

Articles

Titration of Concentrated Dispersions Using Electroacoustic ζ -Potential Probe

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Electroacoustic measurement with a ζ -potential probe offers a quick and accurate determination of the optimal dispersant dose required for preventing aggregation. The most important advantage of this method is its applicability to concentrated dispersions which eliminates dilution. Traditional methods based on the dilution protocol are often inadequate because dilution affects the ζ -potential value. It is shown experimentally how this method works on the example of various kaolin slurries at 40 wt %. In combination with acoustic spectroscopy, this method yields a complete and consistent characterization of the aggregation stability.

Introduction

Stabilization of a dispersed system against aggregation can be achieved using various chemical reagents, such as dispersants, phosphate salts, and polymers. These substances change the properties of the surface of the dispersed phase and increase its affinity to a liquid. Dispersed systems with such modified surfaces become thermodynamically stable. The critical issue in this modification is the amount of dispersant which should be added to the particular dispersion. There is an optimum value of this amount. An underdose of the dispersant leaves some patches of the surface uncovered which might lead to aggregation through the particles' contact at these places. An overdose of the dispersant is also undesirable because it might cause either bridging flocculation¹ or aggregation due to a higher ionic strength.

Determination of the optimal dose is not an easy task. Regular adsorption isotherm measurement is time consuming and rather laborious. Electrokinetics offers another way by measuring the variation of a ζ potential. This method has not been used widely because traditional measurement of the ζ potential with microelectrophoresis is also very slow. In addition, it might be misleading because microelectrophoresis requires dilution which basically destroys the original dispersion.

The situation has drastically changed thanks to the new electroacoustic method of characterizing the ζ -potential.^{2–5} This electroacoustic method opens an opportunity

to measure the ζ potential in the intact concentrated dispersion with a volume fraction up to 40 vol %.⁶ It becomes very simple and fast with a new electroacoustic probe DT 300 designed by Dispersion Technology Inc.⁷ for measuring colloid vibration current (CVI).

We will show in this paper several examples of the titration performed for various industrial slurries.

CVI Measurement

The electroacoustic spectrometer DT-300 consists of two parts, the electronic part and the sensor part.

All electronics are placed on two special-purpose boards (signal processor and interface). It also requires a conventional data acquisition card (DAC). The signal processor board and DAC are placed inside of a personal computer which performs interface with the user through Windows-based software.

The electroacoustic sensor probe contains a piezoelectric transducer with a critical frequency of 3 MHz and a sensing electrode which is placed on the surface of the transducer. This electrode is separated from the external reference electrode with a nonconducting rigid ceramic insert. Internal electric impedance between these electrodes can be selected depending on the conductivity range of the samples by means of an internal transformer. The transformer is selected so that the input impedance is significantly less than the external impedance of the sample such that the resultant signal is proportional to the short circuit current. This transformer is located just behind the central electrode in order to minimize the stray capacitance.

There is a special plastic rod between the transmitting transducer and the sensing electrode with a low acoustic impedance. This rod adjusts acoustic impedance of the

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(6) Dukhin, A. S.; Shilov, V. N.; Ohshima, H.; Goetz, P. J. Electroacoustics Phenomena in Concentrated Dispersions: New Theory and CVI Experiment. *Langmuir* **1999**, *15* (10), 3445–3451.

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probe and dispersion, eliminating a high reflection on this surface. This additional rod opens a way to calibrate an absolute power using reflection on the transducer-rod surface.

The signal processor generates the transmit gate which defines the 1 W pulse generated in the interface module as well as the necessary signals to set the frequency. Electroacoustic measurement can be performed either for one frequency or for the chosen set of frequencies from 1 to 100 MHz. The transducer converts these pulses to the sound pulses with some certain efficiency. The sound pulse propagates through the quartz delay rod and the acoustic impedance rod and eventually through the sample. The acoustic pulse propagating through the sample excites particles and disturbs their double layers. Particles gain dipole moments because of this excitation. These dipole moments generate an electric field. This electric field changes the electric potential of the central sensing electrode. The difference of the electric potentials between the central electrode and the external reference electrode causes an electric current. This current is registered as colloid vibration current. The value of this current is very low. It takes averaging of at least 800 pulses in order to achieve a high signal to noise ratio. The number of pulses depends on the properties of the colloid. Measurement of CVI in low conducting oil based systems requires averaging of millions of pulses. In principle, this method makes it possible to measure any low energy signals.

The general expression for the local CVI for concentrated (up to 40 vol %) and polydisperse systems has been derived in ref 6:

$$\text{CVI} = \frac{\sum_{i=1}^N \frac{\varphi_i h(\alpha_i)}{j\alpha_i I(\alpha_i) \left(\rho_p - \rho_m \left(\frac{3H_i}{2I_i} + 1 \right) \right)}}{9\epsilon_0 \zeta K_s (\rho_p - \rho_m) \nabla P} \cdot \frac{4K_m \eta (1 - \varphi)}{1 - \frac{\rho_p}{\varphi} \sum_{i=1}^N \frac{\varphi_i \left(\frac{3H_i}{2I_i} + 1 \right)}{\rho_p - \rho_m \left(\frac{3H_i}{2I_i} + 1 \right)}} \quad (1)$$

where ϵ and ϵ_0 are dielectric permittivities of the media and vacuum, K_s and K_m are the conductivities of the dispersion and media, φ is the volume fraction of solid, ρ_p and ρ_m are the densities of the particles and of the media, j is an imaginary unit, and special functions h , H , and I are defined in the paper.⁶

This expression contains one unknown parameter, P , the pressure. The piezocrystal converts the initial 1 W electric signal to the sound with low efficiency, about 40 dB loss. The efficiency of this conversion is frequency dependent which makes an additional problem for frequency CVI spectra measurement. The sound intensity after the piezocrystal is rather low and not very well-defined. Each piezocrystal has a unique efficiency. Then, the pulse propagates through the delay rod and the acoustic impedance rod and partially reflects from the sensor-liquid surface. This changes the amplitude of the pressure again. As a result, we do not know the exact pressure at the point of the measurement.

Colloid vibration current can be presented in the simplified form

$$\text{CVI} = C \zeta \nabla P G(\varphi, a) Z_{\text{dis}} / (Z_{\text{dis}} + Z_{\text{rod}}) \quad (2)$$

where C is a geometry calibration constant which characterizes the complex distribution of the electric and sound fields near the electrode surfaces, the multipliers with acoustic impedances of the dispersion Z and impedance of the rod Z characterize reflection on the probe surface, and function G is defined with eq 1.

Neither of these parameters (C and P) is known. To exclude them, we use the calibration procedure described below.

To eliminate the unknown constants C and P , we use calibration with Ludox at 10 wt % diluted with KCl (10^{-2} mol/L). The silica particles have a ζ -potential of -38 mV at pH 9.3. The CVI value for this colloidal silica can be expressed as the following:

$$\text{CVI}_{\text{sil}} = C_{\text{sil}} \zeta_{\text{sil}} \nabla P G(\varphi_{\text{sil}}, a_{\text{sil}}) Z_{\text{dis.sil}} / (Z_{\text{dis.sil}} + Z_{\text{rod}}) \quad (3)$$

From this equation, we can calculate unknowns C and P and use them for calculating CVI for other samples:

$$\text{CVI} = \text{CVI}_{\text{sil}} \frac{\zeta / \zeta_{\text{sil}} G(\varphi, a) / G(\varphi_{\text{sil}}, a_{\text{sil}}) Z_{\text{dis}} (Z_{\text{dis.sil}} + Z_{\text{rod}})}{(Z_{\text{dis}} + Z_{\text{rod}}) Z_{\text{dis.sil}}} \quad (4)$$

Expression 4 can be used for calculating ζ potential only from the magnitude of the CVI.

In addition, DT-300 measures a phase of the CVI signal. This phase yields particle size information. In the case of a single frequency, this measurement provides only a mean particle size. In the case of multiple frequencies, more detailed information about the particle size distribution is available. However, according to our experience acoustic spectroscopy is much more suitable for characterizing the particle size distribution.³

Titration Protocol

The software of DT-300 has several optional titration protocols for running two burets. These burets are able to inject chemicals with increments as low as $0.2 \mu\text{L}$.

The most common is pH titration. The user should specify maximum and minimum pH, number of points, number of sweeps, and direction. This software assumes 1 N acid and base. In addition, the user can change the equilibration time, tolerance, sample volume, and so forth.

Equilibration time is a very important parameter. Titration makes sense only if it follows the equilibrium route. Some systems exhibit a very long equilibration time. A good example is a concentrated zirconia dispersion. Figure 1 shows the evolution of the ζ -potential and pH of the 3 vol % zirconia dispersion in time. The equilibration time is about 30 min. For comparison, silica Ludox reaches equilibrium in a fraction of a minute. A typical equilibrium titration of the silica Ludox at 10 wt % is shown in Figure 2. It is clear that it is almost impossible to make a similar equilibrium titration for zirconia because it takes a lot of time.

For the purpose of this paper, another protocol is important. It is called the "ml protocol" in the DT software. The user specifies a total amount of the injected substance and the number of points. The buret automatically injects this substance and waits the specified equilibration time, and then the CVI sensor measures the ζ -potential. In addition, DT-300 monitors pH and temperature continuously. A typical titration of this kind is shown in Figure 3. It has been made using hexametaphosphate with precipitated calcium carbonate at 3 vol %.

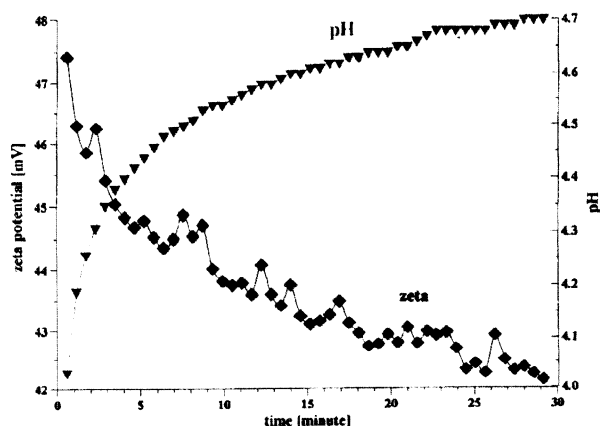


Figure 1. Equilibration of 3 vol % zirconia slurry prepared in KCl (10^{-2} mol/L) with pH adjusted initially to 4. Equilibration takes about 2 h.

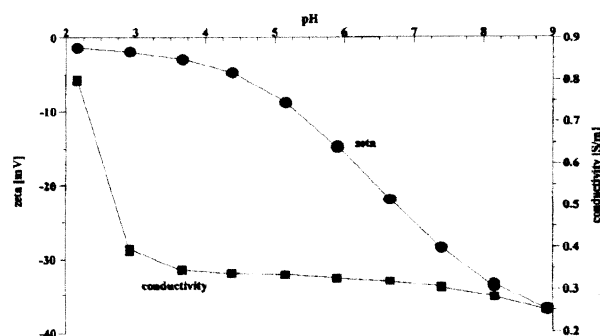


Figure 2. Titration of the 10 wt % silica Ludox using 1 N HCl and KOH.

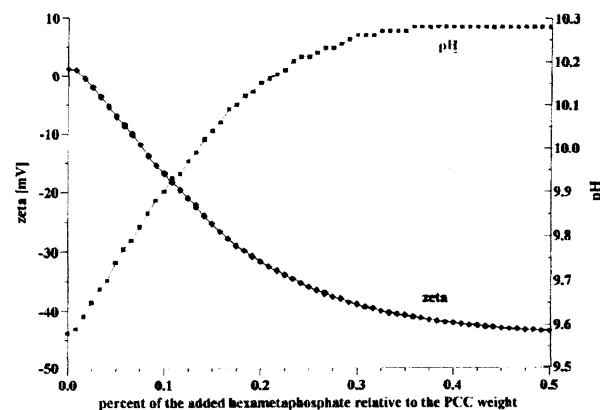


Figure 3. Titration of the 3 vol % PCC slurry with 0.1 g/g hexametaphosphate solution.

The most complicated problem for titrating concentrated dispersions is mixing. Mixing is absolutely necessary for successful titration. However, it becomes hard to mix especially in the ranges of instability.

We know only one solution of this problem: pumping the sample through the measuring chamber. Traditional propeller mixers do not work with the pastelike samples. Pumping makes it possible to involve a complete sample, whereas a propeller performs mixing only its own vicinity. Pumping functions properly only when the measuring chamber does not have hydrodynamically stagnated spaces. Otherwise, deposits built up in these spaces can interrupt the flow.

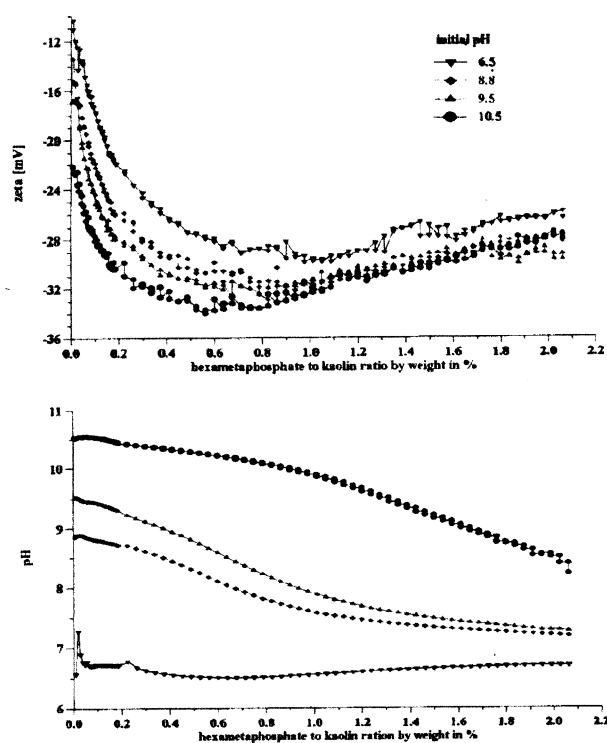


Figure 4. Titration of the 40 wt % kaolin EC1 slurry using hexametaphosphate.

Materials and Experimental Protocol

The kaolin used in this study was obtained from the Engelhard Corp. and was categorized as a fine grade crude with a high iron content. Kaolin, in general, is defined by platelet crystals in which one of the dominant faces is made up of octahedral alumina and the other consists of tetrahedral silica. Particle aggregation thereby occurs when the negative platelet faces (negative because of isomorphic substitutions) interact with positive charge sites on the crystal edges (because of pH sensitive aluminol and silanol sites). The two dispersants used to study this aggregation phenomenon were both common to the kaolin industry and consisted of 2.0 modulus silicate (Occidental Chemical Corp.) and sodium hexametaphosphate, SHMP (Albright & Wilson Americas Inc.). The 2.0 modulus silicate was expected to interact with the positive edge sites of the kaolin platelet through electrostatic interactions. The SHMP was a cyclic polyphosphate, which is expected to adsorb to the positive charges along the kaolin edges through both electrostatic and covalent bonding.

Results and Discussion

Titration of the kaolin EC1 slurry with hexametaphosphate revealed a strong pH dependence. The titration curve shifts depending on the initial pH value. It is illustrated in Figure 4 for both the ζ potential and pH. It is not surprising because pH is a strong charge factor for kaolin. For instance, Figure 7 presents pH titration of the 40 wt % EC2 kaolin slurry. It is clear that ζ potential goes up with pH.

The titration of EC1 kaolin slurry is a good example showing the importance of various factors, not only dispersant concentration. It is convenient to illustrate this

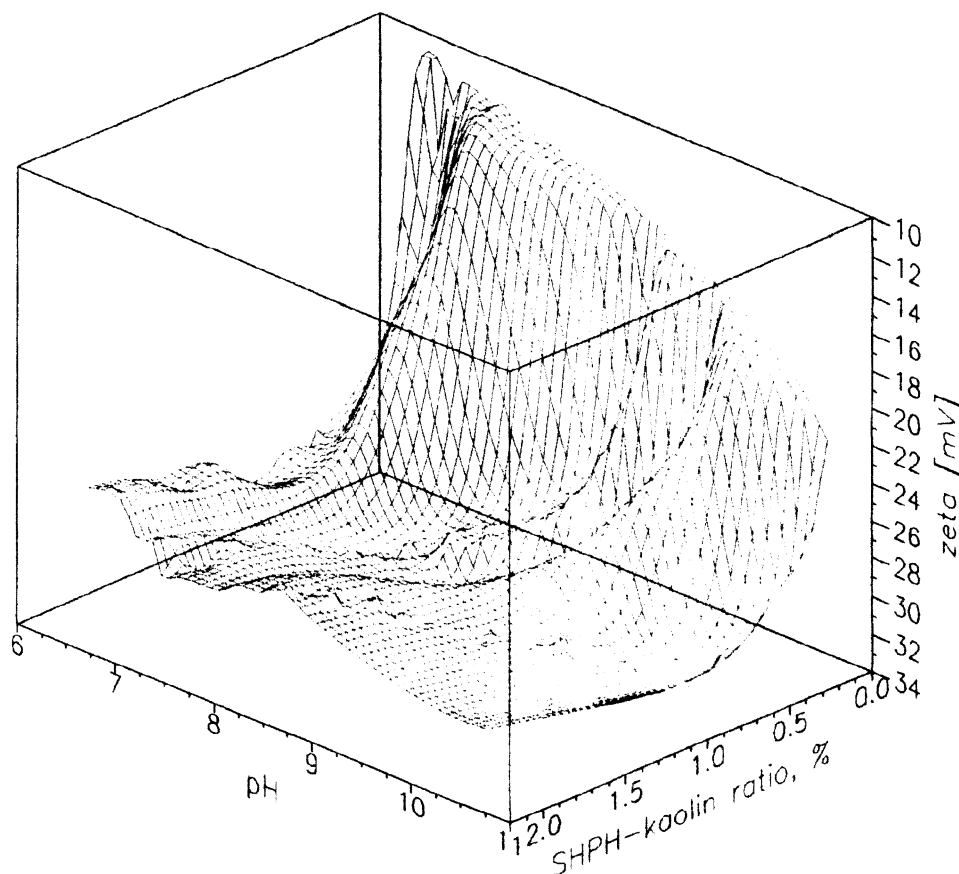


Figure 5. Titration ζ -pH-hexametaphosphate fingerprint of the 40 wt % kaolin EC1 slurry.

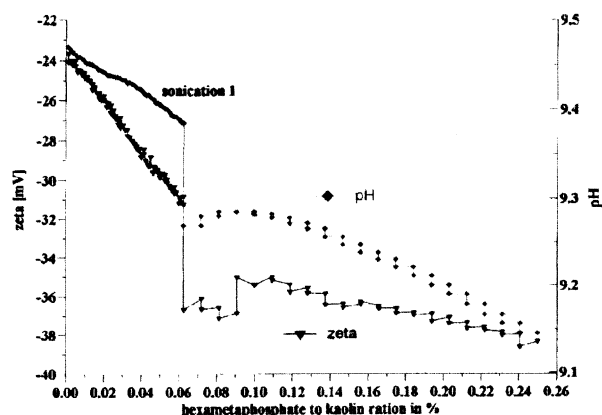


Figure 6. Effect of sonication on the EC1 40 wt % kaolin titration with hexametaphosphate.

complex titration using a three-dimensional fingerprint. Figure 5 shows this fingerprint for the kaolin EC1 titration.

The titration of EC1 slurry illustrates the existence of the optimum concentration of dispersant. One can see that increasing the hexametaphosphate concentration leads eventually to decreasing ζ -potential. In this particular case, it is related to the increasing ionic strength and collapsing double layer.

The dependence of ζ -potential on pH is an additional factor which might be exploited for reaching higher ζ -potential values. From this viewpoint, hexametaphosphate has a disadvantage because it reduces pH. Another dispersant, silicate, is more advantageous from the pH

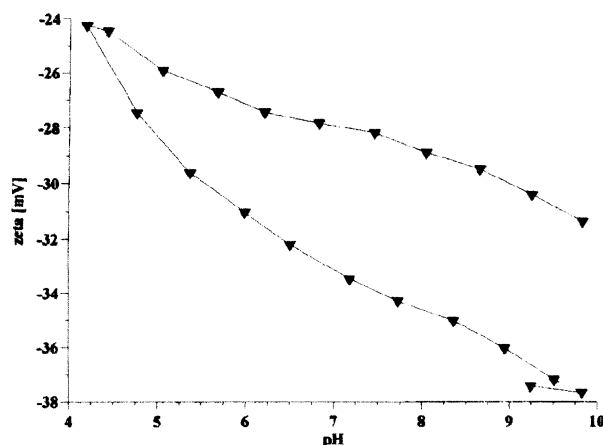


Figure 7. pH titration of the 40 wt % EC2 kaolin slurry.

viewpoint because its addition to the slurry increases pH, as shown in Figure 8. However, even the combined silicate-pH effect is not sufficient to gain ζ -potential values created with hexametaphosphate. The maximum value for silicate titration is -28 mV, whereas hexametaphosphate yields -34 mV at maximum.

Hexametaphosphate is more efficient in terms of optimum amount as well. The maximum value of the ζ -potential can be reached by adding 2 times less hexametaphosphate (0.6% by kaolin weight) than silicate (1.3% by kaolin weight).

There is one more factor which affects the stability of the kaolin dispersions: sonication. Apparently none of

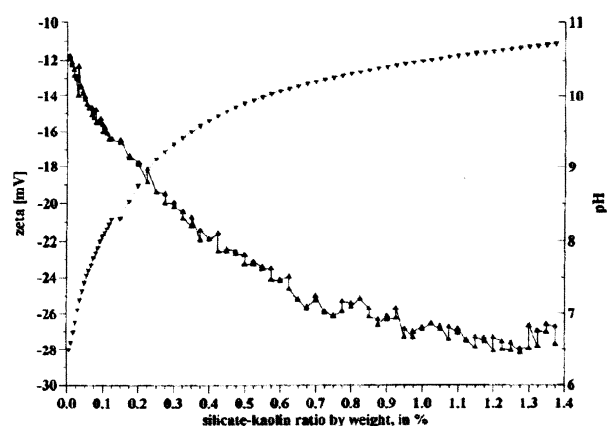


Figure 8. Titration of 40 wt % EC1 kaolin slurry using silicate.

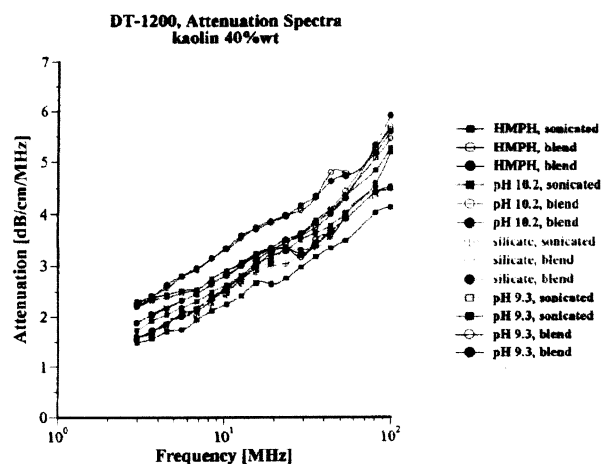


Figure 9. Attenuation spectra measured for EC1 40 wt % kaolin slurry stabilized with pH, hexametaphosphate, or silicate.

the tested chemical factors (pH, hexametaphosphate, silicate) destroys initial aggregates. These chemical factors create an environment which is potentially beneficial for gaining a full stability, but in order to take advantage of this environment one should apply a strong agitation which would destroy aggregates. It turned out that just mixing does not help. Only powerful sonication is able to

Table 1. Median Particle Size Calculated

chemical name	median log	chemical name	median log
hexa, sonicated	0.2122	silicate, sonicated	0.2362
hexa, blend	0.2621	silicate, blend	0.2627
hexa, blend	0.2621	silicate, blend	0.2586
pH 10.2, sonicated	0.2658	pH 9.3, sonicated	0.3063
pH 10.2, blend	0.3002	pH 9.3, blending	0.3671
pH 10.2, blend	0.2978	pH 9.3, blending	0.366
pH 10.2, blend	0.3017		

break aggregates. This effect is illustrated in Figure 6. It is seen that sonication causes a large 5 mV jump in the ζ -potential value. Actually, it is somewhat misleading. Sonication does not affect surface charge. It creates a new surface and reduces particle size. The appearance of the new surface with the same ζ -potential leads to the larger CVI signal. This larger CVI signal can be interpreted as a larger ζ -potential if we keep the same particle size. So far, particle size was assumed to be 300 nm for all EC1 kaolin slurries.

There is an opportunity to prove independently that sonication affects particle size distribution. To do this, we can use acoustic measurement which is a part of DT-1200. This acoustic sensor measures attenuation of ultrasound. Attenuation spectra contain information about particle size. There are many examples of successful particle sizing using acoustics.^{3,4}

Figure 9 shows attenuation spectra measured for various kaolin EC1 slurries. Slurries with hexametaphosphate and silicate are prepared at the optimum dispersant concentrations. The corresponding median sizes are given in Table 1. It is seen that the smallest size can be reached with hexametaphosphate after applying sonication. This conclusion confirms our observations made with electroacoustic measurement.

Conclusions

The electroacoustic ζ -potential probe is a convenient tool for determining the optimal dispersant concentration corresponding to the saturated surface. It is able to perform this characterization in the intact concentrated dispersions, eliminating dilution. A complete peptization requires additional sonication which destroys initial particle aggregates. Acoustic spectroscopy is an important addition to the electroacoustic spectroscopy yielding information about particle size distribution in concentrates and verifying the optimal dispersant level.

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