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Disperion Technology Inc., 3 Hillside Avenue, Mount Kisco, New York 10549, Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Science University of Tokyo, 12 Ichigaya Funagawara-machi, Shnjuku-ku, Tokyo 162-0826, Japan, and Institute of Biocolloid Chemistry, Academy of Sciences of the Ukraine, Kiev, Ukraine

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## Electroacoustics for Concentrated Dispersions

A. S. Dukhin,<sup>\*,†</sup> H. Ohshima,<sup>‡</sup> V. N. Shilov,<sup>§</sup> and P. J. Goetz<sup>†</sup>

Disperion Technology Inc., 3 Hillside Avenue, Mount Kisco, New York 10549, Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Science University of Tokyo, 12 Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162-0826, Japan, and Institute of Biocolloid Chemistry, Academy of Sciences of the Ukraine, Kiev, Ukraine

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Theories describing the dynamic electrophoretic mobility in concentrated dispersed systems have been discussed. There are two different theories derived recently using two different versions of a cell model. We point out here that these two versions created by H. Ohshima (first) and A. Dukhin with V. Shilov (second) agree with each other. We also provide explanations of this agreement. The cell-model-based theory describes motion of the particle in a frame of references associated with liquid. To compare this theory with experiment, the electrophoretic mobility must be recalculated into a frame of reference peculiar to the experimental technique. There are two possibilities suggested in the literature: a frame based on zero momentum flow or a frame based on zero volume flow. The first was introduced by O'Brien. Both possibilities are discussed and compared to experiment. This experiment was an equilibrium dilution of a rutile dispersion. The following parameters were measured for volume fractions from 40 vol % down to 5 vol %: attenuation spectra, sound speed, phase and amplitude of the colloid vibration current (CVI), temperature, and pH. The attenuation spectra provide independently measured particle size distribution. The sound speed is a measure of the system stability. Temperature and pH confirm the equilibrium status of the dilution. CVI is used to calculate the  $\zeta$ -potential applying a new cell model theory. Since this was an equilibrium dilution, in principle, the  $\zeta$ -potential should remain constant over this volume fraction range unless a double-layer overlap becomes important. Indeed, it is shown that the  $\zeta$ -potential does remain constant up to 35 vol % with variations of only  $\pm 2$  mV if the value is calculated using a zero volume flow frame of reference. In comparison, the  $\zeta$ -potential calculated following O'Brien in a zero momentum frame of reference increases more than 2 times at 35 vol %.

### Introduction

Electroacoustics opens in principle an opportunity to characterize concentrated dispersed systems where particle interaction is significant. To turn this opportunity into reality, a theory is required. This theory must connect the measured electroacoustic parameters such as the colloid vibration current (CVI)<sup>1</sup> or electrosonic amplitude (ESA)<sup>2</sup> with properties of the given dispersed system including  $\zeta$ -potential and particle size. Absence of this theory is a major obstacle for further development of electroacoustic-based techniques.

The first versions of an electroacoustic theory were created by Enderby and Booth,<sup>3,4</sup> but only for dilute systems. Later, O'Brien made an important step<sup>5</sup> by introducing the dynamic electrophoretic mobility  $\mu_d$  and deriving a general expression for this parameter which is valid in concentrated systems:

$$\text{ESA}(\text{CVI}) = C\sigma\varphi\mu_d \quad (1)$$

where  $C$  is a cell constant,  $\sigma$  is the density contrast,  $\varphi$  is

the volume fraction of the solid,  $P$  is the hydrodynamic pressure, and  $E$  is the external electric field strength.

Dynamic electrophoretic mobility can be used as a useful system characteristic. It is sufficient, for instance, for determining the isoelectric point. However, the dynamic electrophoretic mobility provides only a partial characterization. The  $\zeta$ -potential and the particle size distribution are required for more complete characterization.

There are several theories describing the relationship between dynamic mobility and other properties of the dispersed system. The most widely known and tested theory created by O'Brien<sup>5</sup> is valid only for the dilute case with a volume fraction below 2% and only for a thin double layer.<sup>6</sup> Another theory created by Babchin et al.<sup>7,8</sup> removes the restriction of the thin double layer but still does not take into account particle–particle interaction and consequently is applicable still only for dilute systems.

The first attempt to derive an electroacoustic theory for concentrated systems was made by Marlow<sup>1</sup> using a cell model.

Rider and O'Brien<sup>9</sup> used a completely different approach for deriving an expression for the dynamic mobility of a single pair of colloid particles. This work showed that such an approach has many large mathematical complications. Nevertheless, O'Brien chose this approach because he

\* To whom correspondence should be addressed.

† Dispersion Technology Inc.

‡ Science University of Tokyo.

§ Academy of Sciences of the Ukraine.

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concluded that the cell model approach did not work since he was unable to fit theories based on such cell models to experimental data. He published this conclusion<sup>10</sup> without giving any explanations to this surprising fact. There is only one detail about this unpublished theory mentioned in the paper<sup>10</sup> that the Levine–Neale cell model<sup>11</sup> is used.

Despite the negative conclusions reached by O'Brien, several new papers have recently appeared which again address the cell model approach. A new cell-model-based theory was created by Ohshima<sup>12</sup> initially using just the Levine–Neale cell model and was later modified by Ohshima and Dukhin<sup>13</sup> using Onsager relationships. Another cell model version of the theory was developed by Shilov, Borkovskaya, and Dukhin<sup>14</sup> using the Shilov–Zharkikh cell model.<sup>15</sup> We show in this paper that both theories yield the same result.

Importantly, the final versions of these new theories predict a much stronger volume fraction dependence than the initial Levine–Neale cell model,<sup>12</sup> which perhaps explains why the initial unpublished O'Brien theory failed to fit experiments.

However, there is an additional reason for the initial failure of the cell model approach. It is related to the problem of the frame of reference. The cell model enables us to calculate the electrophoretic mobility relative to a liquid frame of reference. However, it is not clear that this frame of reference is appropriate for comparison of the theory to experiment. Two possibilities have been suggested before: a zero momentum frame of reference or a zero velocity frame of reference.

O'Brien and Rider suggested that electrophoretic mobility must be determined in a frame of zero momentum flow.<sup>9</sup>

On the other hand, Zukoski and Saville<sup>16</sup> and Chen and Keh<sup>17</sup> have defined electrophoretic mobility using a zero volume flow frame of reference.

For dilute systems the question of the frame of reference becomes unimportant since they each provide the same result. For concentrated systems, the frame of reference becomes increasingly important. We think that the question as to which frame of reference is most appropriate is still open. For this reason we evaluate both versions in this paper.

Our new theory has been tested using a concentrated rutile dispersion. The initial concentrated dispersion was diluted with supernate in order to maintain the same chemical composition for all volume fractions. As a result,

we would expect that the actual  $\zeta$ -potential would be essentially constant, at least up to perhaps 35 vol % where we might expect some decrease due to double-layer overlap. A correct theory should enable us to calculate a  $\zeta$ -potential which remains constant over a wide concentration range.

However, dilution can change the particle size as well, and this would correspondingly affect the  $\zeta$ -potential calculation. For this reason our equilibrium dilution test must also include an independent monitoring of the particle size. This is not trivial because the particle size measurement must be done in a concentrated system. We know of only one reliable method to accomplish this goal: acoustic spectroscopy.<sup>18–20,27–29</sup> We used this method for calculating the particle size from the measured attenuation spectra.

Acoustic spectroscopy also provides an additional consistency check using sound speed. We showed that the experimentally measured sound speed correlates within 1% with the sound speed calculated for the corresponding particle size using existing theory.<sup>18</sup>

This equilibrium dilution test made it clear that a zero volume flow frame of reference yielded more constant values of  $\zeta$ -potential with volume fraction than a zero momentum frame of reference. The zero volume flow reference provided almost constant  $\zeta$ -potential for volume fractions up to 35 vol % with variations of just 2 mV. In contrast, the  $\zeta$ -potential calculated following O'Brien using the zero momentum frame of reference increased more than two times.

#### Comparison of the Different Cell Model Theories.

Both cell model electroacoustic theories (Ohshima/Dukhin and Shilov/Borkovskaya/Dukhin) are intended to be valid for concentrated systems with a thin double layer (DL) and weak surface conductivity  $\chi^o$ . It follows that they should both predict the same value of the colloid vibration current and dynamic electrophoretic mobility if

$$\kappa a \gg 1 \quad (2)$$

where  $\kappa$  is the reciprocal Debye length,  $a$  is the particle radius, and

$$Du \ll 1 \quad (3)$$

where  $Du = \chi^o/\kappa a$  is a Dukhin number introduced by Lyklema.<sup>21</sup>

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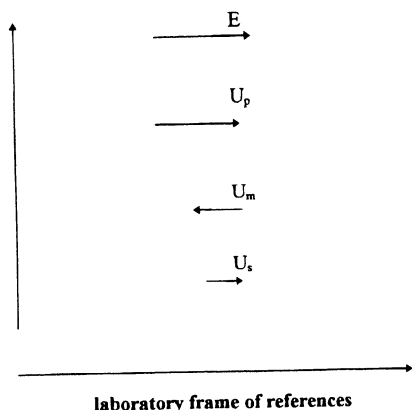
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**Figure 1.** Scheme-illustrating generation of ESA signal and the showing of the relationship between different velocities in a laboratory frame of references.

These assumptions are valid for many real aqueous-based dispersions.<sup>21</sup>

The real situation is not quite that simple. Although we obtain the same value for CVI calculated using either theory, unfortunately, the calculated dynamic electrophoretic mobilities are different.

Let us use the superscripts "oh" and "sh" in order to distinguish the Ohshima theory<sup>12,13</sup> from the Shilov et al. theory.<sup>14</sup> For instance, let us define the dynamic electrophoretic mobilities derived by Ohshima<sup>12</sup> and Shilov<sup>14</sup> as  $\mu_d^{oh}$  and  $\mu_d^{sh}$  correspondingly. First we note that  $\mu_d^{oh}$  differs from  $\mu_d^{sh}$  by the factor  $(1 - \varphi)/(1 + 0.5\varphi)$ :

$$\mu_d^{sh} = \mu_d^{oh} \frac{1 - \varphi}{1 + \varphi/2} \quad (4)$$

In addition to the difference in the dynamic mobilities, these theories apply the different definitions of the dynamic mobility and different relationship with the colloid vibration current. For instance, according to the generalized Ohshima theory,<sup>13</sup>

$$CVI^{oh} = C\sigma\varphi\mu_d^{oh} \frac{1 - \varphi}{1 + \varphi/2} \nabla P \quad (5)$$

This expression was derived using the Ohshima theory for sedimentation potential.<sup>22</sup>

Shilov et al.'s theory<sup>14</sup> applies another expression:

$$CVI^{sh} = C\sigma\varphi\mu_d^{sh} \nabla P \quad (6)$$

The different dynamic electrophoretic mobilities lead to the same values of CVI because of these differences in the definition of the colloid vibration current. As a result, the two cell model theories are identical when they are used for interpreting experimental data. The final expression for CVI in the case of the thin double layer and the weak surface conductivity<sup>13,14</sup> can be presented in the following form:

$$CVI = C\sigma\varphi\nabla P \frac{3\epsilon_m\epsilon_0\zeta}{2\eta(1 + 0.5\varphi)} \frac{(1 - \varphi)H(\alpha) + I(\beta) - 1(\alpha)}{1.5H(\alpha) - \sigma(I(\beta) - I(\alpha))} \quad (7)$$

where  $\alpha = a\sqrt{\omega/\nu}$ ,  $\beta = ba/a$ ,  $\nu$  is the kinematic viscosity,

$$H(\alpha) = \frac{ih(\alpha)}{2\alpha} - \left( \frac{idh(x)}{2dx} \right)_{x=\alpha}$$

$$h(x) = h_1(x)h_2(\beta) - h_1(\beta)h_2(x)$$

$$I(x) = I_1(x) - I_2(x)$$

$$I_1(x) = -h_1(\beta) \exp(x(1 + i)) \left[ \frac{3(1 - x)}{2\beta^3} + i \left( \frac{x^2}{\beta^3} - \frac{3x}{2\beta^3} - \frac{1}{x} \right) \right]$$

$$I_2(x) = h_2(\beta) \exp(-x(1 + i)) \left[ \frac{3(1 + x)}{2\beta^3} + i \left( \frac{x^2}{\beta^3} + \frac{3x}{2\beta^3} - \frac{1}{x} \right) \right]$$

$$h_1(x) = \frac{\exp(-x)}{x} \left[ \frac{x + 1}{x} \sin x - \cos x + i \left( \frac{x + 1}{x} \cos x + \sin x \right) \right]$$

$$h_2(x) = \frac{\exp(x)}{x} \left[ \frac{x - 1}{x} \sin x + \cos x + i \left( \frac{1 - x}{x} \cos x + \sin x \right) \right]$$

It is important to mention that the colloid vibration current defined by expression 7 is a local current. In the real experiment the macroscopic current is a measured parameter. The relationship between this local and macroscopic CVI requires an additional consideration of the frame of reference.

**Dynamic Mobility in Different Frames of References.** The expression for the dynamic mobility derived by either of these theories<sup>12-14</sup> is valid in the frame of reference connected to the liquid. To compare this theory to experiment, the electrophoretic mobility must be recalculated either in the frame of zero momentum or in the frame of zero volume flow. To make an appropriate transition, let us consider particle motion in a new, as yet unspecified, frame of reference (see Figure 1) under the influence of external electric field  $E$ .

Particles move relative to this reference frame with a velocity  $U_p$ . The velocity of the liquid motion is  $U_m$ . The dynamic electrophoretic mobility specified by the cell model theory  $\mu_d^c$  is a part of the following relationship between the velocity of the particle and the velocity of the liquid:

$$U_p + U_m = \mu_d^c E \quad (8)$$

The experimentally measured electrophoretic mobility is defined with the following expression:

$$U_p = \mu_d E \quad (9)$$

The last equation must specify the nature of the frame of reference.

If we employ the zero volume flow assumption, these two velocities are related by the following expression:

$$U_p\varphi - U_m(1 - \varphi) = 0 \quad (10)$$

Alternatively, if we employ the zero momentum flow assumption, we obtain a quite different relationship between the velocity of the particle and the liquid:

$$U_p\varphi\rho_p - U_m(1 - \varphi)\rho_m = 0 \quad (11)$$

where  $\rho_m$  and  $\rho_p$  are densities of the medium and of the

The system of equations, (7)–(9), yields the following expression for the dynamic electrophoretic mobility in the zero volume flow frame of references:

$$\mu_d = \mu_d^c(1 - \varphi) \quad (12)$$

On the other hand, the dynamic mobility calculated in the zero momentum frame using eqs 7, 8, and 10 is quite different:

$$\mu_d = \mu_d^c(1 - \varphi) \frac{\rho_m}{\rho_s} \quad (13)$$

where  $\rho_s$  is the density of the dispersion.

This final expression differs from the expression for the dynamic electrophoretic mobility in the frame of the momentum derived by O'Brien and Rider.<sup>9</sup> The difference arises because O'Brien and Rider used  $\mu_d$  with a different meaning. They derived the relationship between electrophoretic mobilities in the momentum frame and the frame of the zero volume flow at low frequency. Expression 13 relates dynamic mobilities in the momentum frame and the frame of the liquid.

It is important to add that this analysis has been performed for the one-dimensional case. We neglected effects related to the shunt volume flow at the edges of the sound pulse. The width of the sound beam must be much larger than the wavelength corresponding to the frequency of measurement. This condition is certainly valid for DT-1200 which measures CVI at 3 MHz.

### Experimental Technique

We used a combined acoustic and electroacoustic spectrometer DT-1200 developed by Dispersion Technology, Inc.<sup>23</sup> This instrument has two separate sensors for measuring acoustic and electroacoustic signals independently.

Both sensors use the tone-bursts pulse technique.

The acoustic sensor measures attenuation frequency spectra and group sound speed.

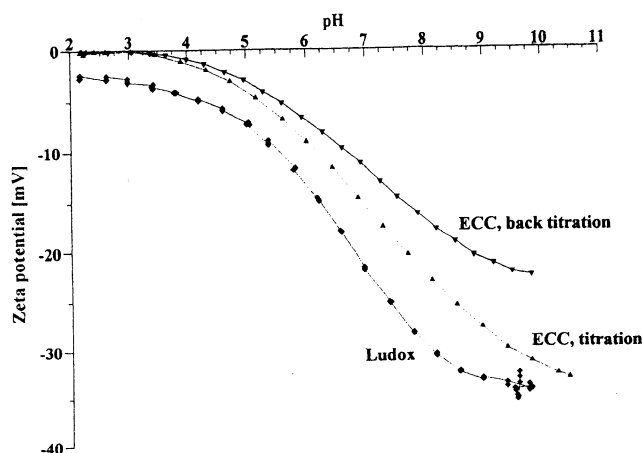
The acoustic sensor has two piezoelectric crystal transducers. The gap between the transmitter and receiver is variable in steps. In default it changes from 0.15 mm up to 20 mm in 21 steps. The basic frequency of pulse changes in steps as well. In default it changes from 3 to 100 MHz in 18 logarithmic steps. The number of pulses collected for the each gap and each frequency is automatically adjustable in order to reach a target signal-to-noise ratio.

The acoustic sensor measures group sound speed at one chosen frequency using the change in transit time of the pulse versus the gap. The instrument automatically adjusts the pulse sampling depending on the value of the sound speed, which is necessary to eliminate artifacts such as excess attenuation at low frequencies.

A single attenuation spectrum is measured using default conditions in about 5 min. The user can speed up measurement by changing the setup parameters, and successive measurements on the same sample are made even faster.

There is a special analysis program which calculates the particle size distribution (PSD) from attenuation spectra. This program tests log-normal, bimodal and modified log-normal<sup>24</sup> particle size distributions. It uses an error analysis in order to search for the best PSD. The goal of the optimization procedure is to minimize the error in the theoretical fit of the experimental attenuation spectra.

The precision and accuracy of the acoustic spectrometer in general depends on the size of the characterized particles and volume fraction. It has been tested with several different systems.<sup>20</sup> For the particular dispersion (rutile in water) which is a subject of this paper, precision of the particle sizing is about 1%; accuracy of the median particle size is about 1%; accuracy of the particle size distribution width is about 5%.



**Figure 2.** Titration of 10 wt % silica Ludox and 20 wt % chemical polishing silica ECC.

The electroacoustic sensor measures the magnitude and phase of the colloid vibration current at 1.5 and 3 MHz.

The CVI measurement at 1.5 MHz is used for determining only the CVI phase and correspondingly the sign of the  $\zeta$ -potential. This phase calculation requires correction for sound speed. It is provided by the acoustic sensor which measures group sound speed which is converted to the phase sound speed according to the following expression:

$$c_{ph} = c_g \left( 1 - \frac{\omega_m}{c_{ph}} \frac{dc}{d\omega_{\omega=\omega_m}} \right) \quad (14)$$

where  $c_g$  and  $c_{ph}$  are the group and phase sound speeds and  $\omega_m$  is the frequency of measurement.

Measured sound speed is more reliable than the calculated one in general. Sound speed might be affected by structural affects. Sound speed theory neglects particle aggregation effects and can produce incorrect sound speed. We use this peculiarity of the acoustic spectroscopy as an independent test of the system stability.

Sometimes the CVI and sound speed are measured at different frequencies. Sound speed is recalculated to the frequency of CVI measurement using theory described in the paper.<sup>18</sup>

The CVI measurement at 3 MHz is used for determining the absolute value of the  $\zeta$ -potential. The acoustic spectrometer provides the particle size and attenuation coefficient which is required for this calculation.

A single CVI measurement can be obtained in as little as 10 s or as long as several minutes, depending on the system properties.

The precision of the  $\zeta$ -potential measurement is about 0.1 mV. The DT-1200 is able to measure very weak signals by collecting more pulses in order to improve the signal-to-noise ratio. One example is shown in Figure 2 which illustrates the measurement of  $\zeta = 0.2$  mV at low pH for a silica slurry used for chemical mechanical polishing.

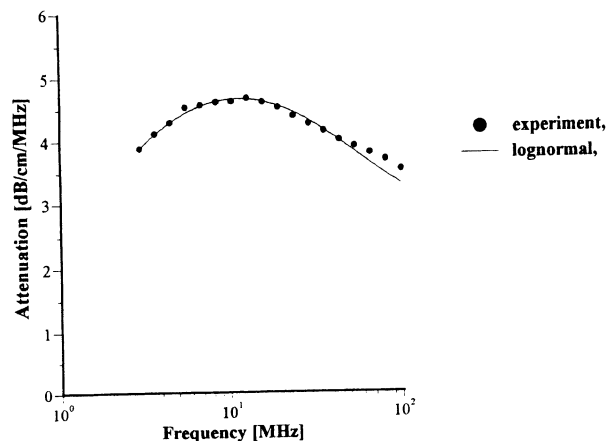
The total required sample volume is about 100 mL. There is a special magnetic stirrer to prevent sedimentation and provide mixing of reagents during titration.

The instrument also has conductivity, pH, and temperature probes as well as digitally controlled burets for dispensing chemical reagents during automated titration.

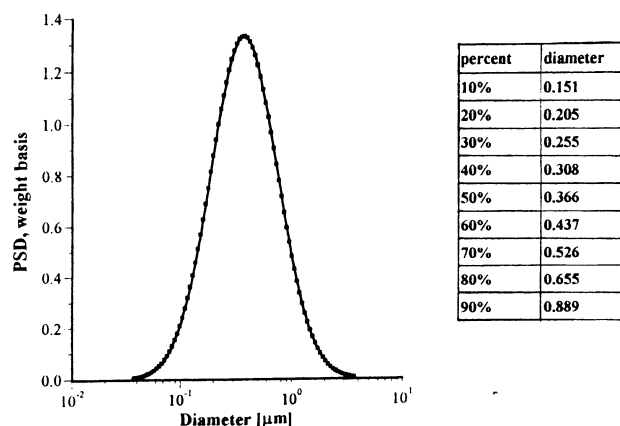
### Experimental Protocol

The experiment was performed using rutile R-900 produced by E. I. DuPont de Nemours. The particle size of this rutile calculated from the attenuation spectra (Figure 3) is shown in Figure 4. This rutile is alumina-covered. As a result, its dispersion is stable at low pH.

We prepared 1 L of the 20 vol % rutile dispersion in  $10^{-2}$  mol/L KCL. It was necessary to adjust the pH several times during the dispersion and sonication. The final dispersion at pH 4 was sonicated for 5 min. The dispersion was aged for 2 days to allow equilibration and separation to occur. There were four fractions



**Figure 3.** Attenuation spectra of the stable rutile R-900 at 5 vol %.



**Figure 4.** Particle size distribution corresponding to theoretical log-normal attenuation in Figure 4.

after this equilibration. The top layer was almost pure supernate, the next layer had an average concentration of 20 vol %, the third layer had a concentration of about 40 vol %, and finally a cake was on the bottom. The final pH was about 4.3.

Three first fractions were used as the basis for the equilibrium dilution. The dilution was made in two steps. First, the 20 vol % fraction was diluted in steps down to roughly 5 vol %. Next, the more concentrated 40 vol % fraction was diluted in steps down to roughly 12 vol %. This procedure gave some overlap between dilution series and allowed us to test the reproducibility. Dilution steps were made almost randomly to avoid any systematic effects, the concentration in each case checked with a pycnometer. The accuracy of the pycnometer deteriorates at low solid content, and therefore we did not go below 5 vol %.

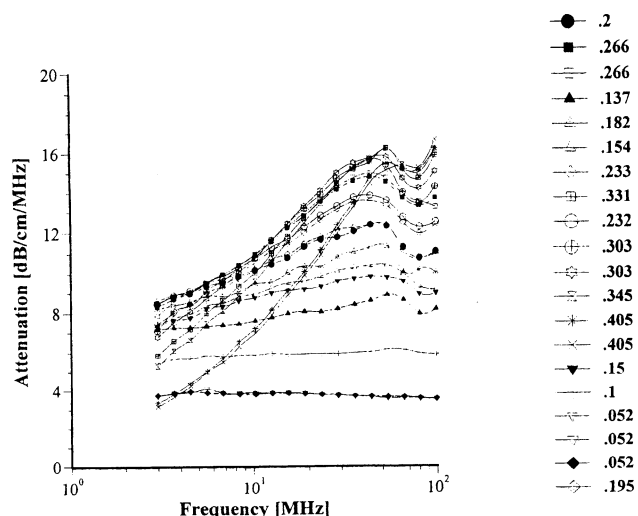
The following seven experimental parameters were measured at each dilution step: attenuation spectra, sound speed, phase and magnitude of CVI, pH, and temperature.

### Results and Discussion

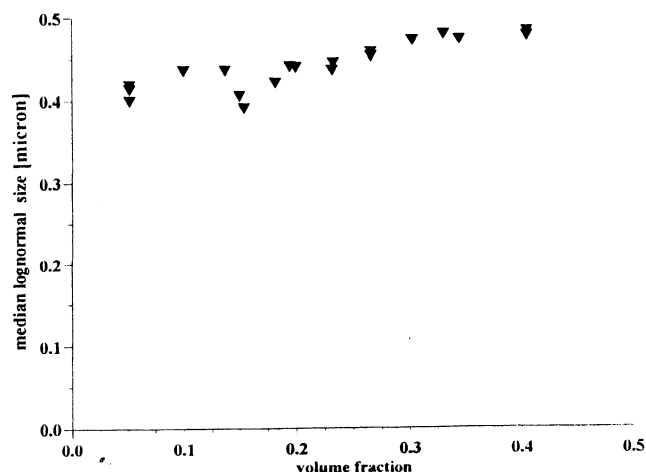
There were no significant variations of the pH of the sample with volume fraction, which supports the equilibrium nature of the dilution protocol.

The measured attenuation spectra are shown in Figure 5. The corresponding median particle size is shown in Figure 6. It is seen that the size increases slightly with volume fraction. This increase can be caused by sedimentation during the equilibration period. The more concentrated 40 vol % fraction might be more enriched with larger particles.

It is important to mention that acoustic theory used to



**Figure 5.** Attenuation spectra for rutile R-900 after 2 days of equilibration.

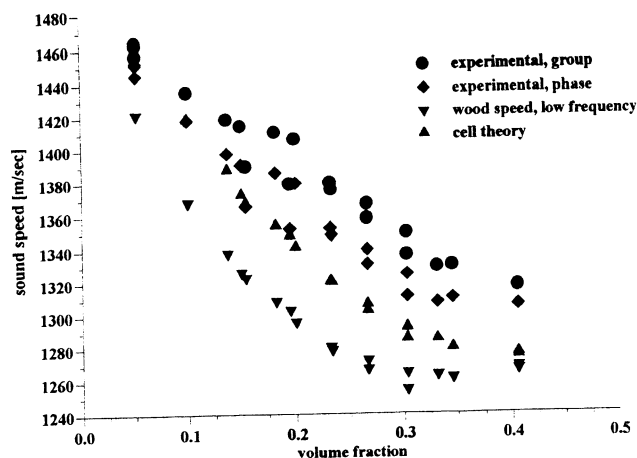


**Figure 6.** Median particle size versus volume fraction for rutile R-900 after equilibrium dilution.

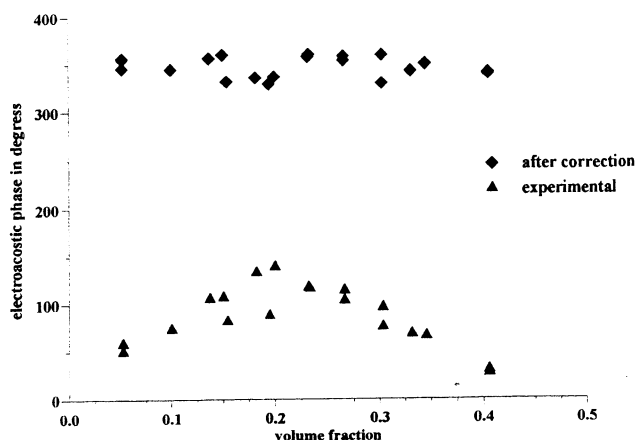
might be wrong which causes error in the  $\zeta$ -potential. According to our experience, neglecting particle-particle interaction causes about 300% error in calculating the particle size for a dispersed system with 40% volume fraction.

The sound speed measurement provides an additional consistency check. Figure 7 shows the experimental and theoretical sound speed at 10 MHz. The theoretical sound speed is calculated using acoustic theory from the paper in ref 18. This calculation requires the particle size distribution. The attenuation measurement provides these data. It is seen that the experimental phase sound speed and theoretical sound speed are very close. The difference between them is less than 1% for almost all volume fractions. This consistency test confirms the calculated value of the median particle size.

We would like to emphasize that it is the first experimental test of the theory determining sound speed with taking into account particle-particle interaction.<sup>18</sup> Usually, so-called Wood sound speed or scattering ECAH theory is used for characterization of sound speed in dispersions.<sup>27-29</sup> The Wood sound speed corresponds to the low-frequency limit. There is a more recent sound speed theory developed in papers in refs 25 and 26. However, there is only one theory which gives the relationship between particle size and sound speed<sup>18</sup> for



**Figure 7.** Experimental and theoretical sound speed of rutile R-900 after equilibrium dilution.



**Figure 8.** Experimental CVI phase and corrected CVI phase of rutile R-900 after equilibrium dilution.

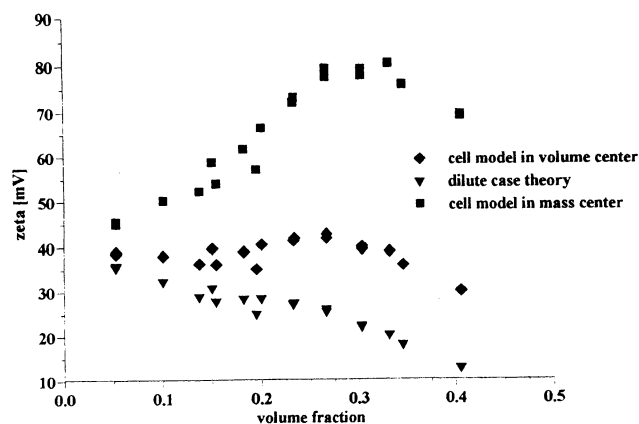
contribution is quite important. There is a substantial difference between the Wood speed and theoretical sound speed.

Sound speed is an essential part of the CVI phase calculation. Figure 8 shows experimentally measured phase and phase corrected for sound speed. This correction has been made with the experimental phase sound speed recalculated to the 1.5 MHz using theory from the paper in ref 18. It is seen that the corrected CVI phase is volume-fraction-independent. It is supposed to be 360° which corresponds to particles with positive  $\zeta$ -potential.

The absolute value of the  $\zeta$ -potential is shown in Figure 9. It is calculated from CVI at 3 MHz using the cell model theory developed in this paper. The calculation has been made using the particle size shown in Figure 6 and the attenuation from Figure 5. The attenuation correction is required because sound attenuates traveling from transducer to the electroacoustic antenna.

It is clear that the  $\zeta$ -potential remains independent of the volume fraction up to approximately 30 vol % using the zero volume flow frame of reference. For comparison, the  $\zeta$ -potential drops to a level of only 10 mV at 35 vol % when calculated with the dilute case O'Brien theory. Furthermore, the  $\zeta$ -potential actually increases more than 2 times at 30 vol % if the O'Brien suggestion of the zero momentum frame of reference is adopted.

We would like to stress at the end that all acoustic and electroacoustic measurements and calculations are consistent and mutually confirming. This experiment has been intentionally designed as overdefined. The amount



**Figure 9.**  $\zeta$ -potential of rutile R-900 after equilibrium dilution, calculated using developed cell model theory.

of experimental information exceeded the requirements for calculating the particle size and  $\zeta$ -potential. As a result we had additional information (sound speed and CVI phase) for consistency tests which makes this experimental test of the developed theory even more meaningful.

We would like to add that there are several sources of the volume fraction dependence of the electroacoustic signal. In this paper we addressed so far only one aspect related to the theory of CVI. Other aspects are related to the measurement procedure. Interpretation software of the DT-1200 takes into account two of them.

The first effect is a partial reflection of ultrasound on the surface of the transducer which is facing the dispersed system. This reflection reduces the intensity of the ultrasound which generates CVI by the factor

$$\frac{I_t}{I_i} = \frac{4Z_t Z_s}{(Z_t + Z_s)^2} \quad (15)$$

where  $I_t$  and  $I_i$  are the sound intensity transmitted to the dispersion and intensity generated by the piezo crystal and  $Z_t$  and  $Z_s$  are acoustic impedances of the transducer and dispersion.

This reflection effect depends on the volume fraction of the dispersed system because of the acoustic impedance  $Z_s$ . The real part of this acoustic impedance equals

$$Z_s = \rho_s c_s \quad (16)$$

where  $\rho_s$  and  $c_s$  are the density and sound speed of the system. These parameters are volume-fraction-dependent.

The second factor which is built into the DT-1200 software is attenuation of the ultrasound. There is a gap between the transducer and CVI antenna. The sound pulse attenuates propagating through this gap. As a result, the intensity of the sound which generates CVI ( $I_{CVI}$ ) decays by the factor

$$\frac{I_{CVI}}{I_t} = 10^{-\alpha L / f^{10}} \quad (17)$$

where  $\alpha$  is the attenuation coefficient in dB/cm/MHz,  $L$  is a gap width between the transducer and antenna, and  $f$  is the frequency in MHz.

Attenuation is a frequency-dependent-parameter in this relationship.

These two additional factors make the relationship between CVI and  $\zeta$ -potential more complicated. We should admit that there might be some additional factors which are missed in the DT-1200 software. Unfortunately,

uncertainties with theory do not allow us to test this measurement procedure completely. All these questions can be resolved only after all theoretical issues about CVI (ESA) would be clarified.

### Conclusions

It is shown that combined acoustic and electroacoustic spectroscopy provide self-consistent and complete characterization of particle size distribution and  $\zeta$ -potential in concentrated dispersed systems with a volume fraction up to 40%. The first step of this characterization is the measurement of the attenuation frequency spectra, sound speed, and colloid vibration current. This set of parameters can be measured reliably and be reproducible in any concentrated-liquid-based dispersed system. This set of parameters contains sufficient information for calculating the particle size and  $\zeta$ -potential when a real system can be modeled as a collection of separate particles in a liquid.

The second step of the characterization procedure is the calculation of the PSD and  $\zeta$  using appropriate theoretical models. The cell model concept provides means for developing acoustic<sup>18</sup> and electroacoustic<sup>12-14</sup> theories

which are valid in concentrated systems. The equilibrium dilution test confirms the validity of these theories.

The attenuation frequency spectra is the data source for calculating PSD independently of any electrical properties of the dispersion.

CVI is a data source for calculating the  $\zeta$ -potential.

There are several links between acoustics and electroacoustics. For instance, acoustics provides information about the sound speed which is necessary for calculating the correct phase of CVI. Acoustics also gives particle size data which is important for calculating the absolute value of the  $\zeta$ -potential.

A combination of acoustics and electroacoustics yield extra information which can be used for testing the basis assumption about system stability. Sound speed is the source of this information. Sound speed is very sensitive to the structural effects. Deviation between theoretical and measured sound speed is an indication that the real system cannot be replaced with the realistic collection of independent particles in a liquid.

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