

Electroacoustic Characterization of Emulsions

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I. INTRODUCTION

Electroacoustics provides a unique opportunity to estimate both the size of emulsion droplets and the state of the surface (kinetic) charge in a single measurement. There are two principal methods used: the colloid vibration potential (or current) (CVP or CVC) and the electro kinetic sonic amplitude (ESA). The CVP and CVC have mostly been used in the kilohertz region and the ESA method in the megahertz region. The theoretical developments are somewhat different in these two regimes, although complete theories should yield identical data from the two sources. Measurements in the kilohertz range have, for the most part, been limited to a single frequency which can only provide measurements of the zeta potential (if the particle size is known). When measurements are taken over a range of megahertz frequencies (0.3-20 MHz, say), as has been done in the ESA mode, the possibility emerges of determining both the particle size distribution and the zeta potential simultaneously. Such measurements, sometimes referred to as *electroacoustic spectroscopy* (1), can be made in concentrated emulsion systems with provision of useful data up to concentrations in excess of 60% by volume. The results can also be used to investigate details of the fluid flow in the neighborhood of the particle surface in the presence, for example, of adsorbed polymer molecules.

Measurement of the stability and anticipated rheological behavior of emulsions has, in the past, been limited by the

difficulty of determining the surface charge on emulsion droplets at the normal concentrations at which they occur in industrial and biological systems. Even the relatively modest concentration of fat droplets in milk (about 3%) produces a fluid which is optically opaque and not measurable by the normal procedures of electrophoresis. More recent developments, in which light-scattering methods are coupled with optical fibers to introduce a light beam into the sample and extract the scattered beam, still suffer from problems of interpretation. The alternative procedure, of diluting the emulsion before measurement, is far from satisfactory. Even if one were able to find the correct diluent (to duplicate the electrolyte solution which bathes the droplets) the dilution process itself changes the phase-volume ratio and hence alters the distribution of any component that is soluble in the oil and water phases. The problem is compounded by the fact that one can never be sure that such redistribution processes are not contributing to the end result (especially if some unusual behavior is being investigated).

The possibility of making measurements directly on an emulsion of essentially any concentration up to around 60% is therefore a very appealing one. When the same measurement can yield a consistent measure of both the size and the electrokinetic charge on the particles, then the method becomes of unique value. That is the present situation with electroacoustic measurements of the ESA effect in the megahertz frequency range.

The two principal electroacoustic processes are the CVP and the ESA effect. The CVP is an outgrowth of the first proposed electroacoustic effect, namely, the *ion vibration potential* (IVP) which was investigated theoretically by Debye in 1933 (2) as a possible method for estimating the hydration numbers of the various ions. Debye showed that if a sound wave were passed through a salt solution it would disturb the ions and their surrounding atmospheres. This would create an array of tiny dipoles which would give rise to a macroscopically measurable potential difference between the peak and trough of the sound wave. Although there were formidable experimental difficulties to overcome (3) before the theory could be adequately tested, some progress was made in this area in the 1960s. It has recently proved possible to develop improvements in the theoretical treatment, which are giving more consistent results (4), although there remain some unresolved inconsistencies in the experimental data.

It was recognized very early (5), however, that the corresponding effect in a colloidal suspension (the CVP) should be much larger and easier to use since in that case the dipole would be created by the particle and its surrounding double layer. That has proved to be the case and the application of the method to the investigation of polyelectrolytes and proteins has been reviewed by Zana and Yeager (3). More recently, the application of the CVP method to colloidal suspensions and emulsions has been reviewed by Marlow et al. (6) and the more recent developments will be discussed in the next chapter. Here, we will concentrate on the developments in the alternate electroacoustic procedure, the ESA effect. This refers to the production of a sound wave when a high-frequency electric field is applied to a suspension or emulsion.

The ESA effect was first recognized in the early 1980s by engineers at Matec Applied Sciences (Hopkinton, MA, USA) who patented the application of the method (7) to colloidal systems. The result was an instrument (the ESA-8000) which operated at a single frequency (around 1 MHz) and was able to do little more than determine the isoelectric point of a suspension, i.e., the point at which the zeta potential (ζ) passes through zero when the suspension is titrated with a reagent capable of changing the effective surface charge. The subsequent development by O'Brien (8) of an adequate theory for the ESA effect made it possible to estimate the zeta potential from the measured ESA signal if the particle size were known. More importantly, the theory showed that if the measurements were made over a range of frequencies and one could accurately measure both the magnitude of the sound signal and the phase relationship between the applied field and the resulting sound response then the method could be used to measure both the zeta po-

tential and the size simultaneously. An instrument which does that, called the AcoustoSizer (Colloidal Dynamics Inc., Warwick, RI), has been available commercially since 1994. Developments in the measurement of the ESA effect have been reviewed elsewhere (9).

A minimal arrangement for observing the electroacoustic effects is displayed in Fig. 1. The application of the electric field to an emulsion of charged particles causes the droplets to oscillate backwards and forwards with the same frequency as the field. The drops are driven in one direction by the field and the surrounding double layer is driven in the opposite direction. This motion causes the formation of an acoustic dipole at each droplet, but in the body of the emulsion the dipoles cancel one another. Near the electrodes the cancellation does not occur and the dipoles reinforce one another to create a sound wave which emerges from the emulsion and travels down the delay rod to the transducer. A second signal, arising from the left-hand electrode, travels through the emulsion and then down the delay rod to the transducer, arriving a few microseconds later.

It must be borne in mind that these effects can also occur in salt solutions, so the resulting signal is the sum of signals derived from the emulsion droplets and the surrounding electrolyte. Normally, however, the size of the electrolyte signal is much smaller than that of the droplets, and can be ignored, unless the charge on the drops is very low.

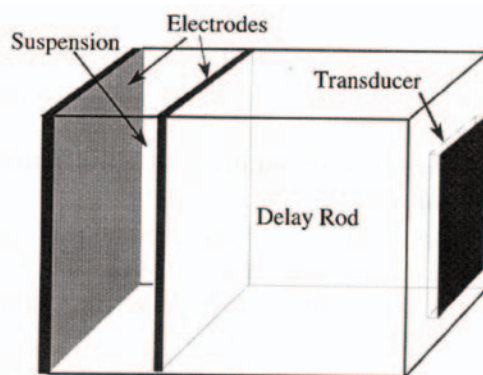


Figure 1 Minimal arrangement for observation and measurement of the ESA or CVP effect.

II. ELECTROACOUSTIC THEORY

O'Brien's theoretical analysis (8, 10) is for a suspension of solid particles, but the evidence to date indicates that emulsion droplets behave in the same way as solid particles at the frequencies involved in the ESA effect. This is understandable on a number of counts. First, it is usually observed that surfactant-stabilized emulsion droplets in a flow field do not behave as though they were liquid. The presence of the stabilizing layer at the interface restricts the transfer of momentum across the phase boundary so that there is little or no internal motion in the drop. Also, the motions which are involved are extremely small (involving displacements of the order of fractions of a nanometer) so the perturbations are small compared to the size of the drop. Finally, O'Brien has shown in some unpublished calculations that if the surface is unsaturated, so that the surfactant groups can move under the influence of the electric field, then the effect on the electroacoustic signal would depend on the quantity $dy/d\Gamma$, where y is the surface tension and T is the surface excess of the surfactant. We have not been able to find any evidence for such an effect, if it exists, so we will assume that the analysis for a solid particle holds also for emulsions.

O'Brien showed in his initial analysis (8) that there was a reciprocal relationship between the CVP and the ESA effects so that essentially the same information could be obtained from either. However, it transpires that the information is easier to obtain from the ESA effect because it appears directly. The same information can be obtained from the CVP only if one knows the complex conductivity of the system. This limitation can, however, be overcome by measuring the CVC. O'Brien's initial analysis was confined to dilute systems, but was subsequently extended to systems of arbitrary concentration as long as the particles were small compared to the wavelength of the generated sound (10). This condition is always fulfilled in practice for the normal emulsion sizes and for frequencies up to 20 MHz for which the wavelength is of order 100 μm . The reciprocal relationship between CVP and ESA has been demonstrated for solutions of polyelectrolytes by O'Brien *et al.* (11).

The particle property which is extracted from the measured ESA response is the dynamic mobility, μ_d of the drops. This is a complex quantity, having a magnitude and a phase angle (just as the ESA signal is a complex quantity). The magnitude of μ_d is analogous to the electrophoretic mobility obtained in, say, an electrophoresis experiment, where a d.c. field is applied. It is essentially determined by

the electrokinetic charge (or the zeta potential) on the drops. As the frequency of the electric field is increased, the particles are able to follow the field quite well up to frequencies in the kilohertz range, but the magnitude of the mobility gradually decreases with increase in frequency. The effect is small for small drops but larger for larger drops. At the same time, the lag between the applied field and the resulting sound signal increases with frequency and this is reflected in the phase angle of the dynamic mobility. It, too, increases from zero for small particles to a value of around 45° for larger particles and/or higher frequencies. It is this effect which enables the size to be obtained from the measured signal. Since both the magnitude and the phase angle depend upon the frequency for drops of a given size, it is possible to use the two effects to obtain a more reliable assessment of both the zeta potential and the size of the particles from a measurement over a range of frequencies.

To determine the precise relationship between the ESA signal and the dynamic mobility one must solve the set of differential equations given by O'Brien in his 1990 paper (10). For the AcoustoSizer that problem is simplified by the geometry because the electrode dimensions and separation are both large compared to the wavelength of the sound (of millimeter order at the frequencies used). In that case the relation is given by O'Brien *et al.* (12) as:

$$ESA = A(\omega)\phi(\Delta\rho/\rho)\mu_d \cdot [Z_e Z_r / (Z_e + Z_r)] \quad (1)$$

where $A(\omega)$ is an instrument function [which depends, among other things, on frequency ($\omega = 2\pi \times$ frequency in hertz) and conductivity], ϕ is the volume fraction of the emulsion, and $\Delta\rho$ is the difference in density between the drops and the surrounding medium (density ρ). The Z functions are acoustic impedances of the emulsion (e) and the delay rod (r), respectively.

The acoustic impedance function measures how effectively the sound signal is transferred from the emulsion to the delay rod. The value of Z_r is well defined and constant (equal to the product of the density and the sound-wave velocity in the medium), and in dilute solutions the value of Z_e is little different from that of the suspension medium. In that case the impedance factor is constant and can be incorporated into the function A which is an instrument calibration factor. That procedure is used in the Matec ESA-8000 device. For more concentrated emulsions, Z_e depends on the density and volume fraction of the drops so it is necessary to monitor the acoustic impedance directly. That is done in the AcoustoSizer so that it is possible to

measure the dynamic mobility accurately up to concentrations of order 60% by volume.

A. Relationship Between Dynamic Mobility and Particle Properties for Dilute Systems

The analysis of the relationship between the dynamic mobility and the particle properties has been made possible by the development of special procedures for dealing with systems in which the double layer around the particle or droplet is thin compared to the radius of curvature. The double-layer thickness is measured by the Debye-Hückel parameter k which is related to the ionic strength of the electrolyte (13). For a 1 mM solution of a 1:1 electrolyte, the double-layer thickness, k^{-1} , is about 10 nm and it decreases as the square root of the concentration, so for a 0.1 M solution it would be about 1 nm. The double layer is regarded as thin if the ratio of radius to thickness (ka) exceeds about 20 and that will be the case for most normal emulsions at most electrolyte concentrations.

O'Brien has shown (10) that for a dilute suspension of spherical particles (less than about 4% by volume, say) with thin double layers, the dynamic mobility is related to the particle properties as follows:

$$\mu_d = \frac{2\epsilon\zeta}{3\eta} G\left(\frac{\omega a^2}{v}\right) [1 + f(\lambda, \omega')] \tag{2}$$

where ϵ is the dielectric permittivity and η is the viscosity of the medium, α is the particle radius, and v is the kinematic viscosity of the suspension medium ($= \eta/\rho$). The functions G and f are both complex and measure the effects of inertia and the bending of the electric field around the particles or droplets, respectively. They are given by the following expressions:

$$G(\alpha) = \frac{1 + (1 + i)\sqrt{\alpha/2}}{1 + (1 + i)\sqrt{\alpha/2} + i\frac{\alpha}{9}\left(3 + 2\frac{\Delta\rho}{\rho}\right)} \tag{3}$$

$$f(\lambda, \omega') = \frac{1 + i\omega' - \left[2\lambda + i\omega'\frac{\epsilon_p}{\epsilon}\right]}{2(1 + i\omega') + \left[2\lambda + i\omega'\frac{\epsilon_p}{\epsilon}\right]} \tag{4}$$

where $\omega' = \omega/K^\infty$ and $\alpha = \omega a^2/v$. Here, ϵ_p is the particle permittivity and K^∞ is the bulk conductivity of the electrolyte suspension. The parameter X will be described shortly.

The G factor is determined by the size of the droplets, α ; the variation of G with the parameter α is shown in Fig. 2. For small particle sizes and or low frequencies ($\alpha \rightarrow 0$) the

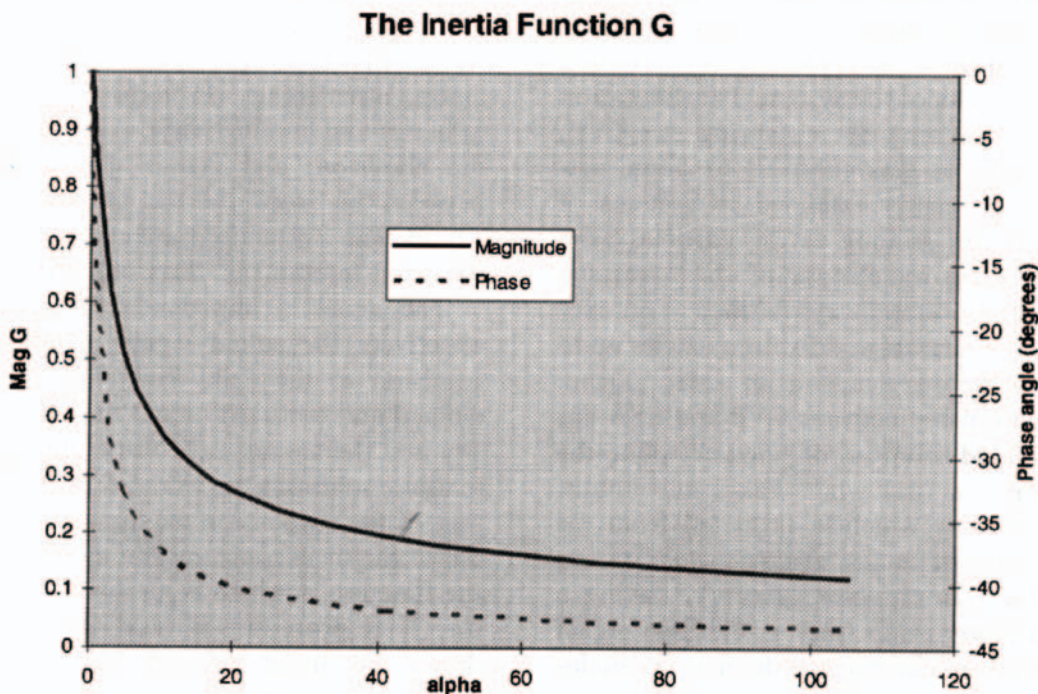


Figure 2 Inertia function $G(\alpha)$ where $\alpha = \omega a^2/v$. At 1 MHz in water at room temperature $\alpha \approx 6a^2$ for a in μm .

value of G is 1 and it has a zero phase angle. The inertia effect is then negligible and the particles essentially behave as they do in a d.c. field. As α increases, the magnitude of G decreases to zero and the phase angle becomes more negative, ultimately reaching a value of 45° . For a $1\text{-}\mu\text{m}$ droplet in water at 20°C $\omega a^2/v = 1$ at a frequency of 0.15 MHz. For a $0.1\text{-}\mu\text{m}$ droplet the corresponding frequency is 15 MHz. The frequency range of the AcoustoSizer (0.3-11 MHz) thus corresponds to a size range (for dilute systems) from 0.1 to 10 μm diameter. The range is, however, shifted to larger values for more concentrated systems. There is some contribution (mostly positive) to the phase angle from the function f , especially for higher values of the ζ -potential and lower electrolyte concentrations. In principle, the phase angle of μ_d alone could be used to determine the drop size, and the magnitude then used to determine the ζ -potential. In practice it turns out to be better to use the variation of both elements of μ_d to determine both parameters simultaneously.

The factor $(1 + f)$ in Eq. (2) measures the tangential electric field at the particle surface. It is this component which generates the electrophoretic or electroacoustic motion. For a fixed frequency, it can be seen from Eq. (4) that $(1 + f)$ depends on the permittivity of the particles and on the function $\lambda = K_s/K^\infty\alpha$, where K_s is the surface conductance of the double layer; λ measures the enhanced conductivity due to the charge at the particle surface. It is usually small unless the zeta potential is very high, so for most emulsions with large $k\alpha$, λ has a negligible effect. The ratio ϵ_p/ϵ is also small for oil-in-water emulsions. Equation (4) can then be reduced to $f = 0.5$ and hence the dynamic mobility becomes:

$$\mu_d = (\epsilon\zeta/\eta)G(\omega a^2/v) \tag{5}$$

Now the frequency dependence and the phase lag are determined entirely by the inertia term G , and the zeta potential is calculated from a modified form of the Smoluchowski formula (41) which takes account of the inertia effect for the larger particles, especially at the higher frequencies. The determination of size and charge is particularly simple in this case.

Figure 3 gives a good indication of the validity of the theory, for solid submicrometer spherical particles of silica. The spherical nature of emulsion drops means that particle shape is not likely to be a problem under most circumstances.

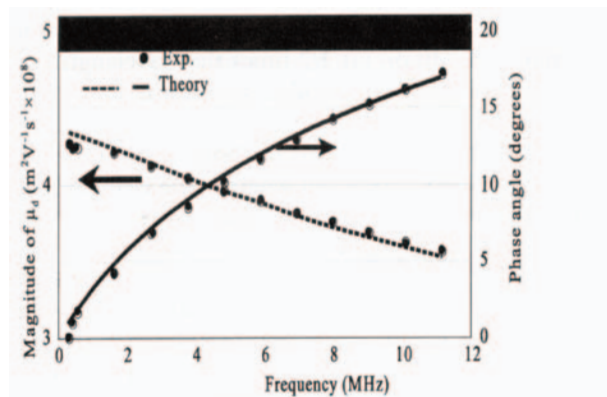


Figure 3 Comparison of theoretical (10) and experimental values of the magnitude and phase of the dynamic mobility for a silica sol of radius 300 nm.

III. INSTRUMENTATION

A. The Matec ESA-8000

A number of descriptions of this instrument have already appeared in the literature (14, 15), including a full description of its main features by Cannon (16). Sayer (17) also provides a general block diagram. The instrument comes in a number of different configurations: a flow-through cell (the PPL-80 sensor) and a dip-type probe (SPP-80). The

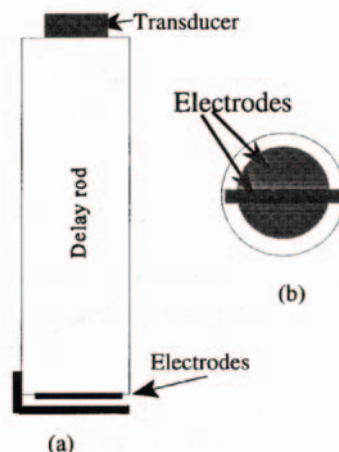


Figure 4 Dip-type probe for the ESA-8000 device. The electrode spacing is a few millimeters, corresponding to 1.5 wavelengths of sound in the liquid medium.

flow-through cell has flat electrodes separated by a few millimeters, while the dip probe (Fig. 4) has a circular disk electrode and a thin-bar counter-electrode again a few millimeters away. In each case the electrode spacing is designed to establish a resonance condition (at 3/2 times the wavelength) in the space between the electrodes, so that the sensitivity is enhanced.

The ESA-8000 can be used for both CVP and ESA measurements, depending on whether the electric field (in the form of a short pulse, or more strictly a "tone-burst") is applied to the transducer or to the electrodes of the cell. In the latter case (the ESA mode) the generated sound wave travels along the delay rod to the transducer and the resulting voltage pulse is then sent to the signal processor unit for estimation of the magnitude and phase angle, using quadrature detection (16). The delay rod is essential because the application of the field to the cell electrodes results in an immediate signal in the transducer due simply to electromagnetic coupling. The delay rod must be long enough so that that "noise" has died away before the sound signal arrives for measurement.

When the ESA-8000 was first introduced there was no adequate theory on which to base interpretation of the signals. Since the instrument measures at only one frequency it does not provide enough information to estimate the size. It seemed reasonable to assume, however, that the magnitude of the sound signal was related to the amount of charge on the particles and this could be calibrated to some extent by using a standardizing colloid of known charge (or ζ -potential). For this purpose, a commercial nanometersized silica sol (Ludox) was normally used. After O'Brien's theory became available (10) it became possible to obtain quantitative estimates of zeta potential. For the larger particles (above about 1 μm) the zeta potential depends strongly on size and a suitable average value must be provided to enable a valid estimate of ϵ to be made. A spreadsheet program (in Lotus-123 or Excel 5) is now available (18) for estimating the appropriate average size from data provided by some other size measuring method, such as light scattering.

The ESA-8000 can make accurate estimates of zeta potential in both aqueous and nonaqueous environments, but it has a number of limitations. Since it measures at only one frequency, it cannot determine both the size and the charge. It is also unsuitable for handling concentrated systems since it has no provision for estimating the acoustic impedance of the suspension which is required to obtain μ_d from Eq. (1). Determining the acoustic impedance is relatively easy, but estimating the phase angles with the necessary precision (about 1°) is quite difficult. Both those problems were ad-

dressed in the design of the AcoustoSizer.

B. The AcoustoSizer

The AcoustoSizer is designed to measure in the ESA mode over a range of frequencies around 1 MHz. The original version of the instrument performed measurements at 13 frequencies from 0.3 to 11.2 MHz which gave a size range from 0.1 to 10 μm (diameter). More recent versions have extended both the hardware (to 20 MHz) and the software to expand the range from 0.07 to 15 μm . That range is shifted upwards somewhat in systems at higher concentration.

The cell of the AcoustoSizer is made of a highly chemically resistant epoxy resin and has a capacity of about 400 mL. Its contents can be stirred by an overhead propeller/impeller stirrer with a variable speed drive. Probes dip into the cell to measure the temperature, electrical conductivity, and pH. Provision is also made for conducting pH and other titrations using built-in, computer-controlled microburets of high (0.1 μL) precision. The electrodes in this case are embedded in the cell walls and are about 5 cm apart so that there is no resonance in the cell and the signals from the two electrodes are quite separate. When the electric field is applied across the cell (again as a short pulse lasting a few microseconds) the droplets of the emulsion will oscillate backwards and forwards. As we noted above, the motions induced by the applied field are extremely small. In a typical field of around 40V/cm the particles will oscillate through distances of less than 0.1 nm, which is less than the size of a single atom. The amplitude of the sound wave moving along the right-hand delay rod is therefore very small and its effects must be greatly amplified before processing. The complex Fourier transform of the signal is first calculated (to determine what the response would have been to a continuous sine wave rather than a pulse of limited duration). The result can then be compared with O'Brien's equation [Eq. (1)], which is derived for a continuous sinusoidal field (8). To do that we also need, in the general case, the acoustic impedance of the suspension. That is obtained using the transducer on the left-hand side of Fig. 5. In this case the field is applied to the transducer and the resulting sound wave travels down the delay rod and is reflected at the interface with the emulsion. The ratio of the (complex) amplitude of the reflected wave to that of the incident wave is the reflection coefficient, and by comparing the reflection coefficient of an empty cell with that from the cell containing an emulsion one can determine the function Z_e (12).

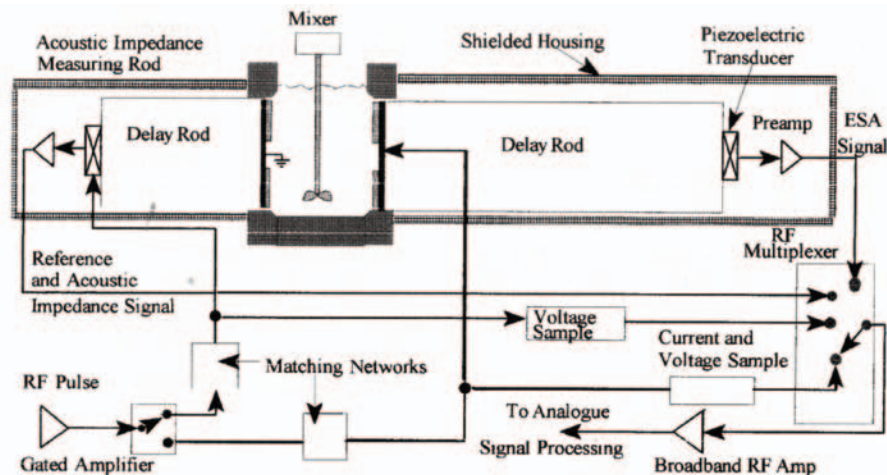


Figure 5 Schematic diagram of the arrangement of electrodes and transducers in the AcoustoSizer. The ESA signal is taken from the right-hand side transducer while the left-hand side is used for determination of the acoustic impedance.

IV. CALIBRATION

A. Determining the Function $A(\omega)$

Before the dynamic mobility can be obtained from Eq. (1) we need to be able to determine the function $A(\omega)$, which depends on the length of the delay rods, on the transducer characteristics, and on the amplifier settings in the signal-processor scheme. It also depends to some extent on the electrical conductivity of the emulsion, especially at low and high conductivities. (At very high conductivities, the current required to establish the standard field strength may exceed the capacity of the driving amplifiers so the field decreases in magnitude. At low conductivities the field lines in the cell become altered because it is then possible for some of the field to leak into the plastic walls of the cell. The field arrangement inside the cell is very complicated because of all the probes in there so any alteration to the disposition of the field alters the particle response.)

The calibration is performed using a special salt solution. As noted above all salt solutions give an ESA signal, but usually it is small compared to the signal from colloid-sized particles or droplets. There are, however, some salts for which the ESA signal is quite large because there is a large difference in the sizes of the cation and anion. The one used for the AcoustoSizer (12) is the potassium salt of a-dodeca-tungstosilicic acid. The octadecahydrate ($K_4[SiW_{12}O_{40}] \cdot 18H_2O$) tends to lose some water of crystallization, but is still an effective standard so long as it is very pure (i.e., has no extraneous ions). The loss of water from the crystal is unimportant because the anticipated ESA

signal can be calculated from the electrical conductivity of the salt. Changes in the salt concentration due to efflorescence are therefore taken into account by the measured conductivity.

The details of the calculation are given by O'Brien et al. (12) so we will not repeat them here but merely quote the value of $A(\omega)$:

$$A(\omega) = \frac{ESA}{M(S_a - S_s)} \quad \text{with} \quad M = -3.02 \times 10^{-9} K \tag{6}$$

where K is the (low frequency) conductivity measured in SI units, S is the measured reflection coefficient, and subscripts "s" and "a" refer to the salt and the empty (air-filled) cell, respectively. [Note that in the original paper (12) the constant in the expression for M in Eq. (6) was misquoted.] The calibration procedure has been shown to be consistent with the independent method developed by James et al. (19), who used a colloidal dispersion to calibrate the ESA-8000.

It would be hard to overestimate the significance of this new procedure, however. There is a great deal of difficulty attached to the problem of finding a suitable standard material, especially for the zeta potential. Different manufacturers and standardizing bodies have produced different materials: the National Institute of Standards and Technology in Washington, for example, provides a standard iron oxide which, if made up to a defined recipe, is reported to give reproducible results for ζ . Here, we have a procedure

which couples the zeta potential back to the classical methods of measuring the transport numbers of ions in solution and the electrical conductivity of a simple salt. It may well prove to be a more viable and robust standard than any other currently available in electrokinetics.

B. Behavior of Polydisperse Systems

In a polydisperse system, the ESA signal is related to the volume average dynamic mobility of the particles, $\langle \mu_d \rangle$ which is defined as:

$$\langle \mu_d(\omega) \rangle = \int_0^{\infty} \mu(\omega, a) p(a) da \quad (7)$$

where $p(a)da$ is the mass fraction of particles with radius between $a + da/2$ and $a - da/2$. For a dilute system, Eq. (2) can be used for $\mu_d(\omega)$ for each value of a provided only that the double layer is thin. The only unknown terms in Eq. (7) are then ζ , and the function $p(a)$ which must be adjusted until the best fit is found to the dynamic mobility spectrum.

The AcoustoSizer software assumes that the size follows a lognormal distribution and adjusts the median and spread of the distribution, along with the zeta potential, to give the best fit to the mobility spectrum, by minimizing the relative root mean square error (superscript “th” is the theoretical):

$$\sqrt{\frac{\sum_1^{13} |\mu_j - \mu_j^{th}|^2}{\sum_1^{13} |\mu_j|^2}}$$

O’Brien et al. (12) show that good agreement can be achieved between the ESA lognormal size distribution and the ‘true’ distribution for a pair of ground quartz standards supplied by the Bureau of Common Reference of the EEC. In the same paper they also describe the results on a variety of industrial samples of ceramics, paper coatings, and pigments, indicating good agreement between sizes obtained by the ESA method and by an alternative sedimentation technique (the Horiba Capa-700).

V. ELECTROACOUSTICS OF EMULSIONS

One of the earliest publications referring to the use of the ESA-8000 apparatus in nonaqueous media was that of

Isaacs et al. (20) who successfully monitored the coalescence of water-in-oil emulsions in the dilute concentration regime. There has been little further published work on emulsions with the ESA-8000, although Washington (21) reported a preliminary study of the zeta potential of “Intralipid” (a proprietary phospholipid-stabilized emulsion used for intravenous feeding of postoperative patients). A more detailed study of that system is discussed below. Lopez *et al.* (22) reported on the value of the ESA method for investigating bitumen emulsions (see below) and Do Carmo Marques *et al.* (23) were able to establish a direct relationship between the ESA signal and the asphaltene content of a toluene-in-water miniemulsion. A paper by Goetz and El-Aasser (24), on the behavior of concentrated miniemulsions, will be discussed when we treat the problem of concentrated systems.

A significant amount of ESA work has been in progress in various industrial laboratories but that has not appeared in the general literature until recently. Ho (25), for example, has given a very interesting account of the use of the ESA-8000 for studying the efficacy of various ionic and zwitterionic surfactants as emulsion stabilizers. He prepared hexane-in-water emulsions at about 10% concentration (by weight) and studied the electroacoustic behavior as a function of the stabilizing surfactant. He looked at some 30 surfactants, mostly cationic, but with some anionic and some zwitterionics. The pH behavior was unsurprising, with the zwitterionics showing an isoelectric point (IEP) at some intermediate pH values and the weak-base types increasing in charge at low pH. The inability to measure droplet size made interpretation of some of the results problematic and there would clearly be an advantage in repeating this kind of study using electroacoustic spectroscopy where the size could be determined. With the AcoustoSizer one would also have the opportunity to eliminate any artifacts created by differences in acoustic impedance which were not able to be accounted for in the ESA-8000 study. Nevertheless, Ho was able to make some very interesting findings. The plot of the ESA signal versus concentration of surfactant, c , is very like the typical high-affinity Langmuir isotherm, with a well-defined plateau in most cases. Strictly linear plots were obtained of ESA/c against c and the initial slope of these plots could be related to the number, N , of CH_2 groups in the alkyl chain of the surfactant. The loglinear relation between slope and N is reminiscent of Traube’s rule relating various surfactant-micellization characteristics to chain length. Ho proposes these ESA plots as a means of rapidly assessing the hydrophile/lipophile balance (HLB) values for different ionic surfactants in accordance with the Davies HLB scale (26).

Carasso *et al.* (27) used the AcoustoSizer to determine

the variation in droplet size and zeta potential for an intravenous emulsion (Intralipid, Kabi Pharmacia) as a function of the pH and other variables. This material is a 20% suspension (in water) of a triglyceride fat, stabilized by egg lecithin, and they were able to characterize it successfully, without dilution, using a theoretical development which is discussed below. They were able to show that it is very stable with respect to pH, showing essentially reversible zeta-potential behavior over the pH range 4–10. The zeta potential varied from -14 to -46 mV over that range and was -24 mV at the natural pH of 7. The diameter of the particles was essentially constant, at 0.23 ± 0.02 μm , over the whole pH range. Calcium and sodium salts are often added to these emulsions along with other essential nutrients, and it is important to know when such additions are likely to destabilize the emulsion. Carasso *et al.* (27) were able to show that calcium ions rapidly decreased the magnitude of the zeta potential and produced a reversal of sign at about 5 to 7mM (Fig. 6). At this point the droplet size appeared to increase, though it returned to smaller values at higher concentrations of calcium when the zeta potential became sufficiently positive. Sodium ions at higher concentrations produced some reduction in the magnitude of zeta, but were not able to reverse the sign. Thus, sodium ions would be classed as “indifferent” and calcium ions as “specifically adsorbed” at this interface. These results were consistent with optical microscopic observations of the emulsion and are to be expected on general double-layer theory grounds. They are clearly relevant to deciding the levels of mineral nutrients which may be added to the emulsion before injection or perfusion.

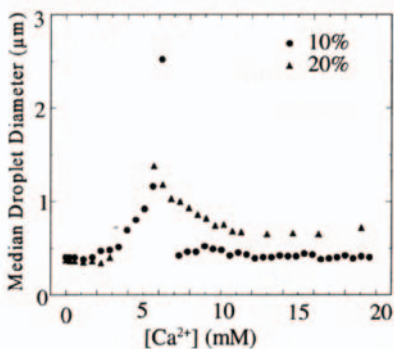


Figure 6 The size of Intralipid emulsion drops as a function of calcium ion concentration.

Of even more significance, perhaps, was some related work by Lilley *et al.* (28) on the destabilizing effect of adding anesthetic drugs to an injectable emulsion (Propofol). The normal injection dose is 20 mL, and this study showed that up to 10mg of the anesthetic lignocaine could be added to 20 mL of propofol, but any increase beyond that caused the magnitude of the zeta potential to fall below 15mV and the droplet size to increase dramatically. This would seem then to be the maximum dosage permitted by this route. A related study (29) was carried out on a mixture of anesthetic, opiate, and muscle-relaxant drugs to determine their mutual compatibility in terms of the stability of the mixed emulsion, using the AcoustoSizer to assess the zeta potential and size of various mixtures, both immediately after preparation and after storage under various conditions. The significance of these studies lies in the fact that the stability can be assessed at the normal emulsion concentration.

Of more general interest are the emulsions natural to the dairy industry, such as milk and cream and their various products. Wade and Beattie (30) have studied such systems using the AcoustoSizer with some interesting results. They examined the fat emulsion separated from homogenized milk (about 4% concentration) and natural cream (about 38% concentration) and also an artificial milk and cream produced by dispersing anhydrous fat in skim milk. The milk emulsions are “dilute” (in the sense that the hydrodynamic interactions between droplets are unimportant). Both the commercial cream and the reconstituted cream were studied at this same concentration (4%) at the natural pH (6.7). The behavior of undiluted cream will be discussed when we deal with the problem of concentrated systems.

The fat droplets in raw milk are stabilized by a thin protective layer known as the milk fat globular membrane (MFGM). Cream produced by simple separation from the raw milk should retain that membrane intact. Milk which has been homogenized will have smaller droplet size and a larger surface area so the membrane will only partially cover the droplet surface and the exposed surface will become covered with a protein mixture from the milk plasma. When artificial milk and cream are prepared from anhydrous milk fat, there would be little, if any, MFGM and the entire surface would be expected to be covered by proteins from the plasma. One would expect therefore that the zeta potential would show significant differences between the surfaces of these products. Table 1 shows the results obtained by Wade and Beattie (30) for the homogenized and reconstituted milk and for the dilute samples of the natural and reconstituted cream. To obtain these results the total ESA signal must be corrected for the contributions from the salts, the serum proteins, and the casein micelles. The

Table 1 Particle Size and Zeta Potential of Natural and Reconstituted Milk Fat Emulsions; d_{50} , d_{15} , and d_{85} Are the Median, and the 15th and 85th Percentiles of the (Lognormal) Size Distribution. All Samples Measured at 4% Volume Fraction and Natural pH (6.7).

Emulsion	Zeta (mV)	d_{50}	d_{15}	d_{85}
Commercial cream	-27	3.4	3.1	3.8
Recombined cream	-24	2.5	2.3	2.8
Commercial milk	-18	1.0	0.9	1.1
Recombined milk	-35	1.0	0.9	1.1

Source: Ref. 30.

zeta potential obtained for the homogenized milk sample agrees well with that obtained by Dalglish (31) using laser Doppler electrophoresis, but the ζ value for the cream emulsion is significantly different. Dalglish observed some time dependence, but the ζ value settled to -10 mV after about 10 min. There are considerable problems associated with dilution of these very complex systems and since both of them were diluted before measurement we will suspend judgment for the moment on which is the more reliable of these two estimates.

Another interesting application of the electroacoustic procedure is given by Hunter and O'Brien (32) in a study of a highly charged emulsion system. The emulsion droplets were produced by stabilizing perfluorodecalin droplets with sodium dodecyl sulfate (SDS) and passing the resulting (rather unstable) emulsion several times through an homogenizer. This has a very small orifice which so constricts the flow that the oil droplets are drawn out and broken down to sizes in the submicrometer range. When measured with the AcoustoSizer after several passes through the homogenizer, the emulsion showed a droplet diameter of about $0.7 \mu\text{m}$ and a zeta potential of about -175 mV at a solution concentration of around 1.4×10^{-3} M, corresponding to a ka value of about 43. Such very high zeta potentials have seldom been reported previously and Fig. 7 shows why this is so. The computer calculations of O'Brien and White (33) show that when the d.c. electrophoretic mobility is plotted as a function of zeta potential, for ka values around 50, there is a pronounced maximum in the curve. In a d.c. measurement yielding a reduced mobility of about 4.7 one would be unable to determine whether the appropriate zeta potential was -103 or -175 mV. Figure 8 shows that there is no such ambiguity in the dynamic mobility, for which both the magnitude and the phase angle clearly indicate -175 mV rather than the lower value. Note, however, that the magnitude curves in both cases ap-

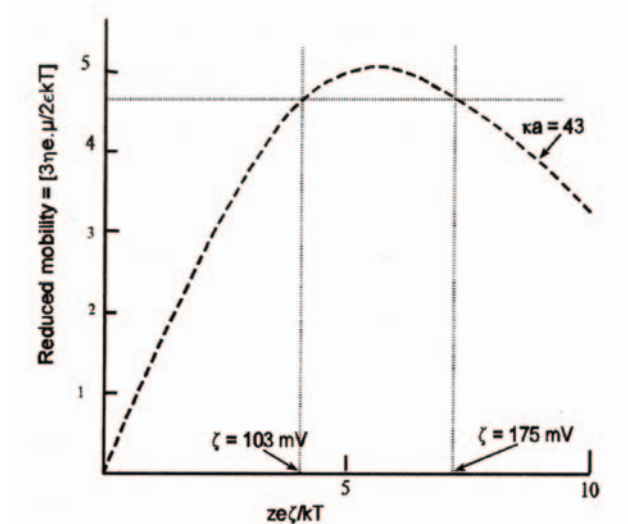


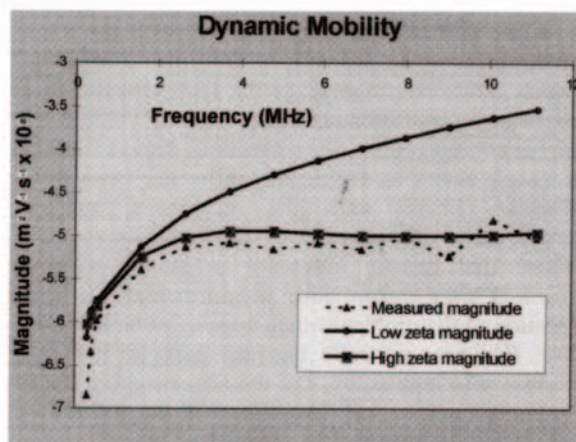
Figure 7 Dimensionless d.c. mobility as a function of dimensionless ζ potential according to the numerical calculations of O'Brien and White (33) for the value of ka relevant to the highly charged emulsion system (see text).

pear to converge to the same low frequency value as would be expected from Fig. 7.

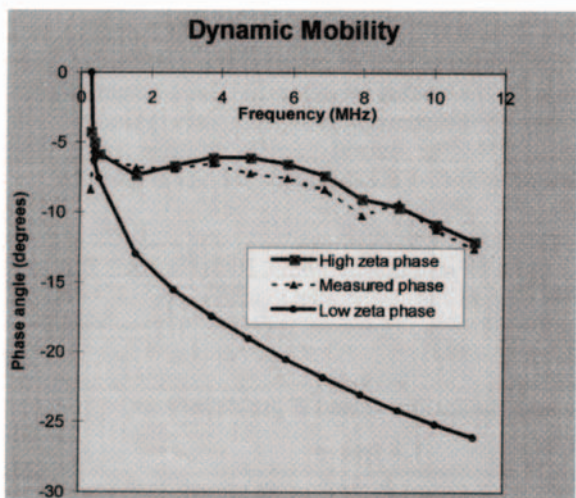
VI. EFFECT OF CONCENTRATION OF PARTICLES

A. Acoustic Impedance

One immediate effect of increasing the particle concentration in the emulsion is that the acoustic impedance, Z_e , can no longer be approximated as equal to that of the dispersion medium. Since Eq. (1) remains valid at all concentrations commonly encountered, it is important that the correct value of Z_e is used, so that the correct value of the dynamic mobility is obtained from the measured ESA signal. In principle, the value of Z_e for the emulsion could be a complex function of the frequency and the properties of the suspension, but the exact behavior is of little consequence for measurements with the AcoustoSizer, since it measures the value at each frequency before calculating μ_d from ESA signal.



(a)



(b)

Figure 8 (a) Comparison of the magnitude of the dynamic mobility of the emulsion with the calculated values for low (103 mV) and high (175 mV) zeta potential; (b) the same for the phase angles.

B. Effect of Concentration on Dynamic Mobility

Equation (1) shows that the ESA effect should be proportional to the volume fraction Φ for dilute systems, and the measurements of Klingbiel *et al.* (15) suggest that this holds for at least some spherical particles up to concentrations of order 5%. Texter's nonspherical particles were linear only up to about 2% by volume (34) but one would

expect nonspherical particles to show departures from the simple relation at lower concentrations than for spherical particles. Departures from sphericity will not be important in emulsion systems until one reaches very high concentrations indeed so we may reasonably assume that the dilute formula should hold up to at least 5% by volume. Even this value is a great deal higher than the normal concentrations at which d.c. electrophoresis is conducted* but it is at the lower end of the range of the ESA method.

A limited number of studies have been carried out on more concentrated systems using variations of the traditional electrophoretic method, e.g., the tracer and mass-transport methods. Reed and Morrison (35) have shown that, for d.c. fields, even in highly concentrated systems, the hydrodynamic and electrostatic interactions cancel one another when the double layers are thin, and the only effect which must be taken into account is the reverse flow of fluid displaced by the moving particles. Zukoski and Saville (36), using red blood cells mixed with ghosts, have verified that this is so and that the d.c. mobility, μ_c , of a concentrated system of volume fraction Φ is given by the simple relation:

$$\mu_c = \mu_0[1 - g\phi] \tag{8}$$

where μ_0 is the mobility at infinite dilution, and g is, within the limits of experimental error, equal to unity. Marlow and Rowell (37) working with coal/water slurries and using the CVP technique have shown that, at the frequencies of their measurements (200 kHz), the effect of particle concentration can be adequately described by introducing a factor $(1 - g\Phi)$ into their equivalent of Eq. (1) where again, g was very close to unity. In their review article Marlow *et al.* (6) discuss the way the cell model of Levine and coworkers (38, 39) is introduced into the CVP theory and show that, for thin double layers, the result is that the hydrodynamic and electrostatic interactions essentially cancel one another and one is left with only the factor $(1 - \Phi)$ to take account of the backflow of liquid caused by the particle motion.

*Traditional methods of determining the electrophoretic mobility in a d.c. electric field have involved particle concentrations with $\Phi \ll g$ 0.001. This provides the infinite dilution limiting value, and the appropriate theoretical analysis is for an isolated particle in an infinite volume of electrolyte.

Unfortunately, no such simple solution is available for the ESA effect at the high frequencies at which it is currently used. Goetz and El-Aasser (24) attempted to compare the electroacoustic and electrophoretic behavior of concentrated miniemulsion systems of toluene in water, stabilized by cetyl alcohol and sodium lauryl sulfate. They concluded that the simple correction which works well for CVP does not produce a similar reconciliation in the case of the ESA effect. Their conclusions are, however, suspect because of uncertainties arising from the dilution of the emulsion system; this can so easily lead to changes in surface properties, no matter how carefully it is done. Texter's results (34) referred to above are perhaps more definitive in this case. He showed that in the range from 2 to 5% by volume where his particles showed a nonlinear dependence of the ESA signal on volume fraction, the Levine and Neale model (38) was unable to account for the nonlinearity. His particles were, however, nonspherical and that may at least partially explain the discrepancy.

Nonetheless, there are good reasons to believe that the concentration correction for the ESA method is not as simple as Eq. (8) would suggest. The Levine approach uses Kuwabara's "zero vorticity" model (40) in which the vorticities of both the hydrodynamic and the electric fields are zero on the defining surface of the cell which encloses each particle (41). At frequencies in the megahertz range, the vorticity of the flow field stretches out beyond the confines of the cell so that hydrodynamic interactions between the particles are very much more significant. O'Brien *et al.* (42) showed that the Levine cell model drastically underestimates the effect of concentration on both the magnitude and the phase angle of the dynamic mobility in the range 0.5–11 MHz. It should be noted that the reciprocal relationship makes it clear that precisely the same limitations would apply to the CVP in the same frequency range. Those experimental studies should be borne in mind in considering Ohshima's calculations of the concentration effect using the Kuwabara model (43). He gives the results of his numerical calculations of the magnitude of the dynamic mobility (but not the phase) for various ka values from near zero (10^{-3}) to infinity (10^3) for values of $\alpha = \omega a^2 / \nu$ from 0.1 to 100 and for Φ values from 0 to 0.7 assuming that ζ is small. He also provides an approximate analytical solution valid for low ζ potentials and insulating particles ($\epsilon_p = 0$). The experimental results (42) would suggest that the frequency range over which those results can be used is rather limited.

Rider and O'Brien (44) have extended the dilute-solution theory to incorporate the order Φ correction which allows one to describe the ESA behavior up to particle concentrations of order 10% by volume. For higher con-

centrations, the corrections depend to a considerable extent on the density difference between the disperse phase and the dispersion medium. Fortunately, in the case of the emulsion systems, where that density difference is usually relatively small, O'Brien has provided an approximate analytical solution to the problem which appears to be very effective. For near-neutrally buoyant particles it is only necessary to take account of the near-neighbor hydro-dynamic interactions. The effect of the particles in modifying the electric field experienced by each particle can also be relatively easily taken into account, using the Clausius-Mosotti approach, familiar from the theory of dielectric permittivity. Using the Percus-Yevick approximation (47) to estimate the distribution function for the nearest neighbors $[g(r)]$ and assuming additivity of the contributions from each particle in the vicinity of the central particle, O'Brien *et al.* have shown (45) that the dynamic mobility is given by:

$$\mu_d = \frac{\epsilon \zeta}{\eta} H \left[\frac{1 - \frac{2\beta^2}{(2+\phi)(3+3\beta+\beta^2)} - \frac{3\phi}{2+\phi} F}{(1+\phi) \frac{\Delta\rho}{\rho} HF} \right] \quad (9)$$

where the factors H and F are defined as:

$$H = \frac{3+3\beta+\beta^2}{3+3\beta+\frac{1}{3}\beta^2 \left(1+2\frac{\rho_p}{\rho}\right)} \quad (10)$$

$$F = \frac{2}{3} \left[(4\beta^2 I + (1+2\beta)e^{-2\beta}) J^2 + \frac{1}{2} \right] \quad (11)$$

Here

$$J = \frac{e^\beta}{1+\beta+\frac{\beta^2}{3}} \quad \text{and} \quad I = \int_1^\infty (g(r)-1) r e^{-2\beta r} dr \quad (12)$$

where $\beta = (1+i)\sqrt{(\omega a^2/2\nu)}$.

The results of the theory are shown in Fig. 9 where it is apparent that increasing particle concentration reduces the variation of the signal with frequency (both in magnitude and in phase angle). The effect is to make the particles appear smaller in size as the concentration is increased. It also makes the measurement of their size dependent on increas-

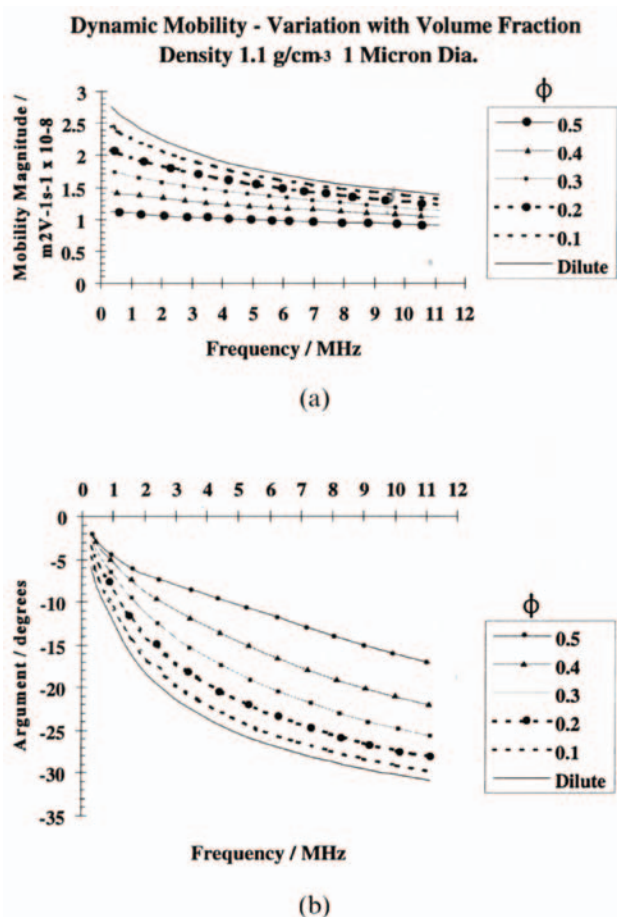


Figure 9 (a) Magnitude of the dynamic mobility as a function of frequency for various volume fractions for a particle of radius 1 μm; (b) phase angles for the same conditions as in (a).

ingly precise measurement of both the magnitude and the phase. Fortunately, the magnitude of the ESA signal increases with Φ so the signal-to-noise ratio is improved, though there is no doubt that there are limits to the concentrations at which sizing will be successful. Only one of Ohshima’s sets of numerically calculated results (43) (his Fig. 9) is in a region where it can be compared with the O’Brien calculation ($ka = 50$) and there appears to be little or no correlation between the two calculations.

The efficacy of O’Brien’s analysis is demonstrated by the data in Table 2 which shows a comparison of the estimated values of zeta potential and of size using the dilute-solution theory and the more elaborate theory of Eqs. (9) to

(12). One of the systems used in this study was the same parenteral/intrave-nous emulsion used by Carasso *et al.* and referred to above (27). This is a very stable material and it is supplied as a 20 or 10% (w/v) emulsion which was carefully diluted with the suspending fluid and measurements made at varying particle concentrations. It is clear from Table 2 that using the concentrated-suspension theory gave rise to almost identical zeta and size values at all dilutions whereas the dilute theory would suggest rather unlikely variations of order 15% in both size and zeta potential.

The other systems used in the study were somewhat more variable in composition. Some were standard examples of common dairy products (30): full cream and reconstructed cream (made by mixing cream with skim milk). They too gave much more consistent results when analyzed using the concentrated formula than were obtained with the dilute formula [Eq (2)]. It should also be noted that the zeta potential and size data obtained for the concentrated systems (cream and reconstituted cream) before and after dilution are reasonably consistent (comparing Tables 1 and 2). Both show almost the same size, and the zeta potentials differ by only 5 to 6 mV, which suggests that the dilution procedure used in preparing the data for Table 1 is more satisfactory than the alternatives but that one should still favor the results obtained on systems which have not been diluted at all.

The bitumen cited in Table 2 was an “emulsion” prepared industrially by mixing hot (140°C) bitumen with surfactant and water (~ 20°C) to produce an emulsion (at ~ 90°C) and then cooling it to room temperature. The disperse phase in that case had a very high viscosity and behaved essentially as a solid.

VII. CONCLUSIONS

Electroacoustic spectroscopy offers the prospect of studying the size distribution, and electrokinetic and stability behavior of emulsion systems while avoiding the very real problems associated with dilution of such systems. Studies are as yet in their infancy but they have already revealed new insights into electrokinetic processes, especially for the very highly charged systems used in industry. The possibility of studying polymer adsorption on emulsion systems, as an extension of the work already performed at the solid-solution interface (46) opens up entirely new prospects for the examination of both biological and technological emulsion systems.

Table 2 Particle Size Distributions and Zeta Potentials Calculated

from Dynamic Mobility Data According to O'Brien's Concentrated Formulas [Eqs (9)-(12)] Compared to the Dilute Relation [Eq. (2)]. Particle Sizes are Given as Diameters in μm , Where d_{50} , d_{15} , and d_{85} Represent the Median, and 15th and 85th Percentiles of a Lognormal Distribution. Zeta Potentials Are in mV.

Emulsion	Volume fraction ^d	Concentrated formula				Dilute formula			
		ζ	d_{50}	d_{15}	d_{85}	ζ	d_{50}	d_{15}	d_{85}
1. Reconstituted dairy cream ^a	0.38	-36.8	1.49	1.04	2.12	-19.7	0.82	0.74	0.90
	0.27	-37.6	1.38	1.13	1.68	-25.0	0.95	0.86	1.05
	0.16	-40.0	1.33	1.20	1.47	-32.0	1.08	0.98	1.20
	0.11	-40.5	1.32	1.17	1.46	-35.0	1.15	1.05	1.28
2. Dairy cream ^b	0.38	-23.0	3.08	2.79	3.41	-12.9	1.86	1.68	2.06
	0.04	-25.3	3.14	2.84	3.48	-24.2	3.05	2.75	3.37
3. Intravenous fat emulsion (Intralipid 20% w/v)	0.217	-40.8	0.40	0.36	0.44	-29.4	0.28	0.26	0.31
	0.163	-40.3	0.40	0.36	0.44	-31.9	0.31	0.28	0.35
	0.109	-40.2	0.40	0.30	0.53	-34.2	0.35	0.31	0.38
	0.054	-40.6	0.40	0.26	0.60	-37.5	0.39	0.28	0.53
4. Intralipid ^c	0.109	-40.4	0.33	0.23	0.48	-34.4	0.28	0.21	0.38
5. Bitumen A1 Bitumen A2 Bitumen A3	0.40	67	5.9	2.6	13	32	2.9	1.5	5.4
	0.40	65	5.3	2.5	11	31	2.6	1.5	4.5
	0.40	45	6.6	2.0	21	21	3.2	1.2	9.1
6. Bitumen B Diluted B	0.60	43	3.5	2.6	4.7	12	1.0	0.9	1.1
	0.40	55	3.9	2.2	6.7	26	1.9	1.4	2.5

^aIn commercial skimmed milk.

^bIn a centrifugate.

^c10% (w/v) as supplied.

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