# CHARACTERIZING CLAY MINERAL SUSPENSIONS USING ACOUSTIC AND ELECTROACOUSTIC SPECTROSCOPY − A REVIEW

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**Abstract**— Recently, significant advances have been made in the theory and application of acoustic and electroacoustic spectroscopies for measuring the particle-size distribution (PSD) and zeta potential ($\zeta$ potential) of colloidal suspensions, respectively. These techniques extend or replace other techniques, such as light-scattering methods, particularly in concentrated suspensions. In this review, we summarize acoustic and electroacoustic theory and published results on clay mineral suspensions, detail theoretical constraints, and indicate potential applications for the study of environmentally significant clay mineral suspensions. Using commercially available instrumentation and suspension concentrations up to 45 vol.%, acoustic spectroscopy can characterize particle sizes from 10 nm to 10 μm, or greater. Electroacoustic spectroscopy can determine the $\zeta$ potential of a suspension with a precision and accuracy in the mV range. Despite the clear potential for their use in environmental settings, to date, acoustic methods have been used mainly on clay mineral colloids with industrial application, typically combined with similar measurements such as isoelectric point (IEP) determined from shear yield stress or $\zeta$ potential from electrophoretic mobility measurements. Potential applications in environmentally relevant suspension concentrations are significant, as PSD and $\zeta$ potential are important factors influencing the transport of mineral colloids and associated contaminants through porous media. Applications include determining the effects of suspension concentration, surfactants, electrolyte strength, pH and solution composition on soil clay properties and colloidal interactions, and determining changes in PSD, aggregation and $\zeta$ potential due to adsorption or variations in the clay mineralogy.

**Key Words**—Acoustics, Aggregation, Electroacoustics, Electrokinetics, Particle-size Distribution, PSD, Zeta Potential.

## INTRODUCTION

Recently, significant advances have been made in the theory and application of acoustic and electroacoustic spectroscopies to characterize colloidal PSD and $\zeta$ potential (Dukhin and Goetz, 1996b, 2002; Dukhin *et al*., 1999a; Hunter, 1998; O'Brien *et al*., 1995; Ohshima, 1998; Ohshima and Dukhin, 1999; Oja and Alba, 1998). These acoustic techniques extend or replace other techniques, such as light-scattering methods, particularly in concentrated colloidal suspensions. Optical techniques fail in this case, due to the requirement of extreme dilution. To date, the use of electroacoustics on clays and clay minerals has been confined mainly to industrial applications, despite the clear potential for the technique to characterize clay mineral suspensions with environmental or agricultural significance (Galassi *et al*., 2001). For example, the size and surface charge of particles in the clay fraction of soils are important in sorption mechanisms and in transport properties of mineral colloids and associated contaminants (Bertsch and Seaman, 1999; McCarthy and Zachara, 1989; Seaman and Bertsch, 2000). Interactions between clay minerals may be complicated, and not predictable from the characteristics of the individual minerals (Anderson and Benjamin, 1990). The effects of different electro-

lytes may be critical, and dependent on the ratio of solution to clay minerals in a suspension (Barrow, 1985; Barrow and Shaw, 1979; Roy *et al*., 1991). Surfactants can be used to modify the surface chemistry of clays and clays minerals in the environment to control the transport of contaminants (Seaman and Bertsch, 2000).

Acoustic spectroscopy measures the speed and attenuation of sound waves interacting with a colloidal suspension. The resulting spectrum yields a quantitative measure of the PSD. Electroacoustic spectroscopy measures either colloid vibration potential/current (CVP/CVI) or electrokinetic sonic amplitude (ESA), each of which is quantitatively related to the mean $\zeta$ potential and PSD. The ESA effect arises when an alternating electric field applied to a suspension generates a sound wave of the same frequency. Conversely, when a sound wave passes through a suspension, tiny dipoles created on charged particles sum to yield a macroscopic electric field alternating at the same frequency. The electric disturbance can be sensed by two appropriate electrodes as a colloid vibration potential (CVP) or, alternatively, as a colloid vibration current (CVI) (Dukhin and Goetz, 1996a; Dukhin *et al*., 1999a, 1999b; Hunter, 1998; O'Brien *et al*., 1995).

Before the introduction of electroacoustic spectroscopy and appropriate theoretical models, $\zeta$ potential was typically measured only in extremely dilute colloidal suspensions using micro-electrophoresis methods.

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Sedimentation potential measurements are also restricted to relatively dilute suspensions in order to ensure free settling and uniform particle flow. Unfortunately, suspension dilution may affect both PSD and ζ potential. Conversely, high solid concentrations of very large particles (*e.g.* sand) are required for electro-osmosis and streaming potential measurements due to the requirement of a tightly packed, immobile porous plug (Johnson *et al.*, 1999a). In contrast to these earlier methods, electro-acoustic spectroscopy is applicable in either relatively dilute or quite concentrated suspensions. Measures of the PSD can also be made with techniques such as scanning electron microscopy (SEM), sedimentation, field-flow fractionation and light scattering. However, electroacoustic spectroscopy has advantages over each of these, particularly in concentrated suspensions.

In this paper, the theory behind acoustic and electroacoustic spectroscopies is summarized with an emphasis on practical considerations important in application. The experimental literature on the application of these techniques to clays and clay minerals is reviewed, and measurement acquisition constraints are discussed. For practical reasons, this article is biased somewhat to the theory and application of the DT-1200 (Dispersion Technology) equipment used in our laboratory (Dukhin and Goetz, 2001b). Several different theoretical approaches and acoustically based instruments are available, such as the DT-1200 (Dukhin and Goetz, 2000), the ESA-8000 (O'Brien *et al.*, 1995), the Malvern Ultrasizer (Oja and Alba, 1998), and the AcoustoSizer (Hunter, 1998). The reader is referred to a recent review focusing on the ESA-8000 and the AcoustoSizer (Hunter, 1998) and to more technical papers and summaries for theoretical detail (Babick *et al.*, 2000; Babick and Ripperger, 2002; Dukhin and Goetz, 2001a, 2002; Hunter, 1998; McClements, 1991; Stolojanu and Prakash, 2001). Similarly, the reader is referred to papers by Hunter (1998), O'Brien (1995), O'Brien *et al.* (1995), O'Brien and Rowlands (1993), O'Brien and White (1978), Rowlands *et al.* (1997), Rowlands and O'Brien (1995) for other theoretical approaches and techniques for sizing particles and measuring ζ potential, and to Dukhin and Goetz (2002) for the relationship between acoustics and rheology. A companion article (Guerin and Seaman, 2004) (the following paper in this issue) illustrates the use of these spectroscopies to suspensions of clays and clay minerals obtained from highly weathered sediments.

## THEORY OF ACOUSTIC AND ELECTROACOUSTIC SPECTROSCOPIES

### Theory of acoustic spectroscopy

When a sound wave in the range of kHz to MHz interacts with a suspension of particles, the acoustic attenuation and sound speed can be theoretically related to the PSD of the suspension. Acoustic attenuation depends on particle size, volume fraction, size dispersivity, and particle-particle interactions, and is measured as a function of frequency of the emitted and detected sound waves. Schematic attenuation spectra for three ranges of particles sizes, measured over two orders of magnitude in frequency, are shown in Figure 1a. Figure 1b shows the measured attenuation spectrum of water for comparison.

Acoustic attenuation can be considered as a superposition of six loss mechanisms; viscous, thermal, scattering, intrinsic, electrokinetic and structural losses (Table 1) (Dukhin and Goetz, 1996a, 1998, 2002). For submicron particles, the first two losses are the most significant, and when either the viscous or the thermal loss mechanism predominates, the other may be ignored. Viscous losses are due to shear waves generated as particles and fluid move relative to each other in the acoustic pressure field, whereas thermal losses arise from the thermodynamic coupling between temperature and pressure (Dukhin and Goetz, 1996a). Viscous losses dominate in dispersions with a large density contrast between solvent and particle, such as in clay mineral suspensions, whereas thermal losses dominate in low-contrast systems such as emulsions. Viscous losses are more sensitive to suspension concentration, and when
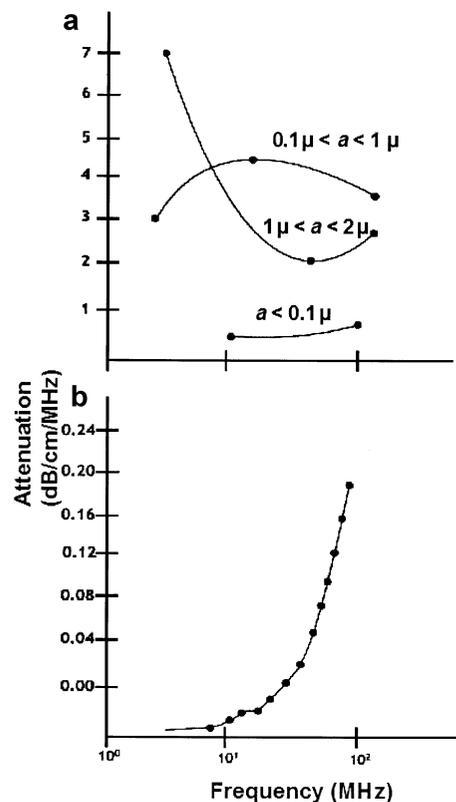


Figure 1. (a) A schematic of acoustic attenuation spectra for three particle-size ranges, *a* (L). (b) The acoustic attenuation spectrum for water.

Table 1. Summary of the loss mechanisms of acoustic waves interacting with colloidal suspensions.

| Loss mechanism | Effect | When significant | Special considerations |
|---|---|---|---|
| Viscous | Shear waves at particle boundary and particle inertia attenuate signal. | In systems with large density differences between colloid and fluid, *e.g.* in clay mineral suspensions. | Dominates attenuation in concentrated dispersions; 'long wavelength' requirement sets 10 nm lower limit on size. Inertial effects dominate at higher frequencies. |
| Thermal | Temperature gradients on both sides of particle surface attenuate signal. | In systems with little density differences between colloid and fluid, *e.g.* in emulsions. | Not important until ~30% volume fraction. |
| Scattering | Long-scale compression waves attenuate signal. Particle-particle interactions shift signal to higher frequencies. | Large, dense particles; particularly >3 μm. | Large particles contribute to long-scale compression waves, especially at high acoustic frequency. |
| Intrinsic | Attenuates signal. | When attenuation is low, such as with small particles, low volume fractions. | N/A |
| Structural | Attenuation and scattering of signal. | In concentrated dispersions with structural scale larger than particles, but smaller than the overall system. | Structural losses dominate signal attenuation when present. Polydisperse suspensions require extra analysis. Links acoustics with rheology. |
| Electrokinetic | Minor effect. | Only in electroacoustic spectroscopy. | N/A |

N/A: not applicable

they are predominant, the so-called 'long wavelength requirement' sets a lower limit of 10 nm on detectable particle size (Dukhin and Goetz, 1996a).

The familiar statistical-mechanical approach is used to model particle-particle interaction in light-scattering and rheological measurements. The 'extended coupled phase theory' is a recent approach to modeling acoustic losses in concentrated polydisperse suspensions (Dukhin and Goetz, 1996a, 1996b, 2000; Ohshima, 1997; Ohshima and Dukhin, 1999). The theory is valid for concentrated systems up to 45 vol.% fraction when the applied sound frequency is in the range 1−100 MHz. It allows for characterization of stable polydisperse systems with or without aggregates, macroscopic structure or floccules, and also for mixed systems of two or more chemically distinct phases. Two models are available for interpreting attenuation spectra as a PSD in suspensions prepared with chemically distinct dispersed phases using this theory, the 'multiphase model' and the 'effective medium' model (Dukhin and Goetz, 2000). The former assumes that the attenuation spectrum of a mixture is composed of a superposition of component spectra, and the PSD is represented as the sum of two lognormal distributions, *i.e.* a bimodal distribution. The latter assumes that only one 'target phase' of a multidisperse system ($\geqslant$ two phases) needs to be determined, while all other phases contribute to a homogeneous system, the 'effective medium'. This model requires additional measurements to determine

the density, viscosity and acoustic attenuation of the 'effective medium' (Dukhin and Goetz, 2000).

Acoustic spectroscopy has several characteristics which make it useful. When the acoustic signal is measured as a function of the transmitter/receiver gap, it requires no calibration. Attenuation spectra are independent of the electrical properties of the particle surface, and supply independent information about PSD (Dukhin and Goetz, 2000). Attenuation spectra can characterize the PSD in uncharged dispersed systems, as well as in systems with conducting particles. Measurement of PSD in concentrated dispersions gives acoustics a real advantage over light-scattering methods (Dukhin and Goetz, 2000). In addition, the large sample volumes and relatively high suspension concentration make the technique much less sensitive to sample contamination than light-based techniques, which can be plagued by contamination with dust particles (Dukhin and Goetz, 2002). Using well characterized samples and commercially available instruments, acoustic spectroscopy can measure the mean of the PSD with a precision and accuracy of 1% and the width of the PSD with an accuracy of up to 5% (Dukhin and Goetz, 1998). There are several shortfalls in acoustic spectroscopy, as information about particle shape is lacking in the spectrum, as it is in many techniques. In some cases, additional physical and thermodynamic information may be needed to interpret acoustic spectra (Table 2) (Dukhin and Goetz, 2001b).

*Theory of electroacoustic spectroscopy*

Electroacoustic spectroscopy deals with electrokinetic losses arising from the interaction of electric and acoustic fields in colloidal dispersions, and theoretical treatments require assumptions about the electrical properties of the colloid surface. The electric double layer (EDL) on colloids in solution is viewed, in a simplified manner, as having two components, an inner, hydrodynamically immobile 'Stern' layer, and an outer, hydrodynamically mobile 'diffuse' layer. The thickness of the diffuse portion, typically denoted '1/$\kappa$' (L$^{-1}$), is dictated by the ionic strength of the solution, and the two layers are considered to be separated by a 'slip plane'. The electrical potential difference between this idealized plane and the bulk solution is associated with the '$\zeta$ potential', and colloid interactions appear to be regulated by this potential (Hunter, 2001; Lykelema, 1995). A more complete description of the EDL can be found in Hunter (1981, 2001) and in Lykelema (1995) as well as in other texts.

In general, electrokinetic properties of colloidal suspensions appear under the application of an external force, such as an electric field for electrophoresis and electro-osmosis, a pressure gradient for streaming potential and current, a gravitational force for sedimentation potential and current, and a sound wave for electroacoustics (Hunter, 2001; Johnson *et al.*, 1999a). In response to an acoustic wave, the density contrast between the particle and the medium causes a polarization of the EDL, creating a dipole moment (Figure 2) the magnitude of which varies with the sound wave amplitude (Hunter, 1998). In superposition, the individual dipoles give rise to the macroscopic alternating electric field measured as a colloid vibration potential, CVP, or a colloid vibration current, CVI (Dukhin and Goetz, 1996a). Conversely, an alternating electric field produces an oscillating electrophoretic motion for particles having a non-zero $\zeta$ potential, thereby generating a sound wave − the ESA effect (O'Brien *et al.*, 1995). In this case, the resulting acoustic field is measured. The CVI, CVP and ESA spectra all contain

Table 2. Summary of constraints on or characteristics of acoustic measurements.

| Acoustic spectroscopy | |
|---|---|
| Particle-size constraint | 10 nm−>10 µm |
| | Upper limit on size lower in concentrated dispersions |
| | Large particles − attenuation appears at low frequency |
| | Small particles have little or no attenuation below 10 MHz |
| * EDL constraints | None |
| * Prior information | Always required: particle density and liquid density, liquid viscosity (c poise), and either weight fraction (g particles/g of liquid) or volume fraction of the colloid suspension |
| | Sometimes required (emulsions, latex): thermal expansion, heat capacity, and heat conductance of particles and liquid |
| * Particle shape | Cannot be determined from attenuation spectra |
| | Assumed spherical, but in practice deviation from this is not a problem for many colloids |
| Particle-size distributions | Monodisperse and polydisperse lognormal, and bimodal lognormal |
| * Dispersion concentration | From ~1 vol.%, up to ~45 vol.% |
| Number of distinct phases | Two or more chemically distinct phases can be characterized − additional information is needed |
| Density contrast | Not a limitation, unless the system is extremely concentrated |
| * Aggregation/structure | Can be identified in many circumstances |
| * Conducting particles/medium | Not a limitation |
| * Accuracy, precision and sensitivity | PS mean accuracy: 1% possible for mean particle size |
| | PS mean precision: 1% possible for mean particle size |
| | PSD standard deviation accuracy: 5% possible for PSD width |
| | PSD standard deviation precision: 1% possible for PSD width |
| | Sensitivity: bimodal distributions detectable with only 2 wt.% of large particles |
| * Advantages | Large sample volumes and high suspension concentrations minimize effects of contamination |
| | *In situ* measurement of aggregation, flocculation in concentrated suspensions |
| | Highly sensitive, very accurate |
| * Problems | Distinguishing large and very small particles – both attenuate the signal at high frequencies |
| | Air bubbles in suspension leads to large attenuation at small frequencies |
| | Large volumes needed |

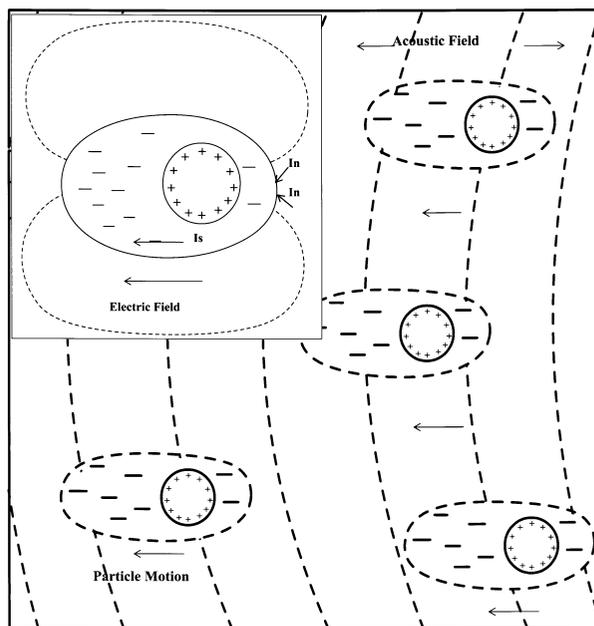* generic considerations, independent of the DT-1200 theory

Figure 2. The outer box is a schematic figure of dipole moments generated on charged particles in response to an applied acoustic field. The inner box indicates the location of the CVI current, $I_n$, external to the EDL (adapted from Dukhin and Goetz, 1996a). The CVI current develops in response to the electric field, generated by the surface current, $I_s$.

essentially the same information about $\zeta$ potential and PSD (Dukhin and Goetz, 1996a; Hunter, 1998). In the DT-1200 equipment (Dukhin et al., 1999a), CVI is measured, while in the AcoustoSizer, ESA or CVP is measured (Hunter, 1998; O'Brien et al., 1995).

Several factors determine the magnitude of the electroacoustic signal. Large differences in the density of particles vs. the medium and high suspension concentration result in larger signals, while a small $\zeta$ potential results in a small signal. The electrolyte contributes a small signal, which may be significant in dilute or low-$\zeta$ suspensions (O'Brien et al., 1995). 'Surface current', the movement of charge within the EDL, may be significant when particle size and/or electrolyte concentration are small (Hunter, 1998). Most theories assume the particles are spherical and the EDL is thin relative to the particle size, $a$ (L). The latter constraint is expressed as $\kappa a \gg 1$. Recall, '$1/\kappa$' ($L^{-1}$) denotes the thickness of the diffuse portion of the EDL, so '$\kappa a$' ($-$) is the ratio of the particle size to the double layer thickness. For most colloids with large $\kappa a$ or with thin double layers, surface current contributions are assumed negligible. Surface current is typically ascribed to diffuse layer ions, but evidence is mounting that anomalous conduction, i.e. conduction in the Stern layer, also contributes (Hunter, 2001; Lykelema, 1995). This phenomenon has been investigated experimentally in the mineral kaolinite (O'Brien and Rowlands, 1993; Rowlands and O'Brien, 1995). High electrolyte concentration may contribute to anomalous conduction (Hunter, 1998).

The CVI is analogous to a sedimentation current, the current arising when the potential generated as charged particles settle under gravity is short-circuited between vertically placed electrodes (Dukhin et al., 1999b). In CVI electroacoustics, an alternating acoustic field supplies the acceleration, instead of gravity. A tangential electric field, $E$ ($V L^{-1}$) is generated by the surface current, $I_s$ (A), and the compensating current, $I_n$ (A), is measured in CVI electroacoustics (see insert box in Figure 2) (Dukhin and Goetz, 1996a). Table 3 summarizes CVI measurement constraints, especially those for the DT-1200 electroacoustic spectrometer (Dukhin and Goetz, 2001b).

Traditionally, $\zeta$ potential was measured by observing the velocity of colloidal particles in a static electric field; the static electrophoretic mobility, $\mu_E$ ($L^2 V^{-1} T^{-1}$), relates the particle velocity to the electric field. The dynamic electrophoretic mobility, $\mu_d$ ($L^2 V^{-1} T^{-1}$), arises in an alternating electric field. At frequencies and/or particle sizes where particle inertia is significant, $\mu_d$ can be used for calculating particle size as well as $\zeta$ potential. It can be obtained from ESA, CVP or CVI measurements (Dukhin et al., 1999b; O'Brien et al., 1995). As the applied field frequency tends to zero, $\mu_d$ approaches the quantity $\mu_E$. Dynamic mobility can be calculated in suspensions above 1 wt.%, though for very small particles, inertial forces may be too small for size calculations to be made. Theoretical analyses have been extended to particles of almost any shape (Hunter, 1998). If the particles are non-spherical, but all orientations under the field are equally likely, theoretical relationships still hold for a 'particle-averaged' mobility. Surface conductance, discussed above, reduces dynamic mobility (Hunter, 1998).

Table 3. Summary of electroacoustic measurement constraints and characteristics.

| Electroacoustic spectroscopy | |
| --- | --- |
| Associated acoustic measurements for particle size | See Table 1 for restrictions |
| Volume fraction | Up to ~40 vol.% |
| * Particle shape and size | $\zeta$ potential difficult to measure for very small particles<br>Deviations from the spherical particle assumption not a problem if all particle orientations are equally likely |
| EDL considerations | Thin double layer assumed<br>Double layer overlap not accounted for<br>All particles assumed to have the same $\zeta$ potential *<br>Assume $\kappa a \gg 1$ (see text)<br>Surface conductance is accounted for in theory<br>Anomalous conductance assumed absent; this is usually true with large $\kappa a$, small $\zeta$ potential, and/or thick EDL<br>Kaolin exhibits anomalous conduction. |
| Accuracy and precision of $\zeta$ potential | Depending on volume fraction and colloid, obtainable limits are:<br>    $\zeta$ potential accuracy: several mV<br>    $\zeta$ potential precision: fraction of a mV |
| Concentration of medium | Restricted by the thin double layer constraint, and the Maxwell-Wagner critical frequency (see text) |
| * Advantages | Unambiguous measurement of $\zeta$ potential<br>Large volumes and high suspension concentrations limit contamination problems.<br>*In situ* measurement of $\zeta$ potential in concentrated suspensions |
| Problems | Theory does not cover case when compression is important (*e.g.* compressible particles, conducting particles, -non-aqueous dispersions)*<br>Anomalous conduction, thick double layers not accounted for in theory.<br>Calibration required.<br>Large volumes required. |

* generic considerations, independent of the DT-1200 theory

Electroacoustic measurements have a great advantage over static mobility measurements of $\zeta$ potential as ambiguities inherent in that technique are resolved by taking measurements over a range of frequencies (Hunter, 2001). Electroacoustic measurements are possible in suspension concentrations of practical interest, well beyond the range of optical techniques, and can be made *in situ*, during the course of titration, for example. In electroacoustics, equipment calibration is required, all particles are assumed to be spherical and to have the same $\zeta$ potential, and simplifying assumptions are made about the thickness of the double layer (thin double layer), and about surface and anomalous conductance. These assumptions affect both electroacoustic PSD and $\zeta$ potential calculations. A major problem in application is that assumptions about EDL properties, notably of a thin double layer, limit the range of validity of theoretical treatments (Table 3). However, the problem of simplifying EDL assumptions is shared by all electrokinetic measurement techniques. As acoustic spectra are in general more accurate for PSD, acoustic information can be incorporated in electroacoustic calculations to obtain better $\zeta$ potential estimates, as the measurements obtained from each technique are independent (Dukhin and Goetz,

1996a). Using supplementary acoustic information, CVI calculations of $\zeta$ potential can be made with accuracies up to several mV and precisions up to fractions of a mV (Dukhin and Goetz, 1998).

## APPLICATIONS OF ACOUSTIC AND ELECTROACOUSTIC SPECTROSCOPY

Table 4 gives a summary of literature applications of acoustic and electroacoustic spectroscopy to clay mineral suspensions. Most acoustic applications include supplementary size measurement techniques. In one study, acoustic PSD for rutile suspensions were validated with Sedigraph measurements up to 30 vol.% solid, but above that, deviations appeared between calculated and measured attenuation (Dukhin and Goetz, 1996a). However, the theory was shown to be valid in some cases up to 45% volume fraction, when the applied frequency was in the range 1−100 MHz. In polydisperse suspensions of silica Ludox and rutile, acoustic attenuation spectra reflected a nonlinear relationship between attenuation and volume fraction. For silica suspensions, there was little change in attenuation spectra above 9 vol.% fraction. For rutile, attenuation

Table 4. The application of electroacoustic (EA) and acoustic (A) measurements of colloidal PSD and/or ζ potential in current literature, along with companion measurements if applicable. In some cases, PSD was determined as a part of electroacoustic measurements of dynamic mobility.

| Acoustic technique | Companion measurements | Application/reference |
|---|---|---|
| EA – ζ potential and dynamic mobility | Shear yield stress<br>Electrophoretic mobility | Examine interrelationship between surface chemistry and shear yield stress<br>Materials – kaolin and alumina suspensions<br>Test new rheological theory<br>Obtain information on inter-particle spacing and pair-wise interactions<br>(Johnson et al., 1998) |
| EA – ζ potential | Adsorption measurements<br>Potentiometric titration | Use EA to quickly find isoelectric point (IEP) of alumina at 0.02 vol.% fraction in various electrolytes<br>Materials – alumina, various electrolytes<br>(Johnson et al., 1999b) |
| EA – ζ potential and dynamic mobility | Electrophoretic mobility<br>Potentiometric titration<br>Streaming potential | Compare EA ζ potential with surface charge density for different Al content in colloidal silica suspensions<br>Examine the nature of the silica surface, and the effects of ageing<br>Materials – colloidal silica and Al-substituted silica<br>(Rasmusson and Wall, 1997) |
| EA – ζ potential | Electron microscopy<br>Titrations | Examine adsorption of cetylpyridimium chloride (CPC) on kaolin<br>(Rowlands and Hunter, 1992) |
| EA – ζ potential, PSD and dynamic mobility | Dielectric response<br>Electron microscopy<br>Photon correlation spectroscopy<br>Centrifugal sedimentation<br>Electrophoretic mobility | Study the effect and measurement of anomalous surface conductance<br>Test measurements against formula accounting for surface conductance and particle shape<br>Materials – kaolin and gibbsite<br>(Rowlands and O'Brien, 1995) |
| EA – ζ potential and PSD | Shear rate and shear stress<br>Titrations | Characterize the dispersing behavior of alumina, with or without ball-milling, and with or without an anionic dispersant<br>Characterize IEP and PSD<br>(Costa et al., 1999) |
| EA – ζ potential | N/A | Determine the ζ potential of precipitated gibbsite particles in various NaCl electrolyte ionic strengths<br>(Rowlands et al., 1997) |
| EA – ζ potential<br>A – PSD | Titration | Characterize optimal dispersant dose to prevent aggregation of concentrated suspensions<br>Materials – zirconia, silica, PCC (precipitated calcium carbonate), kaolin<br>(Dukhin et al., 2001) |
| EA – ζ potential and PSD | X-ray diffraction<br>SEM<br>Titration | Investigate ζ potential and particle size in pH titrations in clays in three different electrolyte solutions<br>Materials – three ball clays<br>(Galassi et al., 2001a) |
| A – PSD | Sedigraph PSD | Test the effects of PSD and volume fraction on acoustic attenuation<br>(Dukhin and Goetz, 1996a) |
| A – PSD<br>EA – ζ potential | N/A | Combine acoustic and electroacoustic measurements to characterize aggregation phenomena in concentrated suspensions<br>Materials – silica, rutile and alumina<br>(Dukhin and Goetz, 1998) |
| A – PSD and aggregation | N/A | Characterize aggregation phenomena in alumina-zirconia, in alumina-PCC, and in silica-PCC slurries using different conceptual models<br>(Dukhin and Goetz, 2000) |
| A – PSD | Photon correlation spectroscopy<br>Laser diffraction<br>Light scattering and ultrasound | Alumina PSD after chemical-mechanical polishing (CMP)<br>Al-coated titania aggregation with pH changes<br>(Oja and Alba, 1998) |
| A – PSD and flocculation | N/A | Flocculated vs. dispersed PSD in concentrated alumina slurries<br>(Takeda and Goetz, 1998) |
| A – PSD | N/A | Concentration effects, illustrating of scattering mechanisms in suspension of 120 μm quartz particles<br>(Dukhin and Goetz, 2002) |

N/A: not applicable

decreased at low frequencies as suspension concentration increased above 16.6 vol.%. The opposite trends with suspension concentration were ascribed to the higher density contrast for rutile compared to silica (Dukhin and Goetz, 1996b). Attenuation of concentrated suspensions of 120 μm quartz particles was dominated by scattering mechanisms (Dukhin and Goetz, 2002). Acoustic attenuation was used to distinguish between dispersed and flocculated particle sizes in highly concentrated slurries (Takeda and Goetz, 1998).

Attenuation spectra from a Malvern Ultrasizer were used to obtain mean particle size and PSD in concentrated colloidal dispersions of industrial interest (Oja and Alba, 1998). The suspensions ranged from 0.5 to 50 vol.% solid, for particle sizes from nm to hundreds of μm. The PSD for a polished alumina dispersion compared favorably with photon correlation spectroscopy measurements. A pH titration of Al-coated titania particles illustrated that a substantial fraction of the small size fraction remained unaggregated near the IEP, and that aggregation was somewhat irreversible (Oja and Alba, 1998). Different types of particle-particle interactions were observed in complex suspensions using the 'multiphase' and 'effective medium' models (Dukhin and Goetz, 2000). When an 'effective medium' of precipitated calcium carbonate (PCC) was combined with a target phase of alumina, interactions between them were minimal, as the PSD calculated was close to the initial alumina particle size (10% error). For three zirconia-alumina mixtures, the effective medium model gave a good fit in two mixtures, while a bimodal distribution (two standard deviations) was hypothesized in the third, indicating that particle aggregation was not occurring. The attenuation spectrum of a calcium carbonate-silica mixture illustrated the effects of aggregation, as each of the models tested yielded a poor fit to the measured spectrum (Dukhin and Goetz, 2000).

Most applications using electroacoustic spectroscopy combined the technique with other electrokinetic measurements, such as electrophoretic mobility (Costa *et al.*, 1999; Johnson *et al.*, 1998) or streaming potential (Rasmusson and Wall, 1997). A common application was to use the ζ potential of a suspension to characterize colloidal stability or aggregation (Dukhin and Goetz, 1998; Rowlands and Hunter, 1992), or to determine optimal dispersant dose to prevent aggregation (Costa *et al.*, 1999; Dukhin *et al.*, 2001). Electroacoustics was also used as a companion technique to standard rheological measurements, such as shear yield stress (Costa *et al.*, 1999; Johnson *et al.*, 1998). Finally, electroacoustics was used to investigate the relationship between electrolyte, sorption mechanisms and ζ potential (Johnson *et al.*, 1999b; Rowlands *et al.*, 1997), and to investigate anomalous conductance (Rowlands and O'Brien, 1995). The most common materials were clays and clay minerals used in industrial applications, such as silica, rutile, gibbsite and kaolin.

Several studies examined the use of dispersants to manipulate the surface charge of colloids. Rowlands and Hunter (1992) investigated the adsorption of the dispersant cetylpyridinium chloride on kaolinite using electroacoustics. The dynamic mobility of the suspension reflected the adsorption onto two layers, and the pH reflected the charge characteristics of basal and cleavage planes. Additions of cetylpyridinium chloride equal to the cation exchange capacity reversed particle charge from negative to positive. Costa *et al.* (1999) investigated optimal dispersant dose for alumina suspensions, combining electroacoustics with ball-milling and rheological measurements. Viscosity and shear yield stress measurements corresponded well with electroacoustic data from an AcoustoSizer, indicating an IEP near pH 9.0. Increasing suspension concentration shifted the IEP downward, in accord with electrophoretic measurements from the literature. Electroacoustic measurements were used (Dukhin *et al.*, 2001) to determine the optimal dose of the dispersants silicate and sodium hexametaphosphate needed to stabilize a kaolin slurry against aggregation. Titration results showed that the latter was a more efficient dispersant, producing a greater gain in ζ potential with a lower optimal concentration.

The combination of acoustic and electroacoustic measurements was used to characterize rutile and alumina suspensions (Dukhin and Goetz, 1998). Both dispersions became unstable within 2 pH units of their isoelectric points, when ζ potential fell below 30 mV in absolute value. Changes in the attenuation spectra indicated particle aggregation, as PSD changed from lognormal to bimodal. Aggregation may have been affected by the rate of mechanical stirring of the suspensions. In another study, acoustic PSD, applied before and after sonication was used to break up particle aggregates, showed that the accompanying 5 mV jump in measured ζ potential was misleading (Dukhin *et al.*, 2001). Sonication increased the electroacoustic signal merely by exposing new surfaces. This effect may have been misinterpreted using PSD from electroacoustic spectra alone.

Electroacoustics has also been used to characterize the effects of volume fraction. Concentrated suspensions of silica Ludox or rutile had nearly constant ζ potential, as measured by CVI, over a wide range of volume fractions (Dukhin and Goetz, 1996a). Costa *et al.* (1999) attributed increases in IEP (measured by electroacoustics) in alumina suspensions at high volume fraction and pH to specific adsorption of aluminum species. A new rheological theory modeling the effect of volume fraction on spherical/oblate (alumina) and plate-like (kaolin) particles was tested on alumina and kaolin suspensions (Johnson *et al.*, 1998). The theory assumed that EDL overlap was small and that surface potential was constant as a function of inter-particle separation. Empirically corrected electroacoustic ζ potentials were calculated using the new theory. The spectra for

2−30 vol.% fractions overlapped, and agreed with data obtained by electrophoresis. Normalized static shear yield (vane technique) stress *vs*. $\zeta^2$ showed a near-linear relationship for alumina suspensions. For kaolin suspensions, the relationship exhibited no correlation (Johnson *et al*., 1998).

Many applications have illustrated the power of *in situ* electroacoustic measurement of $\zeta$ potential in nondilute suspensions. In Hunter and James (1992), the ESA effect was used to provide dynamic mobility measurements of kaolin and crushed quartz in pH titrations. The presence of Co, Cu and Cd ions changed the surface charge. Two charge reversals at high pH were attributed to adsorption and surface precipitation of metal hydroxides. Electroacoustic $\zeta$ potential was measured for various electrolytes at moderate to high ionic strength in 2.0 vol.% fraction alumina suspensions to distinguish between indifferent and specifically adsorbing electrolytes (Rowlands *et al*., 1997). The $\zeta$ potential of gibbsite particles at 10 vol.% fraction in 0.1, 0.5 and 3.0 M NaCl solutions (pH 7.0 to 12.0) was used to indicate IEP (Rowlands *et al*., 1997). The IEP increased with electrolyte concentration, but could not be detected at 3.0 M NaCl. Electroacoustic PSD did not change with pH, possibly because particles were always in close proximity.

Rasmussen and Wall (1997) characterized 3.0−5.0 nm Al-modified (0−16% substitution) or slightly aggregated ellipsoidal silica particles. Neither $\zeta$ potential nor titrated surface charge density correlated with colloid stability. Dynamic mobility was only measured at one frequency (~1 MHz), so was not useful for calculating PSD. Electroacoustic and streaming potential measurements of $\zeta$ potential generally agreed, indicating that polydispersivity and ellipsoidal particle shape had little affect on dynamic mobility. The $\zeta$ potential varied with Al substitution, first increasing and then decreasing past 7% substitution, while surface-charge density increased with Al substitution. Surface charge densities decreased with time but dynamic mobility did not. The difference was attributed to reprecipitation of silica on inter-particle necks rather than aggregation. Using three 'ball clays' with application in the ceramics industry, Galassi *et al*. (2001) presented $\zeta$ potential *vs*. pH curves for the three clays in three electrolytes, each at ~50 wt.% suspension concentration. Mean particle diameters determined from dynamic mobility measurements gave order-of-magnitude agreement when compared with SEM-determined mean diameters.

Advances in electroacoustic spectroscopy have also facilitated the investigation of anomalous conductance. The possibility of anomalously high surface conductance in kaolinite suspensions in low ionic strength electrolytes, <5 mM, was investigated at pH 10.5 (Rowlands and O'Brien, 1995). A new theoretical model accounted for particle shape (oblate spheroid) and high surface conductance. Surface conductance was determined using dielectric response measurements on a high-frequency conductance bridge, and compared with dynamic mobility. Maxima in phase angles and minima in magnitudes of dynamic mobility were taken as an indication of substantial surface conductance. For a given surface conductance, mobility reduction was greater for smaller particles. Calculations for kaolinite resulted in a greater $\zeta$ potential than normally found using static mobility measurements. By comparison, gibbsite particles showed no evidence of anomalous surface conductance.

## EXAMPLES

### DT-1200 instrumentation

In the DT-1200 electroacoustic spectrometer (Dukhin and Goetz, 2000), there are sensors for measuring acoustic and CVI electroacoustic signals separately, though both use the tone-bursts pulse technique. A peristaltic pump assures a well-mixed, dispersed sample, and the sample chamber and associated pump tubing requires a minimum sample volume of ~130 mL. The equipment is controlled by computer software, which includes programs to analyze the spectra after collection. Theoretical assumptions are covered in previous sections of this paper. Air bubbles must be excluded from suspensions, as they strongly scatter sound waves and can produce anomalies in the spectra at low frequencies (Hunter, 2001). For acoustic measurements, ultrasonic pulses from 3−100 MHz are transmitted through the colloidal suspension in logarithmic steps. The resultant signals are collected as transmitter-receiver gaps are typically stepped from 0.15 to 20.0 mm. At each frequency and gap setting, the sensors measure, and the associated software records, the signal (attenuation) and change in transit time of the pulse across the gap (the group sound speed) (Dukhin and Goetz, 1998). The electroacoustic probe is composed of a piezoelectric transducer and a two-element antenna (Dukhin and Goetz, 2002). The CVI signal is averaged over a minimum of 800 pulses, and up to millions of pulses if the signal is extremely small (Dukhin *et al*., 1999a).

### Calibration

Although not necessary, measuring the attenuation of water (Figure 1b) is advisable as a check on equipment function, and is straightforward. Water is a very weak attenuator of sound waves, and has a well defined attenuation spectrum, ranging from <0.05 dB cm$^{-1}$ Hz$^{-1}$ at 10 MHz to ~0.20 dB cm$^{-1}$ Hz$^{-1}$ at 100 Mhz (Dukhin and Goetz, 2001b). The DT-1200 equipment and software allows for calibration of the acoustic geometry, although this is only necessary for weakly attenuating systems at low frequency, such as very dilute dispersions or dispersions of very small particles. For electroacoustic measurements, silica Ludox is used as the calibration colloid, since it has a well-defined PSD and $\zeta$ potential. The $\zeta$ potential of a 10% weight fraction of silica Ludox

in 0.01 M KCl corrected to pH 9.3 (with KOH) is ~−38 mV, and the mean particle size is ~0.03 μm. Figure 3a shows the attenuation spectrum of the silica Ludox standard, and Figure 3b shows the calculated lognormal PSD.

*Acoustic/electroacoustic examples*

Figure 4a illustrates measured acoustic attenuation, and parts b−d show the calculated PSD and electroacoustic ζ potential of three different 1.0 vol.% clay mineral suspensions using the DT-1200. The kaolin (KGa-1, Source Clay Minerals Repository of the Clay Minerals Society, Purdue University) was dispersed with NaCl, and fractionated via centrifugation to obtain a <2 μm fraction. The gibbsite (ALCOA #H-710-B) mean particle size was specified as 1.0 μm, as determined by Sedigraph. The Ottawa sand (20−30 mesh standard) was crushed in a Mixer-Mill using agate containers and balls, and heated to 550ºC for 48 h to remove organic contaminants. The crushed product was fractionated at ~20 μm by settling and decantation in Milli-Q water. The suspensions were dialyzed in an ~0.2 M artificial groundwater (AGW) solution (Seaman *et al.*, 1995a, 1995b; Strom and Kaback, 1992) for ~48 h, followed by dialysis at the final solution concentration for at least 2 days. AGW is a dilute (~1 mM) solution that mimics groundwater from highly weathered sediments found in the Atlantic Coastal Plain Region near Aiken, South Carolina, USA. The calculated PSD values and ζ potentials are within expected values (Dukhin and Goetz, 2002; Hunter, 1981, 2001).

## CONCLUSIONS

Theoretical advances in characterizing concentrated colloidal suspensions reinforce the recent development of automated acoustic and electroacoustic equipment. Acoustic and electroacoustic spectroscopies compare well with alternative measurement techniques, or provide supplemental information. Measurements of PSD, aggregation phenomena, and ζ potential can now be made *in situ* in suspension concentrations of practical importance to the study of clays and clay minerals.

The application of acoustic or electroacoustic spectroscopy for agriculturally and environmentally important clay mineral suspensions covers the same range of issues encountered in industrial application. The particle-size distribution, the reactivity of the mineral surface, the effects of dispersants or additives to manipulate surface charge, and the effect of suspension concentration are important in both settings. The use of these techniques can facilitate the characterization of agriculturally important clays and clay minerals, for example, in the remediation or characterization of contaminated or salt-affected soils. Particle aggregation and changes in particle charge due to the addition of surface modifiers, such as organic matter, organic
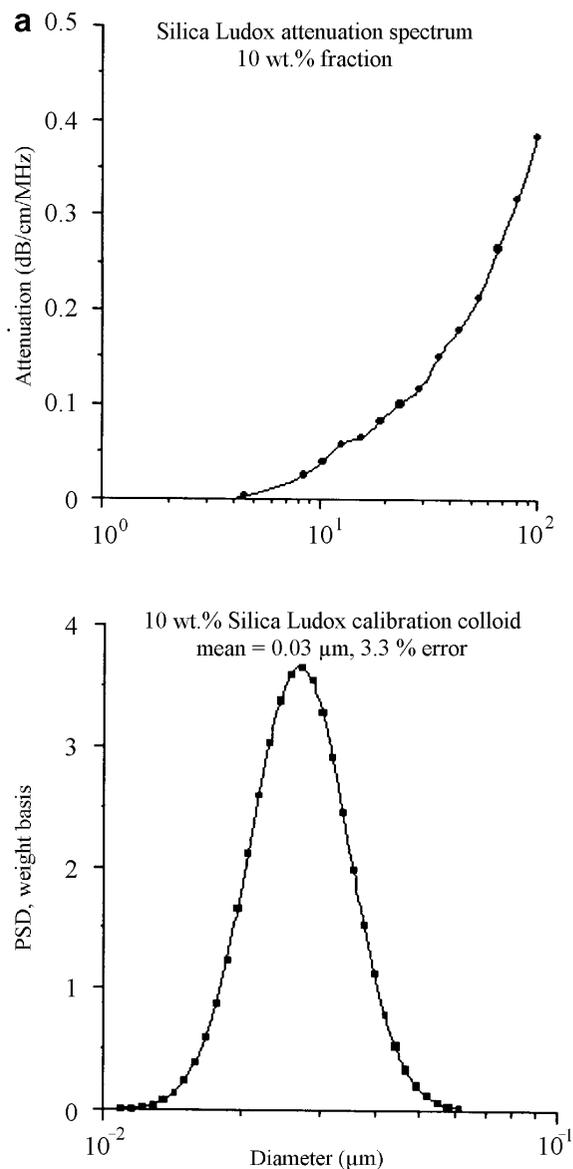
Figure 3. (a) Acoustic attenuation spectrum of a 10 wt.% Silica Ludox standard, at pH 9.3 and 26.7ºC. The ζ potential measurement was −38 mV. (b) The lognormal particle-size distribution calculated from the attenuation spectrum. The mean size was 0.03 μm with a deviation from a lognormal distribution of 3.3%.

contaminants or dispersants, can be monitored to determine critical concentration levels. In addition, the difference between particle aggregation and flocculation may be important, for example, in the transport of contaminant-laden clays through sediments. This distinction can be made using acoustic and electroacoustic techniques (Dukhin and Goetz, 2002). In a companion article in this issue (Guerin and Seaman, 2004), the clay minerals in a naturally occurring variable charge soil are characterized using acoustic and electroacoustic spectroscopies. Suspension concentration effects and the effects
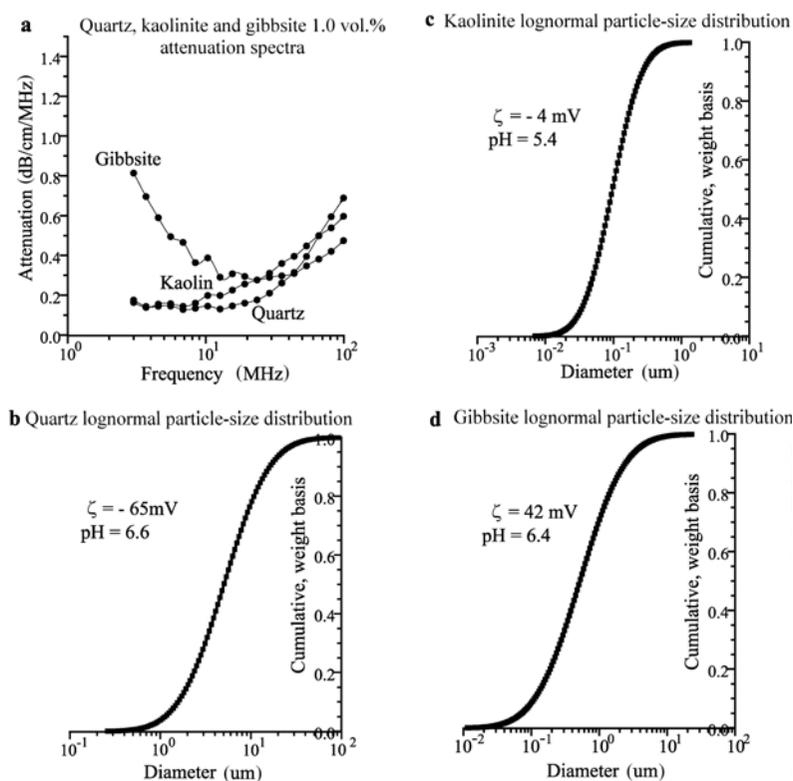
Figure 4. Attenuation spectra (a), $\zeta$ potential and cumulative Lognormal PSD (b–d) for three clay mineral suspensions in AGW: quartz (b), kaolinite (c), and gibbsite (d).

of particle interactions during pH titrations illustrate the advantage of *in situ* characterization. The contributions to suspension stability of the main clay mineral constituents in the soil are identified by comparison with individual mineral standards.

Electroacoustic measurements during titration can be used to monitor changes in $\zeta$ potential due to the adsorption of aqueous species, such as ammonium, nitrate, sulfate, calcium, heavy metals, radionuclides, *etc*., from solution. In addition, measurements can be made of polydisperse suspensions, such as mixtures of clay minerals. Aggregation due to differences in particle charge, for example between goethite and kaolin, or due to addition of di- or multi-valent cations or anions, such as $Ca^{2+}$ or $PO_4^{2-}$, can be measured *in situ*. Attenuation spectra from mixtures can be compared directly, or analyzed semi-quantitatively using models, or simply by superimposing the attenuation spectra from individual components (Dukhin and Goetz, 1998). The effect of suspension concentration on adsorption is a well known problem in obtaining adsorption parameters, and acoustic techniques offer the capability of monitoring changes in suspension characteristics during experiments (Barrow and Shaw, 1979; Roy *et al*., 1991).

Acoustic spectroscopy has recently been established as an important technique for obtaining PSD, particularly in concentrated dispersions. Both SEM and TEM (scanning and transmission electron microscopy) have

extremely important roles to play in particle sizing that acoustics will not supplant, especially for determining particle shape. However, acoustics has the important advantage that *in situ* measurements can be made, and thus are not subject to changes in particle-particle interactions due to drying or due to chemical modifications to achieve dispersion. Other sizing techniques have their place, such as sedimentation under gravity or centrifugal force, Coulter counter, light-scattering methods such as photon correlation spectroscopy, or by capillary hydrodynamic or field-flow fractionation. However, apart from acoustic spectroscopy, each of these techniques requires dilution. In addition, except for electron microscopy, each technique other than acoustics has a limited range of sizes for which the technique is applicable, although the range for light-scattering methods is similar to acoustics (Hunter, 2001). Also, size measurements by acoustics can be made in conjunction with $\zeta$ potential measurements by electro-acoustics. This combination is not possible with most of the other techniques.

The biggest limitation in measuring $\zeta$ potential with electroacoustic spectroscopy is theoretical, but similar problems are encountered for all available techniques. For any measurement method, the interpretation of electrokinetic measurements is problematic when the EDL is thick, when the EDLs for neighboring particles overlap, when the $\zeta$ potential is large, or when anomalous

conduction is present. However, the combination of acoustic and electroacoustic spectroscopies for the independent measurement of PSD and $\zeta$ potential, respectively, potentially allows for fundamental advances to be made in understanding the interactions between mixtures of clays and clay minerals, and between clays and solution constituents in the environment.

## ACRONYMS

AGW: artificial groundwater – a solution whose composition mimics the composition of a particular groundwater

CVI: colloid vibration current – the current generated in a colloidal suspension on application of an alternating acoustic signal

CVP: colloid vibration potential – the electrical potential created in a colloidal suspension generated on application of an alternating acoustic signal (Figure 2)

EDL: electric double layer – a region of variable composition, and physical and electrical potential properties found between the bulk surface and the bulk solution

ESA: electrokinetic sonic amplitude – the acoustic field generated in a colloidal suspension on application of an alternating electric field

IEP: isoelectric point – the pH at the electrophoretic mobility of a suspension is zero

PCC: precipitated calcium carbonate

PSD: particle size distribution – the distribution of sizes in a particulate sample

SEM: scanning electron microscopy

TEM: transmisssion electron microscopy

## ACKNOWLEDGMENTS

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