

Acoustic Attenuation Spectroscopy: A New Technique to Characterize the Stability and Structure of Semi-solid Topical Delivery Systems for Cosmetic and Pharmaceutical Applications

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Abstract

Consistency in the stability/structure characteristics of an emulsion is a necessary prerequisite to achieve the desired final product quality. Two reliable and well-established parameters that are intimately related to the physical stability and structure of an emulsion are particle (droplet) size and zeta potential (surface charge). Topical delivery systems (TDS) are many and varied; they include creams and lotions based on O/W and W/O emulsions. TDS are complex, multicomponent, heterogeneous compositions that require much iteration to attain the final desired formulation; many factors

play a role in determining the outcome. Additionally, cosmetic and pharmaceutical emulsions cannot be diluted without consequence to the droplet size and, hence stability. Additionally, product performance behavior such as delivery of actives, efficacy (e.g. SPF) and aesthetic acceptability (e.g. spreading) is directly affected by the droplet size (distribution). Unfortunately, current non-imaging instrumentation based on light scattering methods is severely limited in its application to such systems because of the requirement to dilute the system under investigation.

We report the results of a preliminary study of a variety of “real-world” cosmetic formulations, both O/W- and W/O-based emulsions, from sunscreens (with and without inorganic particulate actives) to moisturizers measured without dilution using a technique based on acoustic attenuation spectroscopy (AAS). A major advantage of the technique is the ability to study emulsion systems under flow conditions, allowing measurements under different shear conditions. The advantages and limitations of the method will be briefly reviewed. Data will be presented illustrating its relevance as a formulation aid to “fingerprint” emulsion composition. Further, a unique feature is the ability to non-destructively probe in situ structural characteristics of emulsions. This important new development will be discussed in light of its correlation with classical “shear” rheological measurements. AAS has deep common roots with rheology; ultrasound applies an extensional stress to the system on a very short time-scale. The output of AAS can be presented as “extensional” viscoelastic properties of the system at the frequencies within the megahertz region. These “extensional” viscoelastic properties can be used as a system fingerprint similarly to the classic “shear” viscoelastic properties.

11.1 Introduction

The design of a cosmetic or pharmaceutical emulsion is quite complex and often requires several iterations to produce a stable, efficacious, safe, cost effective and elegant product. While product specifications are established to ensure product consistency during manufacture, all too often they are not sufficient to guarantee that a truly high quality product has been manufactured. Formulation is often thought of as a black art rather than an exact scientific discipline based on established physicochemical principles. What is needed is an objective test that will be easy to run, and is predictive—a test that measures *fundamental* characteristics.^{1,2} Any test must, however, not be a function of the instrument used nor of the operator.

Two reliable and well-established parameters are, respectively, particle (droplet) size and zeta potential (surface charge).^{3,4} The techniques devised

to determine them are extremely diverse. Each method has its attractions^{5,6} but it is important to select the one that meets the actual requirements of the application in question; versatile as many current instruments may be, the one that does everything has yet to be invented. Unfortunately, the vast majority of current, commercially available, instrumentation is based on light scattering (LS). This severely limits its application to cosmetic and other emulsions because of the basic requirement to dilute the system under investigation. Only batch measurements can be made; the sample must be stationary or in stop-flow mode.

Each TDS is formulated for a particular application and, therefore, has its own specific advantages and limitations in terms of performance. Cosmetic and pharmaceutical emulsions are complex, multi-component systems that, invariably, cannot be diluted without consequence. The (dilution) process not only destroys any structure characteristics but also can induce instability leading to creaming and, often, breaking/coalescence. Hence the oft-found difficulty of correlating particle/droplet size (PS) and zeta potential (ZP) measurements with flow properties, freeze-thaw and shelf storage behavior. Additionally, many instruments are only suitable for studying O/W emulsions, or may have difficulty evaluating emulsions that contain significant concentrations of dispersed particulates, especially mixed oil/particulate systems as may be found in sunscreen formulations containing zinc oxide and/or titanium dioxide. The size range and heterogeneity also present limitations.

It has been long known that ultrasound based techniques open an opportunity to eliminate dilution.⁷⁻¹⁰ However, instrumentation hardware was too complex and suffered from weaknesses in practical application of the technique to systems of high internal phase concentration. In addition, the theoretical basis of the deconvolution of the raw data was not capable of dealing with particle-particle interaction—an essential feature of concentrated dispersions. The deconvolution of the attenuation spectra to obtain information on particle/droplet size is extremely complex. It is analogous to the problem faced in light scattering but is more straightforward. Unlike the light scattering problem, deconvolution is independent of the particle size range studied; scattering and absorption of the sound signal can be separated and multiple scattering can be eliminated. Recently, all these issues have been addressed and a commercial instrument developed that convincingly demonstrates the advantages of a technique based on a combination of acoustic spectroscopy and electro-acoustics.^{11,12} This innovation offers a new opportunity for characterizing these complicated cosmetic systems; it has the advantage of being able to study turbid emulsions where other techniques, such as light scattering, simply will not work and where dilution of such systems can alter their physical properties. It is also sensitive enough

to determine polydispersity. A major advantage of any technique based on sound is that a sample under investigation need not be stationary—a necessary requirement of light scattering instrumentation. Hence, an acoustic instrument holds promise of being able to study emulsions that are flowing, in-line or on-line. The technique has been successfully applied to the study of simple (three component) model emulsions.^{13,14} Unfortunately, model systems, while of academic interest to the researcher, are often of little practical use to the cosmetic/pharmaceutical formulator.

In this paper we report the results of a preliminary study of a variety of “real-world” cosmetic emulsions, both O/W and W/O, from sunscreens to moisturizers. The aim of the study was to determine the limitations of the acoustic method and to show proof-of-concept in the ability of the technique to help characterize the stability and performance of TDS emulsions without the need for dilution.

11.2 Experimental

A series of emulsions were manufactured; they were formulated to be commercially viable as cosmetic TDS products. The details of the systems are given in **Table 1**. The emulsions varied widely in composition and character viz internal phase weight fraction, viscosity and stability.

Table 1. Cosmetic Emulsion Formulations

Product	Emulsion Type	Emulsion Stabilizer	Internal Phase Wt. Fraction	Viscosity (cP)	Number of Components
A	O/W	Anioni	19%	13,800cP	9
B	O/W	Non-ionic	16%	4600cP	14
C	O/W	Non-ionic	27%	6,400cP	18
D	O/W	Non-ionic	32%	4850cP	13
E	W/O	Non-ionic	74%	134,000cP	10

The instrument used was a DT-1200 Acoustic Spectrometer developed by Dispersion Technology, Inc., Bedford Hills, New York.¹⁵ This instrument has two separate sensors for measuring acoustic and electro-acoustic signals independently; details of the instrument and its operation are given elsewhere.^{13,14} The raw data output is ultrasound attenuation frequency

spectra within a frequency range, from 1–100 MHz that is known to be typical for heterogeneous systems. The attenuation spectra contain information about both the particle size distribution (PSD) and high frequency rheology of the sample. Because the power of the applied ultrasound pulse is very low, the technique is truly non-destructive; it does not affect the stability of a suspension. The technique is suitable for characterizing hard solid particles as well as soft emulsion droplets and latices. The electroacoustic sensor raw data output is Colloid Vibration Current; this measured parameter yields information about ZP. Complete PSD and ZP measurements can be completed in minutes and can be made on flowing systems.

11.3 Results and Discussion

Figure 11.1 gives the results of the raw attenuation data for Emulsion A, an anionic (glyceryl stearate + AMP stearate), basic O/W cosmetic emulsion. The curve A corresponds to an initial measurement of the emulsion at rest whilst the curve B is the result after subjecting the emulsion to shear produced by peristaltic pumping for 30 hours. Clearly, there is a marked change in attenuation indicating that the particle size distribution (PSD) has changed; the emulsion is not “stable” to the level of shear produced by the peristalsis. Figure 11.2 shows measurements made, at two different points on the attenuation curve (at frequencies 4 and 100 MHz), as a function of time of shear. These time dependences are different and this reflects a variation of different droplet

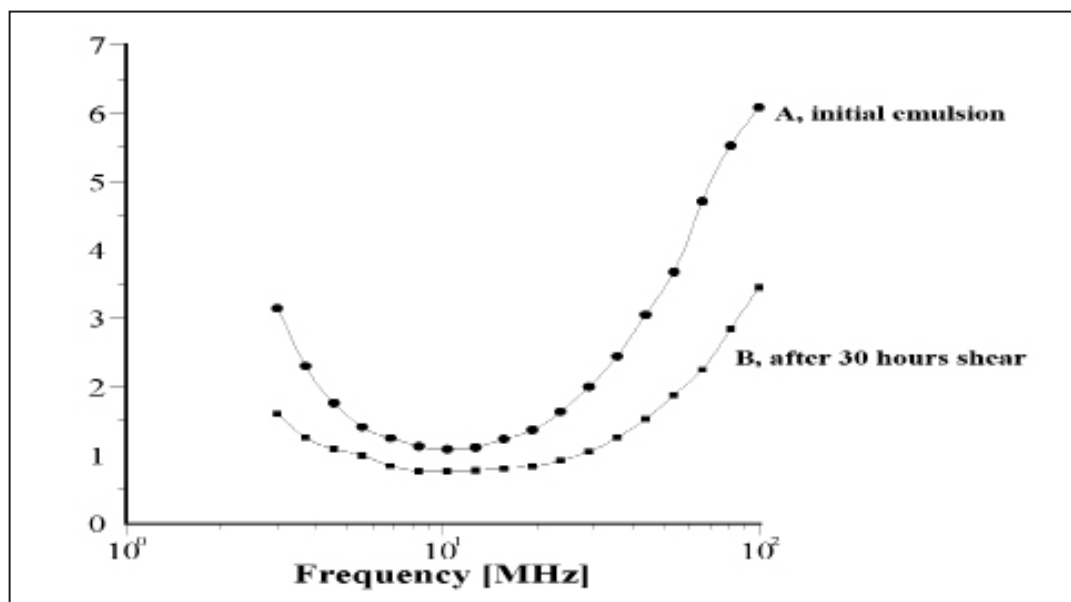


Figure 11.1. Effect of shear on the attenuation spectra of an O/W anionic emulsion

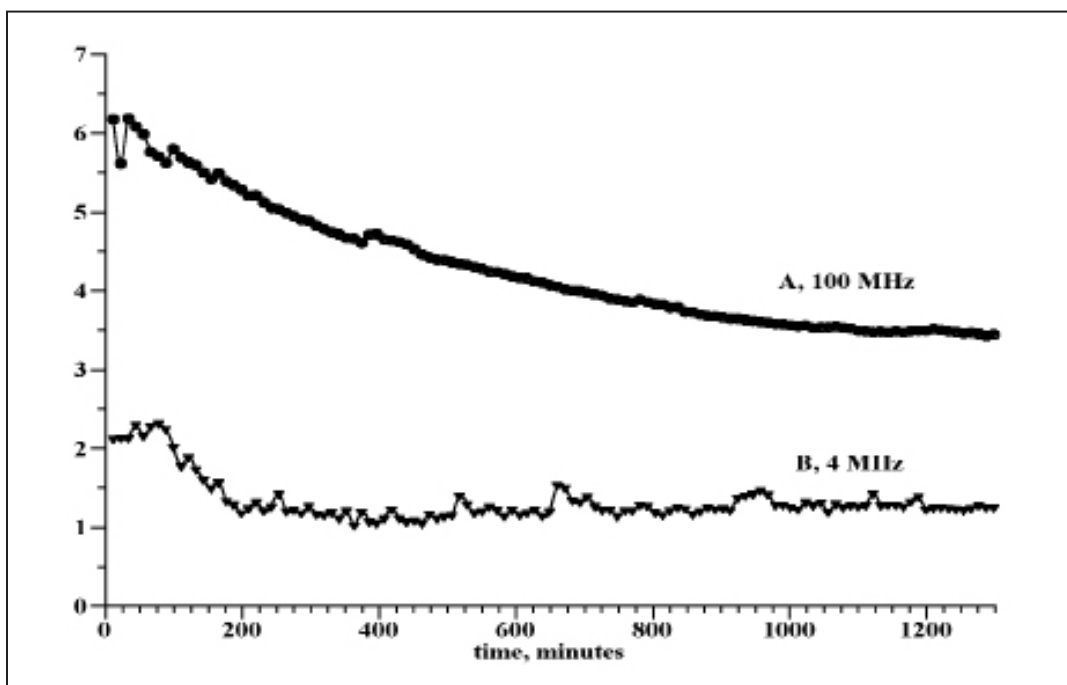


Figure 11.2. Change of attenuation, at 4 MHz and 100 MHz, as a function of time of shear of the anionic emulsion

sizes.

The low frequency attenuation (4 MHz) drops initially rapidly and then levels off (curve B). Attenuation at this frequency is mostly dependent only on the large droplets. The observed time dependence of an initial rapid drop in attenuation indicates that the shearing action has destroyed large size droplets.

The reduction in high frequency attenuation (100 MHz) is much slower (curve A). Attenuation now depends on both small and large droplets. The longer time dependence of the high frequency attenuation is what would be expected if the small droplets were removed by, for example, coalescence. This variance is consistent with the removal of large droplets at the initial much shorter times.

Thus, we conclude that the original emulsion must be bimodal and the shearing action produces two effects: large droplets are broken down into smaller droplets and smaller droplets are coalescing. The overall result is depicted in **Figure 11.3** showing the calculated PSD for the emulsion before and after shear. Initially, the emulsion comprises primarily very small droplets (ca 70nm mean) with a fraction of droplets about $8\mu\text{m}$. After shearing, the PSD changes; there are fewer of the small droplets and considerably more larger droplets but the mean PS of the larger fraction is now around $4\mu\text{m}$. Thus, it is clear that, using acoustic measurements, dynamic changes in

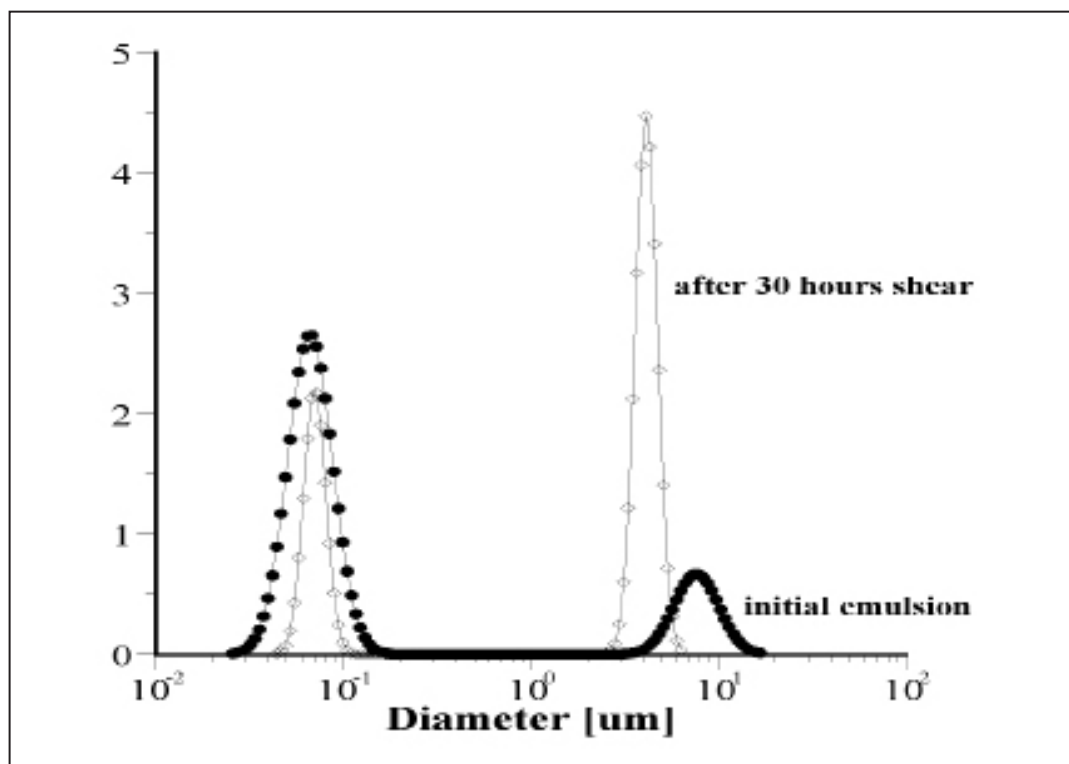


Figure 11.3. Effect of shear on the droplet size distribution of the O/W anionic emulsion

the state of an emulsion can be followed in real time.

The original emulsion was found to have a ZP of -20.0mV , (determined utilizing the electro-acoustic feature of the DT-1200), a not unexpected value given the known facts of the emulsion; it is quite typical of such anionically stabilized systems.⁵

Emulsions B and C are examples of nonionically stabilized O/W moisturizers; primarily they differed in that Emulsion C also contains 3.5 wt% of a particulate sunscreen active—a microfine, hydrophobically coated, zinc oxide (ZnO) added to provide broad spectrum UV protection. The raw attenuation spectra are compared in **Figure 11.4**; they are clearly distinguishable from one another, and it is also apparent that the shapes of the two spectra are dissimilar. The PSD of both the oil droplets and the ZnO, dispersed therein, can be abstracted from the total spectrum for Emulsion C (**Figure 11.5**). The values of ca. $2\mu\text{m}$ and 160nm are typical for emulsion oil droplets and ZnO particles, respectively. Indeed, the ZnO size is very good agreement with the PS measured on a pre-dispersion of the ZnO in the oil phase prior to emulsification. In this latter case the instrument used was an X-Ray disc centrifuge—a high resolution PS analyzer; this technique is ideally suited to the measurement of the PS of oxides and ceramics¹⁶ but is

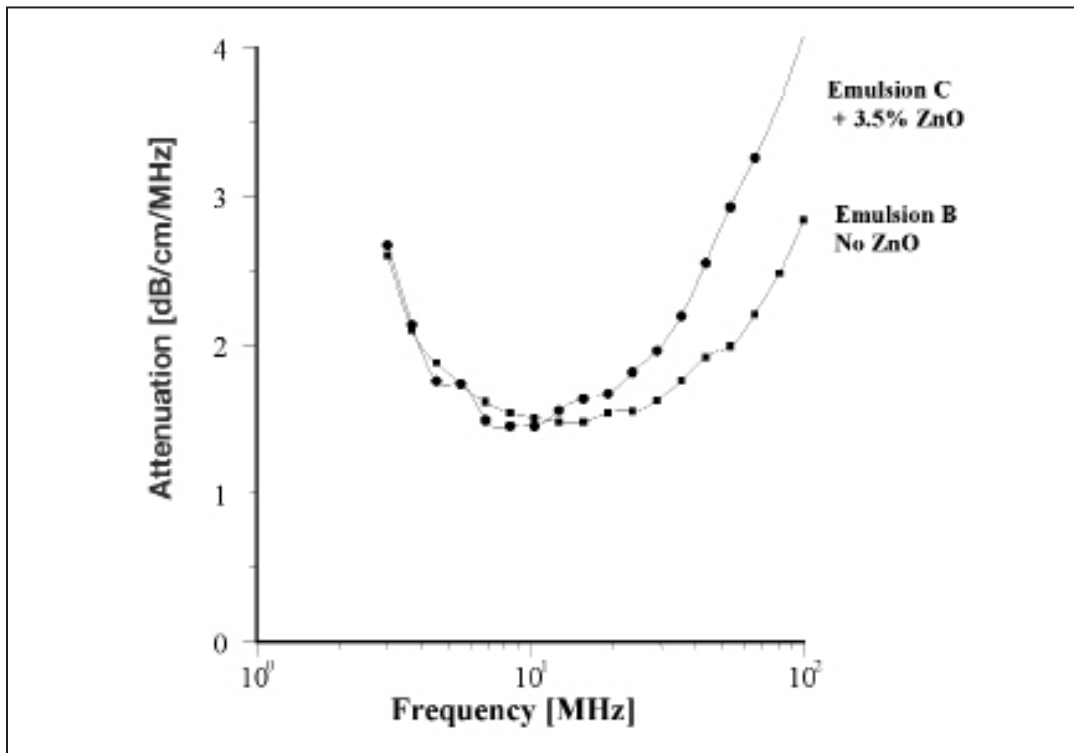


Figure 11.4. Comparison of O/W moisturizer formulations

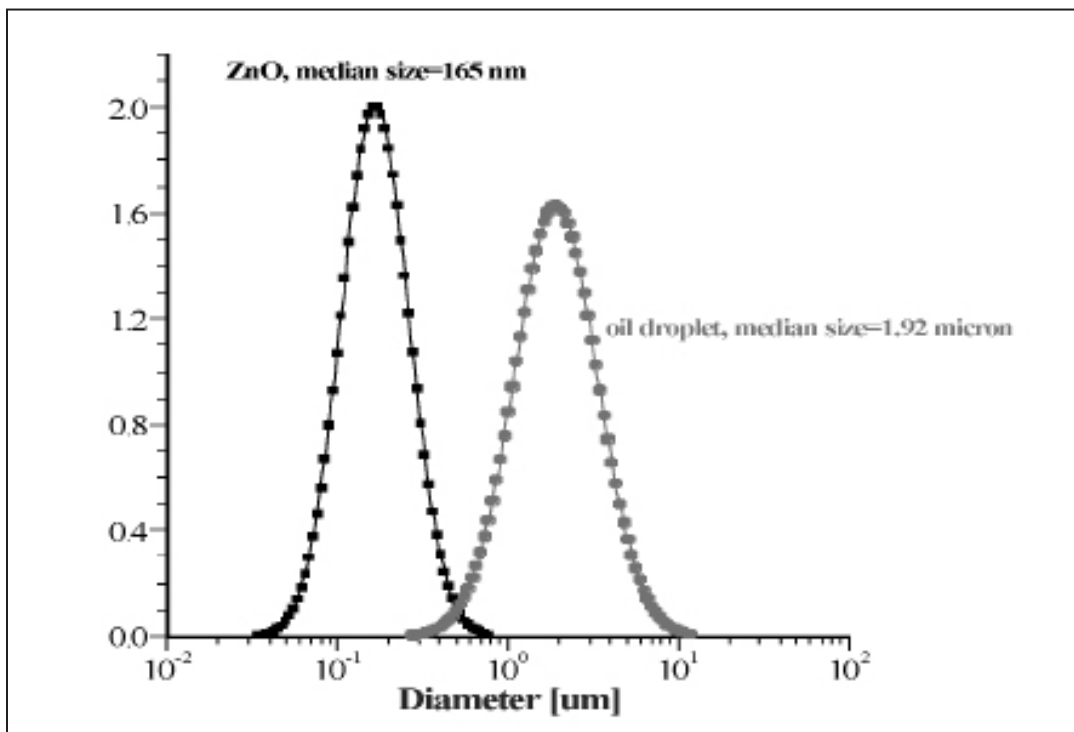


Figure 11.5. Particle size distribution of ZnO suspension within the Oil phase of an O/W moisturizer

limited to working with concentrations less than 2% v/v.

The emulsion C was then re-formulated using 3.5 wt% of a basic USP grade ZnO, such as might be used in a baby diaper cream, in place of the microfine ZnO. USP grade ZnO has a much larger mean PS and a much broader PSD than the microfine grade material. The results are compared in **Figure 11.6**. The mean PS calculated for the USP ZnO was 480nm; again in very good agreement with that measured for a straight aqueous dispersion of the material. Correct pre-dispersion of a particulate sunscreen active, such as ZnO or TiO₂, into the oil phase of an emulsion is critical to obtaining optimum performance (i.e. minimum whitening with maximum SPF/% active).¹⁷ The results of the present study suggest that acoustics might be useful in measuring the state of aggregation of ZnO or TiO₂ prior to emulsification thus allowing a formulator to monitor the efficiency of the homogenization process. It should also find utility in the milling and grinding of pigments

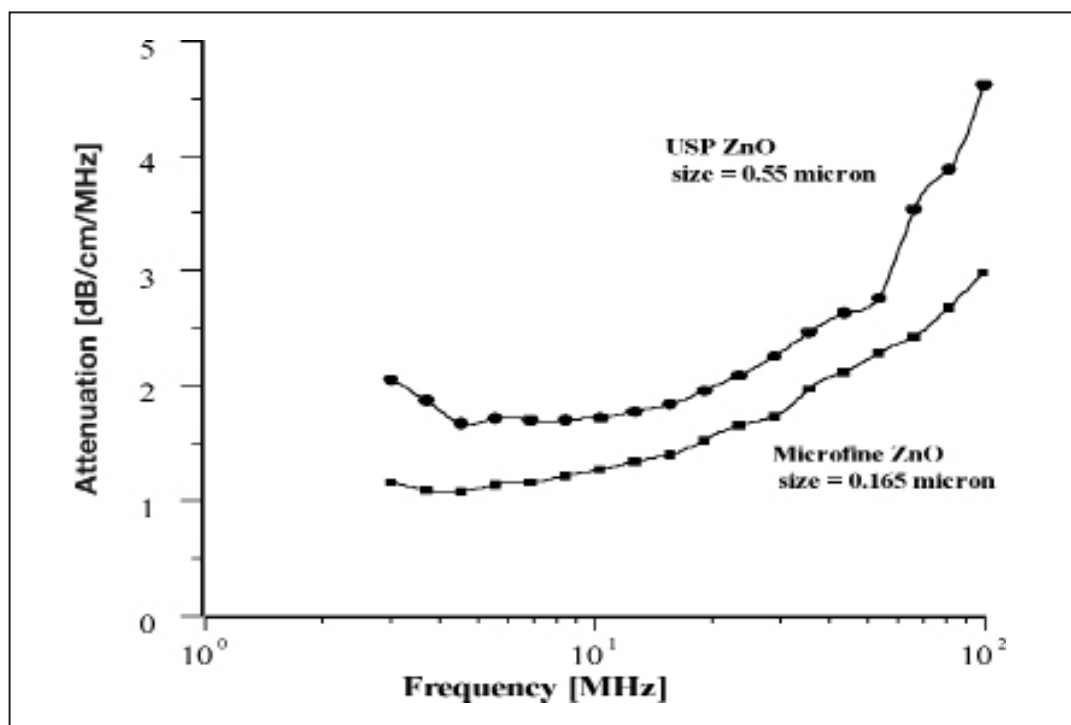


Figure 11.6. Comparison of a moisturizer formulated with different grades of ZnO

used in color cosmetics.

Figure 11.7 shows the attenuation spectrum for the emulsion D, a stable, O/W waterproof sunscreen formulation. The attenuation was measured first under quiescent conditions and then after the emulsion was deliberately

destabilized. The instability was induced by simply diluting in situ approximately 2.5x with deionized water. It can be seen that the attenuation drops by a factor 10, reflecting the observed coalescence and phase separation. Again, the results demonstrate the ability of the acoustic method to characterize the behavior of an emulsion under varying chemical conditions in real

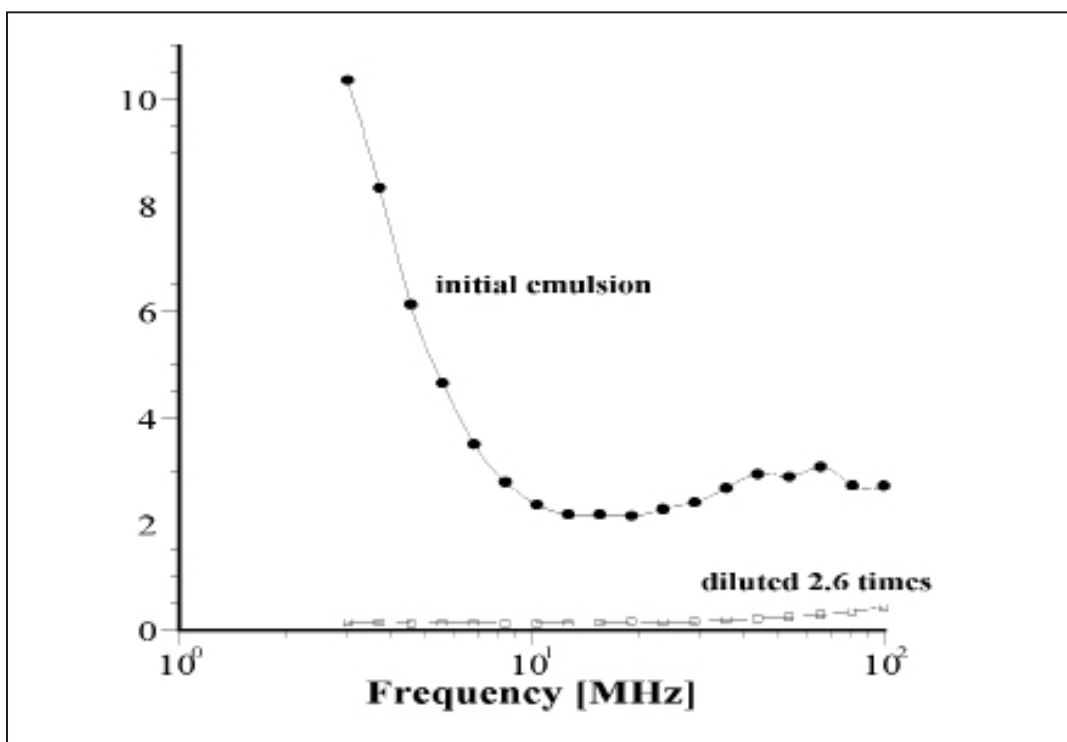


Figure 11.7. Effect of dilution on the attenuation spectra of a stable O/W emulsion (D)

time and under dynamic conditions.

It is interesting to note that, for this system, the measured value ZP was +4.5 mV. This outcome is surprising as it had been assumed that this emulsion was nonionically stabilized because Laureth-23 had been used as the emulsifier and, typically, nonionically stabilized suspensions have a ZP close to zero mV but negative in sign.⁵ On examination of the formulation components for this emulsion, it was found to contain EDTA and TEA. Thus, the only explanation for the positive value of the ZP is that one or both of the amines have specifically adsorbed at the oil/water interface. This result warrants further investigation but, nevertheless, demonstrates the usefulness of acoustics to determine and confirm the charge nature of emulsions.

The W/O emulsion E was a classic (beach type) sunscreen formulation that was found to be unstable and, subsequently, it separated into two

distinct phases. Pumping the emulsion under peristalsis into the DT-1220 allowed the two phases to simply mix; the resultant attenuation spectrum is shown in **Figure 11.8**. An emulsion droplet size of $40\mu\text{m}$ was calculated from the initial attenuation measurement (curve A). Addition of 2% sorbitan laurate (curve B) did little to improve the appearance or stability; the calculated droplet size remained around $40\mu\text{m}$ and the “emulsion” was very thin and of low viscosity. Increasing the surfactant concentration to 5.5% (curve C) resulted in a dramatic change to a white emulsion of very high viscosity

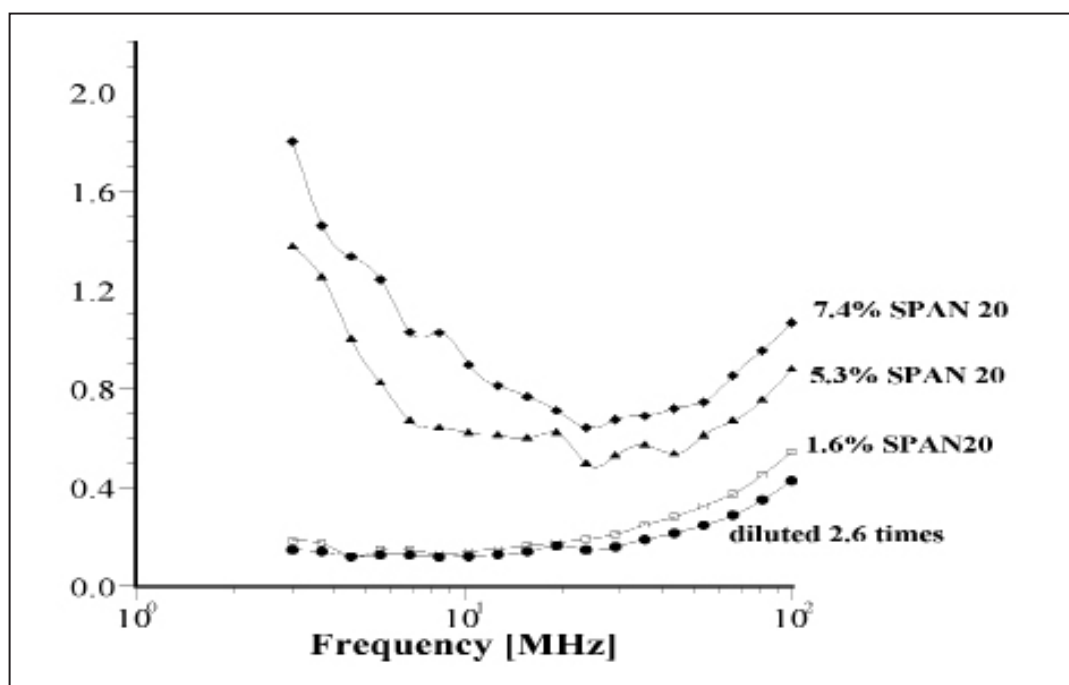


Figure 11.8. Attempt to re-stabilize an unstable (separated) W/O emulsion by addition of emulsifier

having a mean droplet size of only $2\mu\text{m}$.

The forgoing studies strongly suggest that an acoustic measurement might be used as a formulation aid to “fingerprint” emulsion composition. This hypothesis is further illustrated by comparing the attenuation spectra of three different “components” that would typically be produced during the course of formulation or manufacture of a cosmetic. These were an “oil phase”, the oil phase containing pre-dispersed 14 wt% ZnO and the final sunscreen following addition of water and homogenization. The spectra are clearly different (**Figure 11.9**) and track the compositional nature. The attenuation of the oil phase increases upon addition of the particulate ZnO because, as a solid, it has a larger attenuation than any liquid. However, the

final sunscreen has the smallest attenuation; it is considerably less than the oil phase even though it contains ZnO. This is primarily because we have added a large concentration (ca 60 wt%) of water, and it has the smallest attenuation (almost zero) of any liquid. In addition, the oil/ZnO attenuation is also significantly reduced because the concentration of that component is now only about 35 wt%; hence, the actual ZnO concentration in the sunscreen is only 3.5 wt%. This suggests, therefore, that it is possible to use the attenuation spectrum as a measure of reproducibility and repeatability at any stage of formulation; this, in turn, would considerably improve the consis-

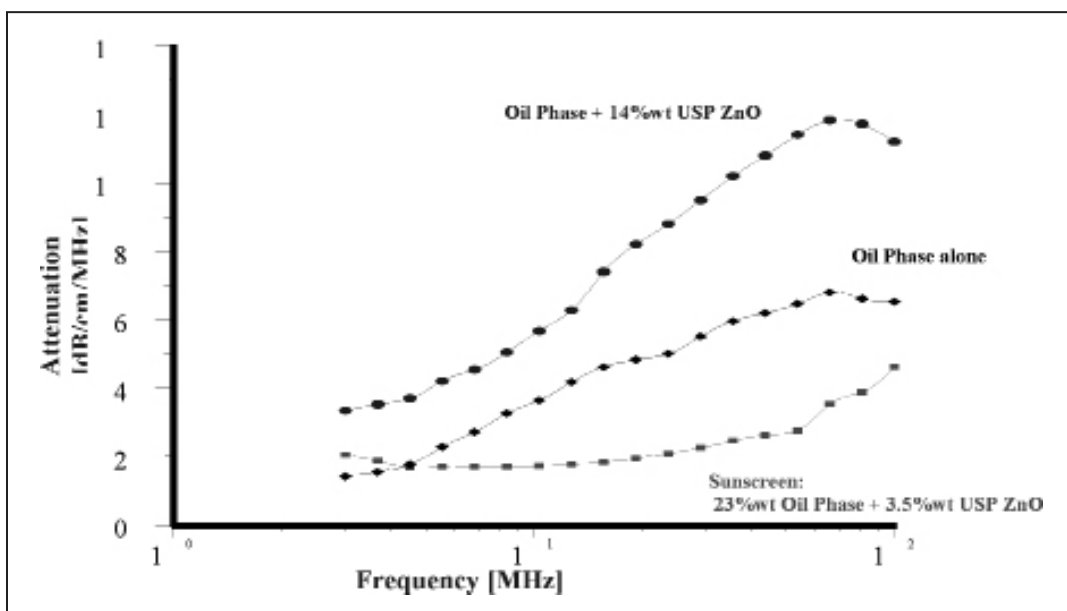


Figure 11.9. Fingerprinting Emulsion Composition

tency of the final product and, overall, lead to a cost benefit.

Using attenuation for such “fingerprinting” purposes is similar to using “shear” viscoelastic properties in rheological characterization. Acoustics and classical “shear” rheology share deep common roots. In both cases we apply stress to the system and measure the corresponding response—strain. The main difference is that, in the case of acoustics, we apply an “extensional” stress instead of a “shear” stress. In this sense the acoustic spectrometer can be considered as “extensional” rheometer. Indeed, dozens of papers are devoted to the acoustic investigation of pure liquids and polymer solution in terms of “extensional” viscoelastic properties. This application has recently been extensively reviewed¹⁸. Despite the availability of information, acoustics remains, practically, an unknown tool with which to characterize the rheo-

logical behavior of emulsions.

Here we present a few expressions that illustrate the common nature of “extensional and “shear” rheology. It is well known that, in viscoelastic media, a shear stress T_{ij} and a shear strain S_{ij} are linked by the shear modulus G :

$$T'_{ij} = GS'_{ij} \text{ where } i \neq j$$

Similarly to this concept, the “extensional” part of the stress P and the “extensional” strain S can be related by the “extensional” modulus K :

$$P = -KS$$

The propagation of an acoustic wave in a viscoelastic medium where both modulus G and K are different from zero can be represented as:

$$\rho \frac{\partial^2 X_1}{\partial t^2} = [K + (4/3)G] \frac{\partial^2 X_1}{\partial x_1^2}$$

where X_1 is the displacement of a point in the medium, ρ is density.

It is also possible to define a complex longitudinal modulus, G^* :

$$G^* = G' + iG'' = K + (4/3)G'$$

Making the assumption that the displacement X_1 is proportional to $\exp\{i\omega\tau - (\alpha + i\omega/V)x\}$, where α is the attenuation coefficient, V is sound speed and ω is the ultrasound frequency, it is then possible to determine relations between G' , G'' , α and V :

$$G' = \rho V^2 \left[\frac{1 - \left(\frac{\alpha V}{\omega}\right)^2}{\left[1 + \left(\frac{\alpha V}{\omega}\right)^2\right]^2} \right]$$

$$G'' = \frac{2\rho V^2 \left(\frac{\alpha V}{\omega}\right)}{\left[1 + \left(\frac{\alpha V}{\omega}\right)^2\right]^2}$$

The parameter $(\alpha V/\omega)^2$ is often very small and can be neglected, which simplifies the previous two equations to:

$$G' = \rho V^2$$

$$G'' = \frac{2\rho V^3 \alpha}{\omega}$$

From this example it is seen that sound speed determines “extensional” elasticity, whereas attenuation coefficient defines “extensional” viscosity. “Extensional” rheology is becoming more recognized as a useful characterization tool; at least one commercial “extensional” rheometer exists (Viscotek Inc). This instrument is based on low frequency using liquid flow through an orifice. Ultrasound offers a much simpler way to measure these parameters. However, it does it at high frequency on the MHz scale. This difference means that it is suitable for characterizing much faster processes with shorter relaxation times.

Importantly, the techniques is non-invasive and non-destructive, hence it should be possible to probe even extremely weak structures. In addition, no extra preparation or measurements are needed; the rheological data are calculated from the same attenuation spectra used for particle and droplet size analysis.

Figure 11.10 shows the measured attenuation for a series of pure liquids as a function of frequency. The relationship is linear as predicted by simple theory¹⁹ for Newtonian liquids. The calculated viscosity value of a few selected liquids is given in **Table 2**. The agreement with the nominal (literature) values is impressive. Next, a typical oil phase of an emulsion was prepared that contained various components including waxes and emulsifiers. To keep it liquid the temperature was raised to 65°C. The measured attenuation is shown in **Figure 11.11**. Though the attenuation is not perfectly linear, the calculated viscosity of 37cP compares favorably with the 35cP measured, at the same temperature, using a Brookfield viscometer. This result, however, may be fortuitous because the “viscosity” measured using an ultrasound technique is based on a longitudinal shear whereas that measured using a conventional rotational viscometer, like the Brookfield, involves a transverse shear. Essentially, a rotational viscometer measures a low frequency loss modulus whereas an acoustic “viscometer” provides a

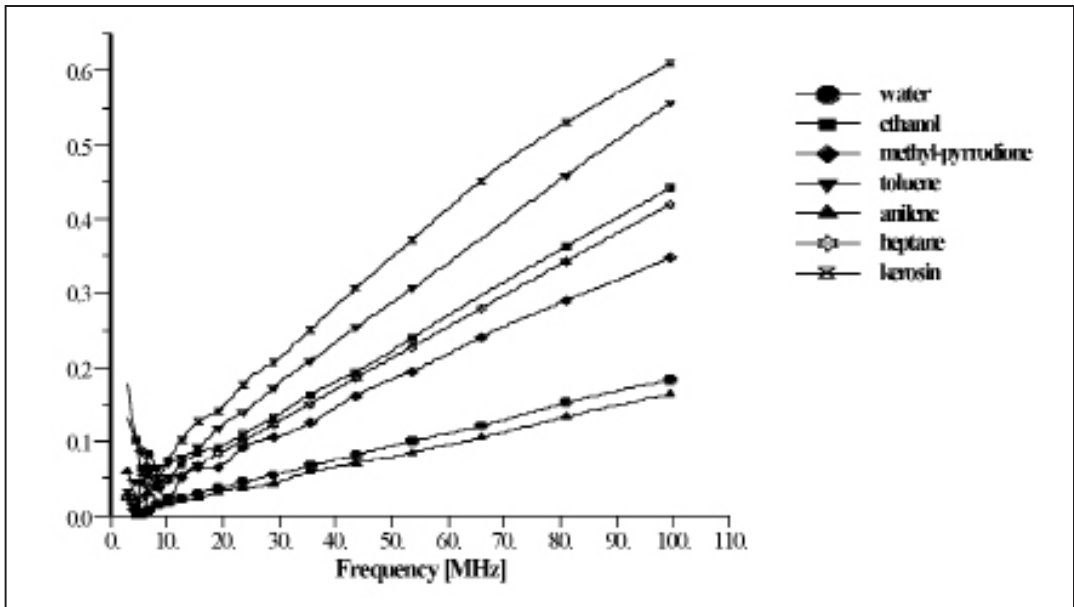


Figure 11.10. Attenuation Spectra for various pure liquids

Table 2. Viscosity of Pure Liquids

Liquid	Viscosity (Nominal)	Viscosity (Calculated)
Kerosene	4.7cP	4.6cP
Silicone Fluid A	4cSt	4.3cP
Silicone Fluid B	10cSt	12.0cP

high frequency loss modulus. Hence the presence of any “dispersed phase” in a liquid, or, indeed, if the pure liquid has any microscopic structure, will result in non-linearity and a disparity with a “normal” viscosity. Indeed, this situation will also occur if the (pure) liquid contains any microscopic structure as can be seen in **Figure 11.12** that shows the loss modulus, G'' , determined from the attenuation spectrum for the two ZnO-based sunscreens (**Figure 11.5**). It is clear that the response is non-linear and hence the system is non-Newtonian. However, it is still possible to calculate a “viscosity” using the measured sound speed through these materials and assuming the simple linear relation between G'' , frequency, ω and viscosity, η ¹⁹. This being so, the viscosity of each sunscreen was determined to be 5600cP and 7900cP for the microfine ZnO sunscreen and USP ZnO sun-

screen, respectively. The viscosities are surprisingly close to those measured using a Brookfield; in fact, the ratio of the two viscosities are 1.41 (acoustic) and 1.40 (Brookfield), respectively. The only explanation is that there must be little or no oil droplet-oil droplet interaction in either emulsion. The

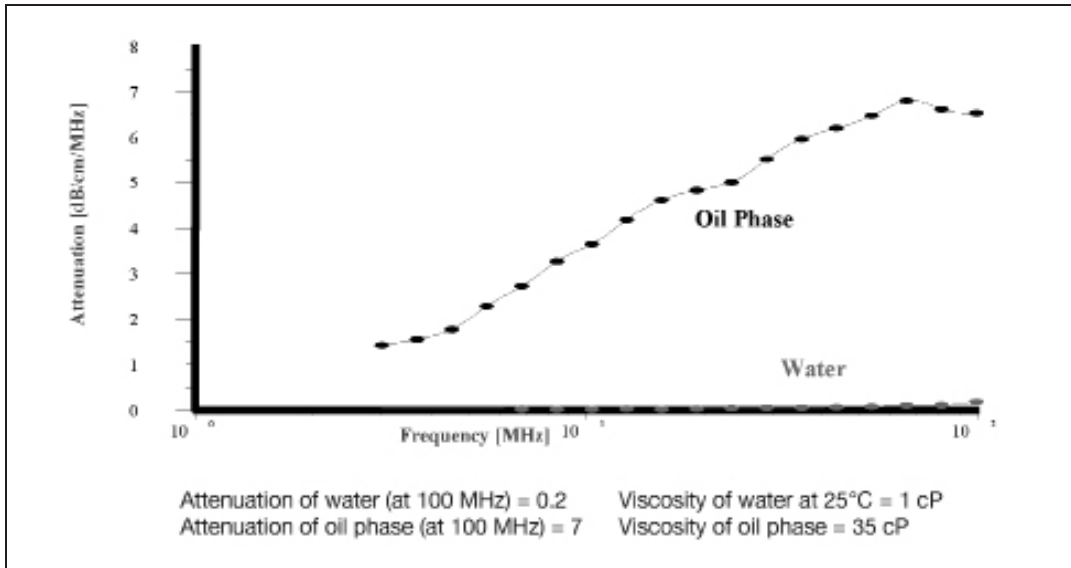


Figure 11.11. Attenuation spectrum of the oil phase of an emulsion

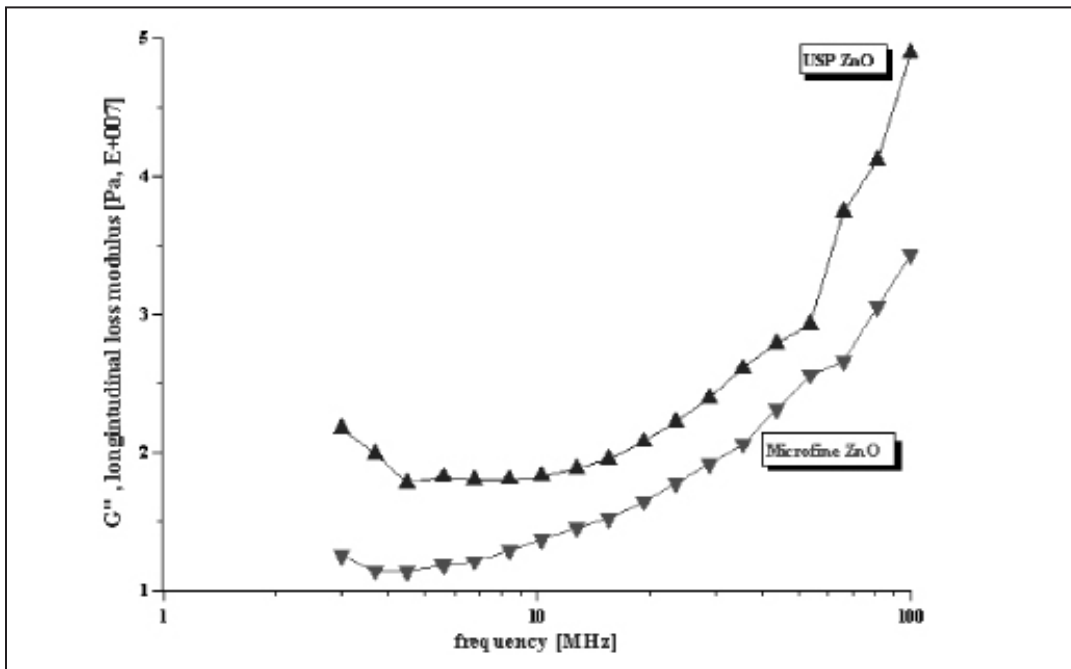


Figure 11.12. Loss Modulus, G'' , calculated from attenuation spectra, for two sunscreen formulations

observed increase in viscosity is pure hindrance arising from the PSD. The presence of the ZnO particles within the oil droplets appears to be irrelevant; this observation warrants further study.

A recent paper²⁰ has demonstrated that AAS can be used to time-finger-print the evolution of a 5% W/O emulsion during 45 hours of continuous mixing. Results are shown on **Figure 11.13**. Detailed analysis presented in the paper suggests that this evolution is driven by ion exchange between

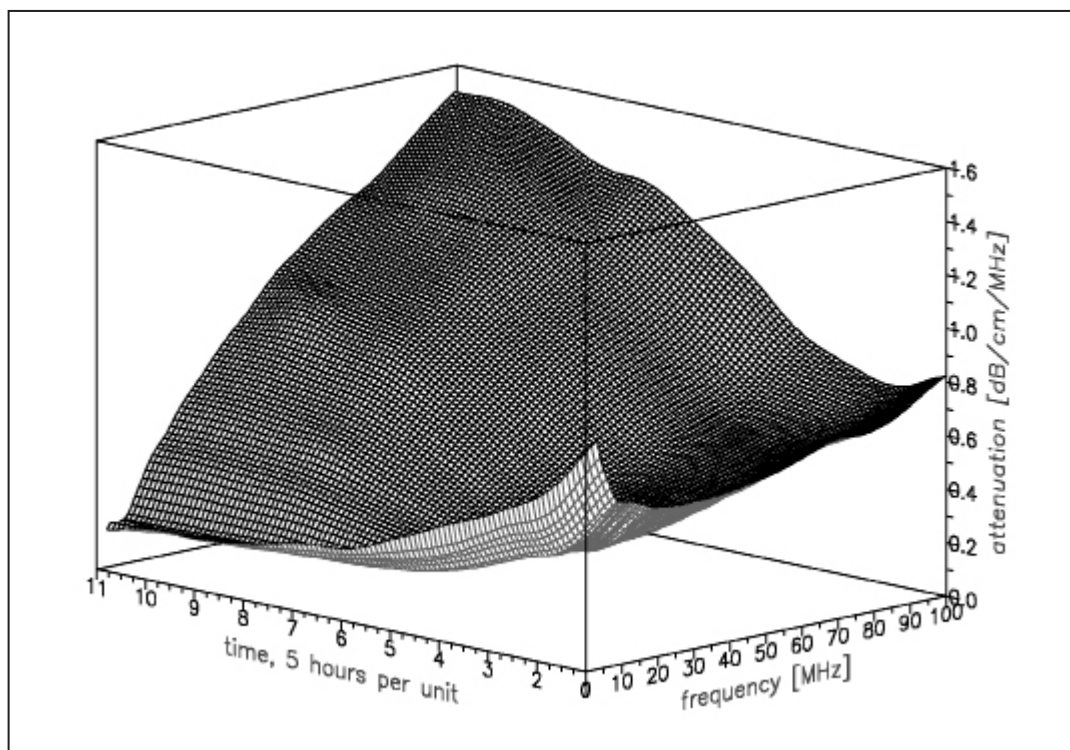


Figure 11.13. Evolution of a 5% vol water-in-kerosene emulsion stabilized with 1%wt SPAN 80

water droplets and oil phase. Electroacoustic measurement played an important role in interpreting these data.

11.4 Conclusions

Initial results, from studies of a series of commercially formulated cosmetic emulsions, suggest that a technique based upon a combination of acoustic spectroscopy and electro-acoustics is a powerful new tool to characterize the stability and performance of semi-solid cosmetic and pharmaceutical topical delivery systems (emulsions) without the need for dilution. Measurements are made in real time and can follow dynamic changes as the system is per-

turbed. PSD and ZP can be easily measured on both O/W and W/O systems; as long as the emulsion can be pumped it can be measured. Indeed, for the systems in the present study, it should be possible to measure them in-line—a potential major advantage for production. It appears feasible to use the attenuation spectrum as a measure of reproducibility and repeatability at any stage of formulation; it, in turn, would considerably improve the consistency of the final product and, overall, lead to a cost benefit and savings.

Acoustic attenuation spectroscopy can also be used to rheologically “fingerprint” the same TDS emulsions. This technique can be considered as an alternative “extensional” rheometer that offers a very simple way to collect “extensional viscoelastic data for probing the microscopic structure(s) in emulsions and suspensions. Importantly, no additional preparation or measurements are needed; the rheological data are calculated from the same attenuation spectra used for PS analysis.

Based on the present work many avenues of investigation suggest themselves. Future studies will probe in more detail the ability of the technique to discriminate the presence of a particulate phase within the emulsion and then to follow this as a function of homogenization. It would be interesting to determine, for a given emulsion, the effect(s) of HLB of emulsifier and addition/variation of thickeners, viscosity/rheology modifiers.

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