One-Dimensional Terahertz Imaging of Surfactant-Stabilized Dodecane-Brine Emulsions

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***Abstract*—Terahertz line-images of surfactant-stabilized dodecane($C_{12}H_{26}$)-brine emulsions are obtained by translating the emulsified region through the focus of a terahertz time-domain spectrometer. From these images, dodecane content, emulsion size, and stability can be extracted to evaluate the efficacy of the surfactant in solubilizing the dodecane. In addition, the images provide insight into the dynamics of concentrated emulsions after mixing.**

***Index Terms*—Commercial applications, industrial and non-destructive imaging, terahertz (THz) imaging and spectroscopy.**

I. INTRODUCTION

THE petroleum industry is increasingly interested in the efficient extraction of petrochemicals from underground reservoirs, especially those reservoirs for which conventional extraction techniques have exhausted the easily mobilized oils. A variety of enhanced oil recovery (EOR) techniques have been developed, including those that rely on injection of gases, steam, and various liquid chemical mixtures to mobilize residual oil in a well [1]. In this latter case, surfactant-brine mixtures are often employed. The surfactants can generate a sufficiently low oil-water interfacial tension to overcome capillary forces, to allow for the formation of a micro-emulsion phase and allow the emulsified oil to escape from porous rocks [2]. One challenge involves the choice of surfactant used for a particular well. This choice depends on various factors including the salinity of the brine and the nature of the oil in the reservoir. Selecting the correct surfactant can have a significant impact on the efficacy of residual oil extraction [3]. However, current industry standard methods for surfactant screening are qualitative, and often rely on laboratory-based oil-water phase behavior tests. Visual inspection, the most commonly employed method for evaluation of these laboratory tests, is challenging because of the opacity of the oil phase, which makes it difficult to see the formation of a micro-emulsion phase [4].

Here, we demonstrate that terahertz (THz) imaging can provide the quantitative data required for surfactant evaluation. Terahertz radiation is uniquely advantageous for studying the properties of these oil-brine emulsions as the oil phase is non-polar and therefore is relatively transparent. Moreover, the radiation can easily be focused to a spot size much smaller than the typical size ($\sim$ cm) of a microemulsion region, so inhomogeneities within the microemulsion can be spatially resolved. Previously, terahertz spectroscopy has been used to study vibrational modes in nanometer-sized water-in-oil microemulsions [5], [6]. More recently, spectroscopic measurements of emulsions with low water concentration have been performed using broadband [7] and single-frequency [8] terahertz sources. Extending these studies into the realm of terahertz imaging, vertical line-images can be used to investigate emulsions of higher water concentration and can provide a full profile of an emulsion, similar to the creaming/sedimentary profiles obtained through ultrasound techniques [9], [10]. Without prior knowledge of the constituent bulk oil phases' physical properties, the THz profiles can be used to determine dodecane content as well as the size and stability of the emulsion region, parameters which are of particular importance for EOR applications.

II. PROCEDURE

Our procedure is to obtain a series of vertical line-scan (one-dimensional) images of surfactant solutions, over an extended period of time, to evaluate the transient and long-term stability of the emulsion. Surfactant-brine solutions of varying salinity are mixed with dodecane (Acros Organics 99%+ purity) inside a quartz sample cell with a height of 14.5 cm and an internal path length of 1.10 mm. The surfactant is a mixture of an internal olefin sulfonate and an alcohol propoxy sulphate, which has previously been characterized for EOR applications and is therefore suitable for validating the terahertz imaging technique [4]. For the salinities and surfactants used in this experiment, mixing results in a three phase system where the bulk brine, an emulsion of dodecane dispersed in brine and/or brine dispersed in dodecane, and bulk dodecane are layered vertically within the cell. With optimal mixing the size of the micro-droplets within the emulsion are much less than the THz wavelengths, so scattering may be ignored ($d < 1\ \mu$m). The sample cell is then translated vertically in 0.5 mm increments in the focus of a THz beam from a conventional time-domain spectrometer in a transmission configuration. The collimated beam from the spectrometer is focused and re-collimated using two PTFE lenses in a confocal geometry. Time-domain waveforms are measured at each of the vertical points, forming a line-scan profile of the solution. The fast acquisition time of the spectrometer coupled with the translation time of the sample cell allows us to measure a complete vertical profile in approximately 40 seconds, depending on the signal averaging. These vertical scans are repeated every 15 to 30 minutes for 6 hours to investigate the evolution of the emulsions' profiles and again after 24 hours to investigate their long-term stability. This procedure is repeated for each brine

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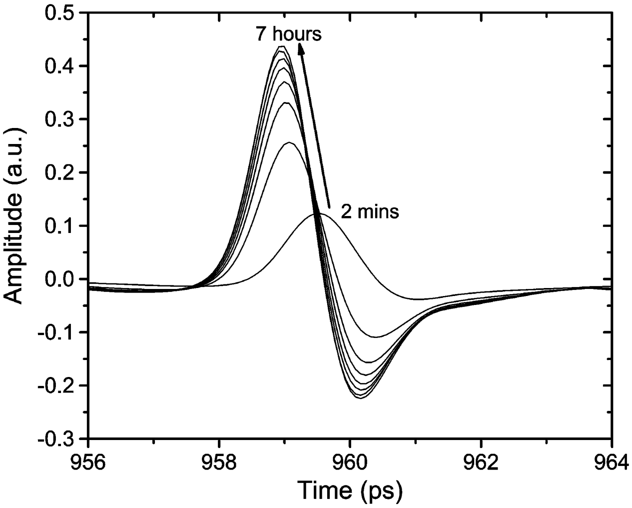

Fig. 1. Time-domain waveforms at a fixed vertical position (center of the emulsified region) for the 3% salinity dodecane-brine emulsion. The lowest amplitude waveform corresponds to 2 minutes after mixing while the highest amplitude waveform corresponds to 7 hours after mixing.

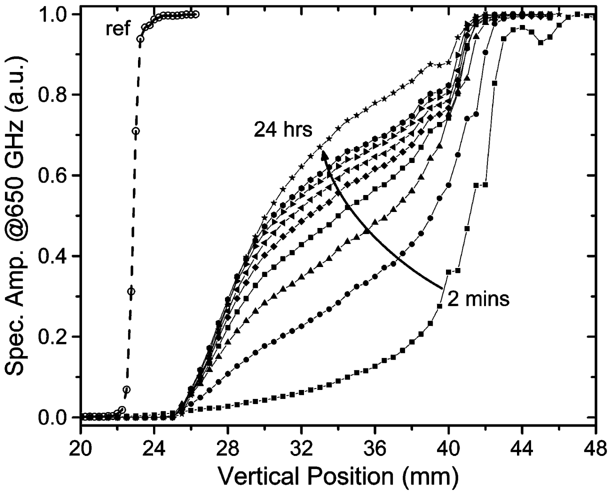

Fig. 2. Normalized spectral amplitudes plotted as a function of vertical position for the 3% salinity dodecane–brine emulsion. A profile was captured every hour for 7 hours and a final profile was captured after 24 hours. The dashed profile, offset to the left, is an unmixed water–dodecane system with a sharp interfacial layer, representing the spatial resolution of the measurement system.

salinity, with NaCl concentrations ranging from 1% to 6% by weight.

III. RESULTS

Fig. 1 shows typical data, obtained in measurements of the 3% salinity dodecane-brine emulsion for a fixed vertical position in the approximate center of the emulsified region. Here, time-domain waveforms are plotted in 1 hour intervals from 2 minutes after mixing to 7 hours after mixing. These waveforms represent the typical behavior of the measured waveforms at a fixed position over time. The change in amplitude with time is indicative of a change in water concentration in the region illuminated by the THz beam. From the Fourier transform of these measured waveforms we extract the desired quantitative information. The spectral amplitude of each waveform at 650 GHz is plotted as a function of position to obtain vertical profiles of the emulsified regions (Fig. 2). A spectral amplitude of zero corresponds to pure brine solution whereas a maximum spectral amplitude corresponds to pure dodecane (for which the THz absorption is negligible in this path length [11]). The reference profile in Fig. 2 is an unmixed pure water/dodecane system which exhibits a sharp interfacial layer and is essentially the edge response function for the imaging system. For this reference image, the distance between the 10% and 90% amplitudes is 0.69 mm, which corresponds to $\sim 1.5\lambda$, the estimated spatial resolution at 650 GHz.

Fig. 2 also shows a typical result for one particular surfactant/brine/dodecane mixture, illustrating the time evolution of the emulsion. Initially after mixing, the THz signal is attenuated strongly throughout the emulsion due to a relatively homogenous distribution of dodecane and brine, resulting in the initial low spectral amplitudes of the first profile. Due to the difference in density of the dodecane and brine, the larger micro-droplets will aggregate toward the top or bottom of the emulsion (dependent on the identity of the dispersed phase) resulting in the curvature evident in the subsequent profiles. Varying micro-droplet sizes may be a result of the mixing process and/or coalescence of the micro-droplets after mixing.

The observed rates at which contours of constant spectral amplitude converge to their limiting values could in principle be used to obtain information about the size of microemulsion droplets. Stoke's Law relates the terminal velocity of a spherical droplet in a liquid to its diameter, the viscosity of the continuous phase, and the difference in density between the two continuous phases. In a well-characterized emulsion with low droplet density, this would allow estimation of micro-droplet sizes and could indicate flocculation or coalescence of the micro-droplets similar to ultrasonic analysis methods used for concentrated emulsions [12]. However, this analysis would assume that there are no retarding effects from collisions between droplets or friction from displaced fluid in the emulsified region and the sample cell walls. These assumptions are probably false for these emulsions. In addition, the identities of the dispersed and continuous phases are not known for this particular system, further complicating the analysis. Thus, an approach based on Stoke's Law is not likely to provide accurate information.

To compare the size of each emulsion, the vertical distance between each profile's 90% and 10% spectral amplitude is plotted as function of time for several values of the salinity (Fig. 3). From this data, we conclude that the 3% salinity brine emulsion is the optimal salinity, as it produces the largest stable emulsion. Over the course of 24 hours the 3% and 5% brine salinity emulsions remain relatively stable with a slight decrease in size while the 2% and 6% emulsions both decrease in size at a faster rate. The 4% emulsion slightly increases in size.

In the limit that the THz absorption of the brine (mostly water) is far larger than that of dodecane [11], the spectral amplitudes at each vertical position are proportional to the dodecane/brine ratio. Integrating the profiles over the emulsified region and normalizing to the value for the 3% brine salinity emulsion gives the total relative dodecane/brine ratio for each emulsion. These ratios are plotted as a function of time in Fig. 4. The 3% and 5% emulsions continue to absorb dodecane

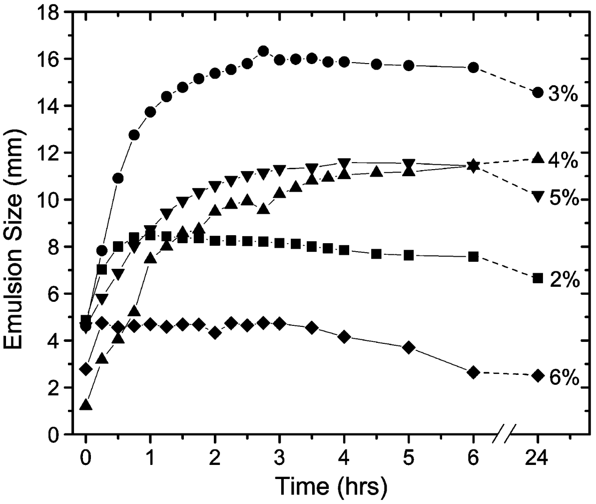

Fig. 3. Sizes of the emulsified regions, defined as the vertical distance between 90% and 10% spectral amplitude for each profile, plotted as a function of time for a few different emulsion salinities.

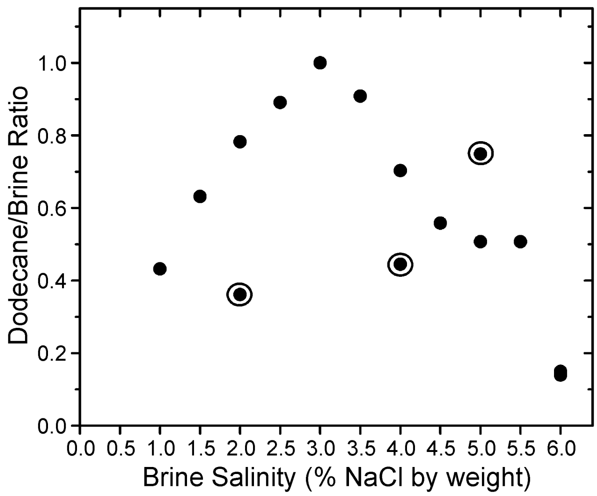

Fig. 5. Final (24 hour) dodecane-brine ratio for each emulsion salinity showing the optimal salinity for solvating the maximum amount of dodecane given the choice of surfactants and mixing conditions. The circled data points indicate the cases where visible inhomogeneities skewed the results.

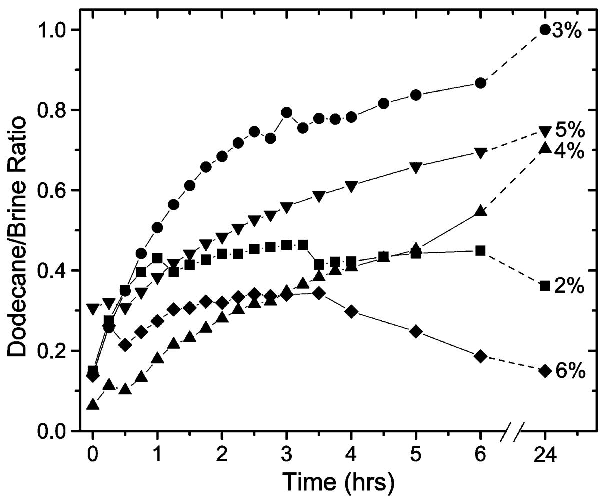

Fig. 4. Dodecane–brine ratios, normalized to the final 3% salinity emulsion dodecane–brine ratio, plotted as a function of time. The 3%, 4%, and 5% salinity emulsions continue to solvate dodecane after mixing. The 2% and 6% salinity emulsions' dodecane-brine ratios decrease after mixing.

well after mixing even with the slight decrease in size, while the 4% emulsion's ratio increases at a faster rate. The 2% and 6% salinity emulsions' dodecane/brine ratios decrease slowly over the 24 hour period.

The final ratios after 24 hours for each of the brine salinities reveal the optimal salinity for maximum dodecane content (Fig. 5), a valuable quantitative metric for EOR applications.

Varying the salinity of the brine in an emulsion alters the distribution of surfactant solvated between the aqueous and oil phases. At optimal salinity, the surfactant will have the same affinity for both the oil and brine phase resulting in the highest concentration of surfactants at the brine–oil interface [13]. Hence, for the given surfactants and dodecane, the lowest possible interfacial tension is achieved with the 3% salinity brine, producing a stable emulsion with the highest relative dodecane content after 24 hrs. As the salinity of the brine is adjusted away from the optimal value the resulting lack of free surfactant molecules at the interface results in larger, inherently less stable, droplets. These droplets tend to coalesce and eventually return to their respective bulk phases. This behavior can be seen most strikingly in the size and dodecane/brine ratio of the 2% and 6% salinity emulsions and, to a small extent, the reduction in size of all the other salinity emulsions, with the exception of the 4% emulsion. The increase of the dodecane/brine ratio for the 3%, 4%, and 5% salinity emulsion may be a sign that excess free surfactant molecules are present after mixing, allowing for the slow formation of more micro-droplets at the dodecane–emulsion interface. This more complex behavior requires further studies beyond the scope of this paper.

In some cases, due to insufficient mixing and the small path length of the sample cell, large bubbles are formed in the emulsions which may eventually collapse or remain adhered to the boundaries of the sample cell, skewing the results. In our case, the samples with large visible inhomogeneities (circled data points in Fig. 5) were re-mixed resulting in homogenous emulsions. Hence, these inhomogeneities can be eliminated with a more robust mixing process and/or a larger sample cell size. If large inhomogeneities are consistently produced after repeated mixing, this would be a strong indication of a non-optimal surfactant-brine mixture, such that THz imaging would not even be necessary. Nevertheless, this technique clearly provides valuable information which cannot be obtained using visible inspection.

The presence of impurities in the formation and behavior of the emulsions has not been tested. However, as long as the impurities are non-polar ($\alpha_{\text{brine}} \gg \alpha_{\text{oil+impurities}}$), the impurities will only effect the value of the optimal salinity and the choice of surfactants and their concentration, values which can be revealed using this technique. THz imaging provides a more robust quantitative metric for evaluating the efficacy of particular surfactants for EOR, without prior knowledge of the properties of the oil phase.

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