequency response of the samples using the Complex Nonlinear Least Square (CNLS) method [23]. More details of the methodology for sample preparation, EIS measurements, and equivalent circuit modeling are explained in our previous work [24, 25]. While EIS has already been proven powerful in analyzing micro-scale physics of multiphase media [10, 11], the experimental approach taken in this study is very effective in determining effective electrical properties (resistance and capacitance) of miscible liquid-liquid mixtures as well as oil-water emulsions reflecting macro-scale phase behavior. The technique is validated using liquids with known electrical properties [24, 25]. In this work, decane-water (dielectric constant 2 and 80, respectively) emulsions, stabilized with surfactants Tween80 (soluble in water) and Tegopren700 (soluble in oil), are prepared to different degrees of emulsification. To achieve different degrees of emulsification, different dosages of surfactant, 0 to 20CMC (Critical Micelle Concentration [19]), and high-frequency homogenization are used. The samples are stirred at 700rpm while adding the dispersed phase dropwise. Some are also homogenized at 13000rpm after stirring. Malvern Mastersizer 2000 is used to measure the droplet size distribution. The median droplet size of fresh unhomogenized and homogenized samples (with or without surfactant) are approximately 90µm and 9µm respectively. Homogenization and different surfactant dosages are used to achieve emulsions with different stabilities so that the effect of stability on dielectric properties could be investigated over time as phase separation occurred. EIS measurements are carried out on each sample over approximately a ten-hour period.

3. Results and Discussion

Over time, the emulsion ripens due to flocculation/coalescence of the oil drops. Larger drops and flocs move towards the upper electrode and are expected to be compressed to spheroids under the influence of buoyancy force. This is depicted in figure 1. Figure 1-a schematically shows the fresh emulsion and figures 1-b to 1-d show the process of
coalescence and creaming, up to the point of phase separation. This behavior can be described in terms of the Bond number [19], represented for spherical droplets (or spheroids of small aspect ratios) by:

\[
Bo = \frac{\text{net gravitational force}}{\text{interfacial forces}} = \frac{\Delta \rho V g}{2 \gamma / R} \approx \frac{\Delta \rho g R^2}{\gamma}
\]  

where \(\Delta \rho\) is the density difference between the dispersed phase and the host medium, \(V\) is the drop volume, \(R\) is the drop radius and \(\gamma\) is the interfacial tension between the two phases. The rightmost term in equation (1) is the ratio of buoyancy force per unit area to the pressure caused by interfacial tension, which is proportional to \(R^2\). Therefore, as the droplet size increases due to coalescence of smaller droplets, the buoyancy force becomes increasingly dominant, resulting in creaming. As schematically depicted in figure 1, coalescence of all droplets is unlikely. Thus, the unseparated dispersed phase progressively becomes more stable, and takes a longer time to phase segregate. Figure 1 also schematically shows that the permittivity of the well-emulsified system can be described by the Boyle model [8] (which is close to parallel-capacitor model for spherical dispersed droplets with significantly different dielectric constant than the medium [24]), and the separated system is close to a serial-capacitor configuration.

\[
\text{(a)} \quad \text{(b)} \quad \text{(c)} \quad \text{(d)}
\]

Figure 1: Schematic of coalescence, partial phase separation and creaming of the dispersed phase. (a) Fresh emulsion. (b) Coalescence of droplets. (c) Large droplets move upwards under buoyancy force and are deformed to spheroids when touching the upper electrode. (d) The separated phase creams at the upper electrode and the system approaches the laminar (serial capacitors) structure.

To experimentally investigate permittivity and resistivity of emulsions during phase separation, oil-water emulsions are allowed to rest and EIS is done approximately every 20 minutes for around 10 hours. Figure 2 shows the Nyquist diagram of 5% decane-in-water emulsion over time. It is observed that the EIS response of the system changes over time. The capacitance \((C)\) and resistance \((R)\) of the emulsion sample is obtained by using equivalent circuit modeling. The variation of the parameters \(R\) and \(C\) during phase separation is depicted in figure 3. It is observed that capacitance of the emulsions decay from a well-emulsified value described by the Boyle model to close to the minimum (serial-capacitor) value. Similar decay is reported in the literature for an experiment studying micro-scale agglomeration of ion carriers [22] where the end capacitance and the decay rate depended on the charge distribution of the micro-spheres. In the present work, however, the dominant phenomenon determining the capacitance decay is the bulk movement and gradual separation of the dispersed phase. As it can be seen in figure 3, the emulsions with higher surfactant dosages are better emulsified and their capacitance converges to a value higher than the serial-capacitor due to stability of the oil present in the water phase and vice versa. The resistance of the emulsions do not show any significant change except for the 0-surfactant case where an increase in the resistance is observed as phase separation became complete. This is attributed to the fact that in the emulsions with surfactant, enough water remains stable in the oil-rich phase to maintain current paths between the electrodes, whereas in the emulsion with 0 surfactant, water is separated to a higher extent. In other words, while permittivity is a strong function of the geometric structure and topology of the complex medium, conductivity remains almost unchanged unless water drops (electric current paths) are completely separated from the oil-rich layer (thus completely preventing
Figure 2: Nyquist curves of the EIS experiment with 5% decane-salt water (KCl $10^{-4}$M) emulsion (homogenized, no surfactant) as phase separation occurs. Symbols and lines represent measurements and equivalent circuit model respectively. Each round of frequency analysis starts at the highest frequency (10MHz) and ends at 1Hz. The $R_s - R_C$ circuit modeling is implemented for the 1MHz-1kHz range before polarization (linear constant-phase fit) becomes dominant.

Figure 3: Capacitance (top) and resistance (bottom) of homogenized 5% decane-salt water (KCl $10^{-4}$M) emulsions versus time for different surfactant dosages as the emulsions undergo phase separation. It is observed that the capacitance of the emulsions that are more stable (with higher surfactant dosages) decay from the well-emulsified value to a value larger than the serial capacitance while the emulsion with 0 surfactant, decays to a value very close to the serial capacitance. The dashed and dash-dot lines show exponential decay functions fitted to the systems’ behavior. Error bars show standard deviation multiplied by 2 (95% confidence).
any percolation of current). The same set of experiments are performed on unhomogenized emulsions. Unlike the previous set of samples, these emulsions are not homogenized after stirring at 700rpm. The capacitance and resistance of these systems over time are shown in figure 4. The behavior of these emulsions are similar to the homogenized ones but the emulsion with no surfactant has already separated when the first EIS test is carried out, and the resistance increase in the unhomogenized 0-surfactant emulsion happens sooner compared to the homogenized sample.

Figure 4: Capacitance (top) and resistance (bottom) of unhomogenized 5% decane-salt water (KCl $10^{-4}$M) emulsions versus time for different surfactant dosages as the emulsions undergo phase separation. It is observed that the capacitance of the emulsions that are more stable (with higher surfactant dosages) decay from the well-emulsified value to a value larger than the serial capacitance while the emulsion with 0 surfactant, decays to a value very close to the serial capacitance. The dashed and dash-dot lines show exponential decay functions fitted to the systems’ behavior. Error bars show standard deviation multiplied by 2 (95% confidence).

The time evolution EIS experiment is also performed on decane-water emulsions with different oil contents. To be able to observe phase separation over time, oil-rich emulsions are stabilized with 1CMC of Tegopren700 dissolved in the oil phase before adding water and homogenization at 13000rpm. Tegopren700 is added to the oil phase of all samples in this experiment for consistency. The permittivity decay is observed in all cases and is depicted in figure 5. It is observed that the higher the oil content, the lower the initial permittivity, the more difficult it is to detect phase separation by using permittivity decay. This is attributed to the fact that dielectric constant of oil (usually below 10) is lower than water (around 80), therefore, the permittivity decay is best observed in oil-in-water emulsions rather than water-in-oil ones. Stability of emulsions is quantitatively described by fitting an exponential decay function to the experimentally measured capacitance. The decay function is:

$$C(t) - C_f = (C_0 - C_f)e^{-mt}$$

where $C(t)$ is the capacitance of the emulsions as a function of time, $C_0$ and $C_f$ are the initial and final capacitances, and $m$ is the decay parameter. The fitted decay functions are depicted in figures 3 and 4 with dotted and dash-dot lines. In the homogenized emulsions, the decay parameter, $m$, of the 20, 1 and 0CMC emulsions are 0.04, 0.10, and 0.26, respectively. In other words, the permittivity decay or phase separation rate of the 0CMC emulsion is estimated to be 3 times faster than that of the 1CMC emulsion, and the same parameter of the 1CMC emulsion is approximately 3
times larger than that of the 20CMC. For unhomogenized emulsions, the decay parameter of the 20 and 1CMC cases are 0.06 and 0.15, respectively. The decay parameter indicates that and phase separation in 1CMC emulsion occurs approximately 2.5 times faster than the 20CMC emulsion. The decay function is not fitted to the 0CMC unhomogenized sample as separation occurs before the measurement is started.

It is worth mentioning that in EIS analysis, a number of physical phenomena can contribute to the frequency response at different frequencies, and therefore can contribute to the equivalent circuit model. The contributing factors can be divided into bulk and interfacial categories. The interfacial effect can be divided into two subcategories of liquid-electrode and liquid-liquid effect. The magnitude of the effect of each phenomenon generally depends on the thickness of the bulk sample, size of the dispersed droplets, amplitude of the signal, and frequency range used for equivalent circuit modeling. In this work, at frequencies below 1000Hz (shown in figure 2), a constant-phase trend started to take place and rapidly become dominant. This is attributed to electrode polarization, a low-frequency phenomenon, that is typically modeled by adding a constant-phase element (or in certain simpler cases an additional capacitor, depending on the electrode material) to the Randles circuit in series with the capacitor. As a result, in this study, the frequency range of 10MHz to 1kHz (a subset of the entire range applied in the experiments) was used for equivalent circuit modeling. As this frequency range is higher than the threshold where the constant-phase behavior began, electrode polarization is not a dominant factor in the changes of the modeled resistance and capacitance. Moreover, the contribution of the interfacial forces between the dispersed droplets and the majority phase cannot not have a significant net effect due to the small size of the dispersed drops and the spherical charge distribution on droplet surfaces. Therefore, unless the sample size is in the same order of magnitude as the dispersed droplets, the liquid-liquid interfacial effect is not as significant as electrode polarization or bulk properties. Based on the above discussion, the changes observed in the equivalent electrical properties of the samples in this study can be attributed to the bulk phase separation.

4. Concluding Remarks

In this letter, permittivity (capacitance) and resistivity (resistance) of oil-water emulsions during phase separation is investigated by applying electrical impedance spectroscopy and equivalent circuit modeling to carefully prepared emulsions which then undergo phase separation over a ten-hour time span. It is observed that the capacitance of emulsions decay from a well-emulsified state described by homogeneous models such as Boyle model or parallel capacitor analogy, to a separated state described by serial capacitor analogy. Therefore, capacitance measurement can be used to detect phase separation in oil-water emulsions and to quantitatively describe emulsion stability. Permittivity measurement is shown to be more effective than conductivity measurements for phase separation monitoring. It is also shown that detecting phase separation based on permittivity decay is most effective in oil-in-water emulsions rather than water-in-oil ones.
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