Electrical resistance tomography for monitoring emulsions and foams

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ABSTRACT

There are several techniques available for monitoring emulsions and foams. Early studies usually referred to global measurement of the volumes of the emulsion/foam and of the separated liquid versus time. However, it was soon understood that phase separation is not only a function of time but also of location. With regard to simplicity and fast response, electrical measurements offer a tempting alternative for determining the longitudinal phase distribution in emulsions/foams. A far more challenging application is electrical resistance tomography (ERT) which involves several non-intrusive sensors across a measuring volume to determine the distribution of the conducting regions inside an emulsion/foam from electrical signals taken from all possible views of the sensing electrodes. In particular, a 2-Dimensional ERT which uses ring electrodes (mounted around the circumference of vessels) at different axial positions to yield the instantaneous longitudinal phase distribution will be presented here. The ability of this technique for real time measurement of foam/emulsion destabilization and separation of the constituted phased is examined in the present work. The technique is applied separately in study of a particular foam and a particular emulsion. In both cases, the evolution of the phase distribution is registered in detail. In addition, in case of emulsion, appropriate theoretical tools allow the estimation of the dominant droplet sizes.

Keywords: foam; emulsion; electrical conductance tomography; electrical resistance tomography

INTRODUCTION

Foams and emulsions are essential constituents of foods so their characterization through their stability identification is an important issue for the food industry. The primary loss of stability reason is the drainage process for foams and the creaming process for emulsions. Both processes are gravity-induced and they are enhanced by the secondary reason of instability, the coalescence process. So the direct experimental measurement of the drainage and the creaming processes is of paramount importance to the study of foams and emulsions stability.

There are quite a few techniques available for foam drainage measurement. Early studies usually referred to global measurement of the volumes of the foam and of the drained liquid versus time. Although this was sufficient from a technological point of view [1], it was soon understood that in a draining foam the liquid fraction is not only a function of time but also of foam height. In subsequent years, magnetic resonance imaging (MRI), γ-ray and X-ray techniques were applied to measure density profiles in draining foams. Despite their high potential, these are expensive techniques that allow measurements only on small volumes and require highly skilled personnel.

Regarding emulsions, several methods have been employed in the past e.g. optical microscopy, laser diffraction, light scattering etc to investigate the progress of emulsion’s destabilization, which determine droplet sizes either from direct visual observations or from measurements performed on withdrawn samples [2]. These methods are limited by the fact that they provide information of droplet sizes only from places where there is either visual access or a sampling mechanism can be inserted. Sampling can alter the emulsion characteristics by exerting forces that can disturb seriously the phases distribution. Additionally, the often required significant dilution of samples before measurement can modify some of the emulsion characteristics (e.g. destroy flocks or aggregates). Moreover, these methods cannot provide information on local phase concentrations. Differential scanning calorimetry is an interesting method for characterizing the morphology of emulsions and also for providing an estimation of droplet sizes. Although, the method is non-intrusive, the emulsion need be transferred to the sample cell unit of a calorimeter where, in addition, there is no possibility to determine volume fraction distributions during the destabilization of the emulsion.
With regard to simplicity and fast response, electrical measurements offer a tempting alternative for determining the longitudinal liquid content profile in draining foams. This is implemented by placing several small electrodes along the vertical direction of the foam and scanning them at a rate faster than the time scale of drainage (usually a scan through all electrodes in less than a second is enough). Another important advantage is the possibility of using non-intrusive electrodes that can be attached to the wall of test vessels of virtually any size. Electrical techniques appear also to be a tempting option for measuring non-intrusively the temporal evolution of local volume fractions inside emulsions (opaque or transparent). Such techniques have been used in the past for monitoring other applications such as mixing, bubble columns, multiphase flows, solid-liquid filtration, and polymerization reactors. In those studies different electrode geometries and possibilities to arrange/configure electrodes have been employed. A pair of ring electrodes running the internal circumference of a vessel and separated by a certain distance in the axial direction constitutes a probe which, apart from being non-intrusive, is particularly sensitive to phase distribution patterns in the cylindrical segment between the ring electrodes. Ring electrodes have been successfully applied to a number of multiphase applications e.g. [3]. It has been reported that in cases of radially homogeneous dispersions the separation distance between electrodes can be significantly reduced in favor of more localized (axially) measurements.

**MATERIALS & METHODS**

Soya protein isolate (SPI, PRO FAM® 974) purchased from VIOTREK is used as the foaming agent without any further purification. The isoelectric point of protein is 5. Xanthan gum (XG) purchased from SIGMA is used to increase the viscosity of the liquid phase since most high molecular weight polysaccharides are hydrophilic and so do not have a high tendency to adsorb at the air water interface. Solutions of SPI are prepared in de-ionized water at 1% (w/v) by gentle stirring for one hour. The insoluble SPI fraction (~50%) is removed by centrifugation at 10000 rpm for 15 min (ROTINA 35, HETTICH) and the supernatant is refrigerated for 24 hours at 4°C. The soluble SPI is then added to prepare the aqueous solution with 1% (w/v) SPI and further gentle stirring for another hour. The resulting liquid serum has viscosity 12 cp (Covette DV-II Viscometer, Brookfield), natural pH 6.9 (MP 220,Mettler Toledo), electrical specific conductivity 0.52 mS/cm (ECM, Dr. Lange) and equilibrium surface tension 44.5 mN/m (ring method, Sigma 70, KSV); all properties measured at 25°C. This serum is then cooled to 4°C for additional 24 hours. Foams are prepared by whipping air into 300 ml of the above solution using a Sunbeam Mixmaster mixer for 10 min at 900 rpm. Part of the produced foam is then decanted to fill a Plexiglas test tube up to its top and is allowed to drain. The Plexiglas test tube has 70 mm internal diameter and 170 mm height. The conductance gauge consists of six parallel stainless-steel rings that are placed at various heights along the tube, flush with its inner surface (Figure 1a). The electrodes are 2 mm wide. The electrodes of the gauge are combined in pairs to give several conductance probes. The separation distances of the probes are: probe 1, 5mm; probe 2, 15mm; probe 3, 10mm; probe 4, 30mm. Assuming a radially uniform foam at all times during drainage, the separation distance between electrodes (dictating the measuring volume also in the radial direction) is not a matter of concern and the selection of pairs is solely based on their relative position along the foam height. Thus, for obtaining data at different heights the four electrode pairs (probes) shown in Figure 1a are selected. Apart from the ring electrodes, a pair of disc-like and a pair of rod-like electrodes are manufactured, each one having the same active (for electrical flow) surface area with a ring electrode. Each disc electrode has available for electrical current flow only its front plane surface whereas each rod electrode only its side cylindrical surface. For all pairs, the electrodes separation distance is large enough to average bubble size undulations yet small enough to preserve the local character of measurements.

The oil-in-water emulsions were prepared using a NaCl aqueous solution, n-hexane and C10E5 as emulsifier. The aqueous solution was prepared by dissolving NaCl at a concentration of 50mg/L into Millipore filtered water. After salt dissolution the electrical conductivity of the aqueous solution was 125 μS/cm, a value typical of tap water. Hexane was spectroscopy grade (purity ≥ 98.5%, Uvasol, Merck). Three different oil-to-water volume ratios: 40/60, 20/80, 5/95 were used for making emulsions. The emulsifier, C10E5 (Nikko Chemicals Ltd), was initially dissolved in water but once in contact with hexane during emulsification it started dissolving into hexane and partitioned between the two phases. The partition coefficient of C10E5 between water and hexane is $K_{wp}=13.9$. To achieve the same final C10E5 concentration when increasing the hexane/water volume ratio, higher initial surfactant concentrations in water have been employed. The final concentrations of C10E5 after partitioning are $C_f=10^{-4}$, $2 \cdot 10^{-3}$, $5 \cdot 10^{-4}$, $10^{-3}$ M, respectively. With only exception the case 5/95 hexane-in-water and final concentration $C_f=10^{-3}$ M, all other cases have initial surfactant concentrations, $C_i$, above the critical micellization concentration (CMC). Emulsification was
conducted inside a cylindrical Plexiglas vessel having 19.5 cm height and 7 cm internal diameter. The vessel was furnished with sixteen stainless steel ring electrodes flush mounted to the inner wall, 1.5 cm apart from each other. Electrodes combined in pairs provide several non-intrusive conductance probes. Electrical signals from multiple probes combined with a multiplexer and a suitable inverse reconstruction algorithm for data reduction constitute a tomographic imaging system. As this was an attempt to employ tomographic measurements to emulsification, tests were initially conducted with signals taken from all possible views of the sensing electrodes. Due to the intense mixing during emulsification virtually no angular or radial variations of volume fractions were found but only variations in the axial direction. To ease the computational effort and increase data acquisition rate, only three probes at different axial locations along the vessel were eventually employed, designated for convenience as high, middle and low (Figure 1b). These probes consisted of adjacent electrodes which offered certain advantages: the 1.5 cm separation distance between rings was large enough to average droplet size undulations yet small enough to prevent the local character of measurements. All probes were located at the lower half of the emulsion, 1, 4 and 7 cm, respectively, from the bottom of the vessel (distances calculated from the center of probes). The free surface of the emulsion was 16 cm above the bottom of the vessel (total liquid volume 616 ml). Emulsification was implemented by intense mixing of water and oil using an impeller (Rushton turbine, d=4.6 cm) placed at the central axis of the vessel. The impeller was placed 1.7 cm above the bottom of the vessel.

![Figure 1. (a) Experimental test tube with flush mounted ring electrodes for foam stability experiments. (b) Schematic representation of the employed experimental set-up for emulsion stability experiments](image)

**RESULTS & DISCUSSION**

Although our foams continue to drain for several hours we have decided for practical reasons to present here results only for the first hour after their formation. Volumetric measurements in our initially uniform and homogeneous foam yield an independent check of electrical data reduction to liquid fraction values. The volumetrically determined initial liquid fraction is 0.25. Figure 2a presents data obtained from the four measuring probes along the foam column. Global volumetric measurements are also presented for comparison. The four probes give qualitatively similar results [4,5]. However, both the time for drainage onset (moment when curves start to decline) and the liquid fraction variation with time show a monotonous trend among probes: The lower a probe is located in the foam the later the drainage starts and the slower the drainage rate. This is normal and is due to hydrostatic effects in the foam.

Interestingly, a slight gradual rise of the electrical signal is observed from time zero until the moment (different for each probe) that the liquid starts to leak out of the measuring volume. This rise corresponds to a liquid fraction increase of about 0.01. This is just a small difference which in terms of accuracy is out of the capacity of determination but in terms of resolution it can be safely sensed. Inasmuch as capillary hold-up effects are restricted to low heights (the capillary length at our bottom foam-liquid interface is estimated around 1 cm) they can not be blamed for the liquid fraction rise with time. Such signal rise could be explained by a slight temperature increase during the experiment but our temperature recordings at the wall
do not confirm this. Nor the ionic strength of the solution has changed with time as conductivity measurements show. Another possible explanation is a bubble size effect (through tortuosity) as bubbles get larger with time. Datye and Lemlich [6] observed a similar small bubble size effect on the conductivity of dry foams. Although qualitatively correct, this remains to be seen from the analysis of the close-up photos. To our knowledge, this is the first time that such a feature is reported regarding electrical signals in foams. The role of the electrode geometry and intrusiveness is examined next. Figures 2b shows the electrical and volumetric measurements, respectively, obtained by employing ring, rod and disc electrodes simultaneously. For comparison, the data obtained when using just the ring electrodes are shown. Beside their different shape, rod and disc electrodes have a much longer vertical surface exposed to the foam compared to the narrow (2 mm) ring electrodes and one may have concerns whether this may enhance drainage. It must be also stressed that rod and disc electrodes are immersion electrodes while ring electrodes are flush mounted at the wall of the container.

Figure 3 present electrical measurements of local water volume fraction obtained by the three probes (high, middle, low) during the destabilization process of hexane-in-water emulsions for a particular C10E5 concentrations for 40/60 (v/v) emulsions. The mentioned v/v proportion refers to the end of hexane addition. Electrical signals from all runs exhibit similar features. Time t=0 is the moment that the impeller is switched-off which corresponds to a well-mixed homogeneous emulsion along the test vessel [7]. This means that signals from the three probes start from the same initial water volume fraction which for the three examined oil/water proportions is 0.95, 0.80 or 0.60, respectively. At long times, electrical curves of water fraction tend to unity which corresponds to presence of water alone. This is because all three probes are located at the lower half of the emulsion volume so at the end of phase separation electrodes are covered only by water. In all curves, a fast rise is observed at the beginning which progressively turns into a slower rise at longer times. The initial fast rise corresponds to large oil droplets that separate rapidly from the aqueous phase whereas the slow rise corresponds to small droplets that take longer to destabilize.

A direct approach to extract problem parameters from experimental data is developed in [8]. The shape of the evolving water volume fraction curve for the low measuring probe (Fig. 3) implies a bidisperse size distribution of droplets. The term bidisperse literally refers to a population with two discrete sizes. Nevertheless, in practice, it is a good approximation for any bimodal distribution with no very broad modes and with limited overlapping between modes. This is apparently the case here since the distinct character of the two modes is clear in the experimental conductance curves (see below). The development procedure to estimate droplet sizes and relative volume fractions from the experimental data of the low probe is briefly described. The first step is to find the slopes of the two linear regions of the volume fraction evolution curve and the corresponding transition point φc between the two regions (see Figure 4). The slopes are related to front (separation line between regions of different oil volume fraction) velocities through a theory for the relation between nonuniform oil volume fraction and liquid conductance. Next, the velocity is related to bubble buoyancy velocity and final to bubble size (through the use of the appropriate drag law).

Following the mentioned procedure one can derive the average diameter of large and small bubbles dL and ds and the corresponding oil volume fractions φL and φs, respectively. The results of the analysis are shown in Table 1. The two droplet size modes appear to have very different values which is compatible with the way of producing the emulsions in the present work. The oil is introduced from a capillary to an intensively stirred tank. The initial large droplets leaving the capillary undergo turbulent breakage (the existence of surfactant prevents coalescence both in the emulsification and the destabilization stage). It is well known that in case of intensive turbulence breakage occurs by dripping tiny droplets from the surface of mother droplets [9]. This type of breakage leads to a bimodal distribution. The large mode corresponds to the continuously decreasing size of the initial droplets and the small mode to the fragments. The above mechanism is imposed by surface energy and capillary pressure criteria [9]. Further to the expected bimodal shape, it is evident from Table 1 that the size of the large mode decreases as the surfactant concentration increases. This is explained by the fact that the reduction of surface energy leads to higher breakage rate and thus to larger breakage extent. Finally, the higher large mode size for larger oil volume fraction probably is due to the well-known damping of turbulence by the presence of the dispersed phase. For very high breakage extent the breakage mechanism changes from dripping to equal size breakage leading to the merging of the two modes to one. This seems to be the case for the 20/80 v/v mixture with 10⁻³ surfactant concentration in which the second mode vanishes. It is noted that the average diameter resulted from the processing of microscope images is also shown in Table 1. The deviation between the diameters dL, ds from the electrical technique and the Dopt can be explained based on the different physical principles of the measuring techniques.
Figure 2. Local electrical conductance measurements: (a) evolution of liquid fraction with time at different heights (probes) (b) Comparison between ring, disk and rod electrodes

Figure 3. Water fraction ($\phi_w$) as a function of time (t) during destabilization of a hexane-in-water emulsion at a 40/60(v/v) (final proportion) oil/water volume ratio at three positions ($C_f=5\cdot10^{-4}$ M is the concentration of surfactant after partitioning between the two phases)

Figure 4. The procedure followed in order to calculate the two slopes and the transition point $\phi_c$. 
Table 2. Results from the theoretical analysis of electrical data from the lower electrode ring based on the assumption of a bidisperse droplet size distribution: bubble diameters $d_L$ and $d_s$ with oil volume fractions $\phi_L$ and $\phi_s$ respectively. $D_{opt}$ is the number average diameter from the optical measurements.

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<th>Concentration of $C_{10}E_5$ (M)</th>
<th>Hexane % (v/v)</th>
<th>$\phi_L$</th>
<th>$d_L$ (μm)</th>
<th>$\phi_s$</th>
<th>$d_s$ (μm)</th>
<th>$D_{opt}$ (μm)</th>
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CONCLUSION

In the present work, the capabilities of the electric resistance tomography technique based on flush mounted cylindrical electrode probes, as a tool for studying the stability of foams and emulsions, are demonstrated. The particular electrode design has the advantage of no interference with the destabilizing process which is the case for immersed electrodes. The use of multiple sensing probes provided accurate measurements of local water fractions at different heights along the test vessel both for foams and emulsions and allows detailed registration of the destabilization process. In case of emulsions, using the appropriate theoretical treatment, the conductance curves obtained from the electrode probe can be used to estimate the two characteristic droplet sizes of an assumed bimodal distribution.

REFERENCES