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Colloids and Surfaces
A: Physicochemical and Engineering Aspects 000 (1998) 000–000

COLLOIDS AND SURFACES A

Characterization of aggregation phenomena by means of acoustic and electroacoustic spectroscopy

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Received 19 September 1997; received in revised form 20 March 1998; accepted 24 April 1998

Abstract

Aggregation phenomena change the particle-size distribution, replacing small particles with larger aggregates. Measuring this evolution of particle size is an apparent way to characterizing aggregation phenomena. It is often desirable to perform this measurement in an intact, concentrated, dispersed system. Until recently, this kind of measurement was impossible, but the situation has improved dramatically with the availability of ultrasound-based spectroscopy. An ultrasound pulse interacts with dispersed particles while propagating through the dispersed system, thereby attenuating. An acoustic spectrometer measures this attenuation for a set of frequencies and calculates the corresponding particle size. An ultrasound pulse also disturbs the particle double layer. As a result, the particles generate an electric current, the so-called colloid vibration current (CVI). An electroacoustic spectrometer measures this current and calculates the ζ potential. We have suggested in our previous papers that combined acoustic and electroacoustic spectroscopy provides the most reliable and complete characterization of concentrated dispersed systems. We show in this paper that this technique is able to determine not only the isoelectric point but also a range of pH where system is not stable. It is found that the system loses stability when the ζ potential becomes less than 30 mV. We prove that a lognormal distribution is not adequate for characterizing unstable systems compared with the performance achieved with a bimodal distribution. © 1998 Elsevier Science B.V.

Keywords: Aggregation phenomena; Acoustic and electroacoustic spectroscopy; Particle-size distribution: Zeta potential

1. Introduction

Acoustic and electroacoustic spectroscopy are developing rapidly as an alternative to light-scattering methods. The ability to characterize concentrated disperse systems provides much of the impetus for these developments. Both techniques are based on a well established scientific background [1–19]. In both methods, the interaction of sound with the dispersed particles provides useful information. However, the set of measured parameters is different. In acoustic spectroscopy we measure the attenuation and/or sound speed [3–5] whereas for electroacoustic spectroscopy it is either the colloid vibration potential/current (CVP/CVI) [6] or the electrosonic amplitude (ESA) [8,9].

Electroacoustic spectra depend on both particle-size distribution (PSD) and ζ potential, which makes this type of spectroscopy very attractive for providing complex characterization of both these parameters. However, there are several disadvantages to this simple approach. We have analyzed

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PII S0927-7757(98)00565-2

and listed these problems in our previous paper [10]. In order to eliminate these limitations we have suggested the combination of electroacoustics with acoustics [10]. This new approach requires more sophisticated hardware. Nevertheless, we believe that it is worthwhile because the reliability of the data improves significantly.

Acoustic spectroscopy based on the attenuation measurement does not require any assumptions about electrosurface properties. As a result, the PSD obtained with acoustic spectroscopy is more reliable than that extracted from the spectra. This means that acoustic spectroscopy is more preferable for the characterization of particle-size distribution. The more reliable PSD coming from acoustic spectroscopy can then be used in interpretation of the electroacoustic spectra. As a result, the improvement in the reliability of PSD determination leads to more reliable ζ-potential data.

In this paper, we characterize the accuracy and precision of acoustics and electroacoustics by using stable, well-defined, concentrated dispersed systems. It is shown that this combined acoustic spectroscopy is suitable for characterizing unstable dispersed systems as well. In order to do this, a titration with a concentrated dispersed system has been performed. The change in both measured parameters (attenuation spectra and CVI) reflects changes in the particle-size distribution and ζ potential. Comparison of these two parameters allows us to determine the value of ζ and range of pH at which the system loses stability.

Calculation of the PSD from acoustic attenuation spectra requires an assumption concerning the shape of the distribution. A lognormal distribution is the most widely used model. Here, we compare the performance of lognormal PSD and bimodal PSD by means of error analysis.

2. Measuring technique

A combined acoustic and electroacoustic spectrometer (DT-1200) developed by Dispersion Technology Inc. was used. This instrument has two separate sensors for measuring acoustic and electroacoustic signals separately. Both sensors use a pulse technique.

The acoustic sensor has two piezo crystal transducers. The gap between 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 the pulse changes in steps as well. In default it changes from 3 to 100 MHz in 18 steps. The number of pulses collected for each gap and each frequency is automatically adjustable in order to reach the target signal-to-noise ratio.

The acoustic sensor also measures the speed of sound at one chosen frequency by using the time of arrival of the pulse at the receiver. The instrument automatically adjusts pulse sampling depending on the value of the speed of sound. This is necessary for eliminating possible artefacts like excess attenuation at low frequencies.

The electroacoustic sensor measures the magnitude and phase of the colloid vibration current at 2 MHz. It has a piezo crystal sound transmitter and a specially designed electric antenna. The distance between the transmitter and antenna is 5 mm. There is provision for automatic correction for the speed of sound and attenuation measured with the acoustic sensor.

All experimental data are stored in an Access database. A special analysis program calculates PSDs from attenuation spectra and ζ potentials from the CVI. This program tests lognormal, bimodal and modified lognormal [20] particle-size distributions and uses an error analysis to search for the best PSD. The goal of the optimization procedure is to minimize the error of the theoretical fit of the experimental attenuation spectra.

The analysis program takes into account a PSD correction when calculating the ζ potential. It uses either the PSD calculated from the attenuation spectra or a PSD known a priori. It makes also correction for attenuation of the sound pulse resulting from backflow caused by moving dispersed particles. An additional correction is made for the volume fraction effect, which is required in concentrated dispersed systems.

The instrument also has a special prediction program. This is an educational tool that gives the opportunity to calculate attenuation and CVI spectra for any system specified by the user. This program is suitable also for a manual search of the best PSD for the given experimental attenua-

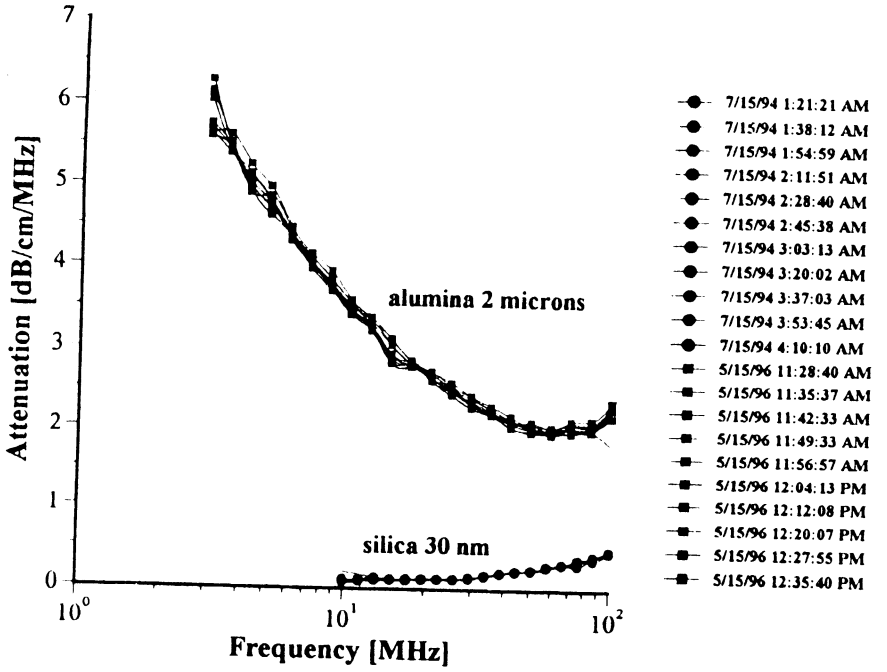

Fig. 1. Attenuation of the multiple measurements with alumina Sumitomo AA-2 and silica Ludox.

tion spectra. It helps to overcome the problem of a local minimum which might be an obstacle for the automatic optimization program.

The total volume of sample required is about 100 ml. A special magnetic stirrer prevents sedimentation and ensures mixing of the chemicals during titration. The instrument is equipped with two burettes and appropriate software for automatic titration. It also has conductivity and temperature probes.

Measurement of one attenuation spectrum with the default set-up takes about 5 min. The user can speed up the measurements by changing the set-up parameters. One CVI measurement takes from 10 s to 1 min depending on the system's properties. The precision and accuracy of the DT-1200 are described in the following sections.

2.1. Precision

Precision is a measure of the reproducibility. This section presents results concerning the precision of both the acoustic and the electroacoustic sensors.

The attenuation spectra in Fig. 1 illustrate the precision of the acoustic sensor. These spectra were measured on alumina Sumitomo AA-2 and silica Ludox. The alumina sample was measured 10 times in a row, while the silica sample was measured 11 times in a row. Corresponding median particle sizes are given in Table 1. It is seen that absolute variation of the median particle size is 0.9% for alumina and 1.5% for silica. These numbers illustrate the precision of the acoustic sensor.

Figs. 2 and 3 illustrate the precision of the

Table 1
Median particle size

Alumina	2.015	2.076	2.057	2.092	2.065	2.047	2.035	2.075	2.039	2.085	
Silica	0.03	0.029	0.029	0.029	0.029	0.03	0.03	0.029	0.03	0.03	0.03

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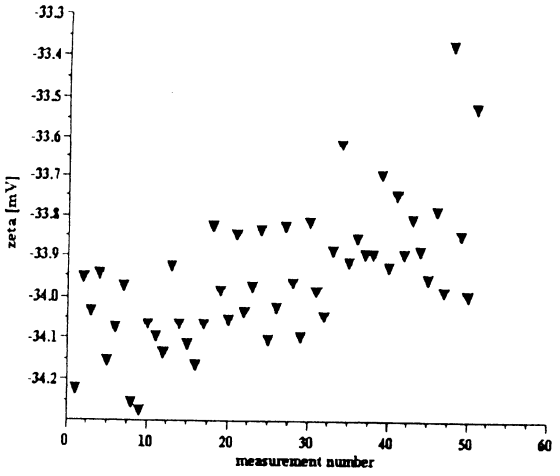

Fig. 2. Multiple ζ-potential measurements of 10 wt.% silica Ludox.

electroacoustic sensor. Fig. 2 shows the results of 51 continuous CVI measurements for silica Ludox. It is seen that the precision of the absolute value of the ζ-potential measurements is a fraction of a mV. Fig. 3 shows titration curves for three identical samples of 6 wt.% alumina with particles about 100 nm in size. It is seen that the precision in determining the isoelectric point is about 0.1 of a pH unit.

2.2. Accuracy

Accuracy characterizes the correlation between real and measured values. The accuracy of PSD measurement is a measure of the adequacy of the measured particle-size distribution. In order to determine the accuracy of PSD one needs a standard system with a known particle-size distribution. We used BCR silica quartz with a median size of about 3 μm; this is a PSD standard in Germany.

Fig. 4 shows the standard particle-size distribution and that measured with the DT-1200. The difference in median particle size between the standard and DT-1200 measurements is less than 1%. At the same time there is some difference in the amount of small particles. The results indicate that the acoustic sensor determines the median size with an accuracy of 1% and the standard deviation with an accuracy of about 5%.

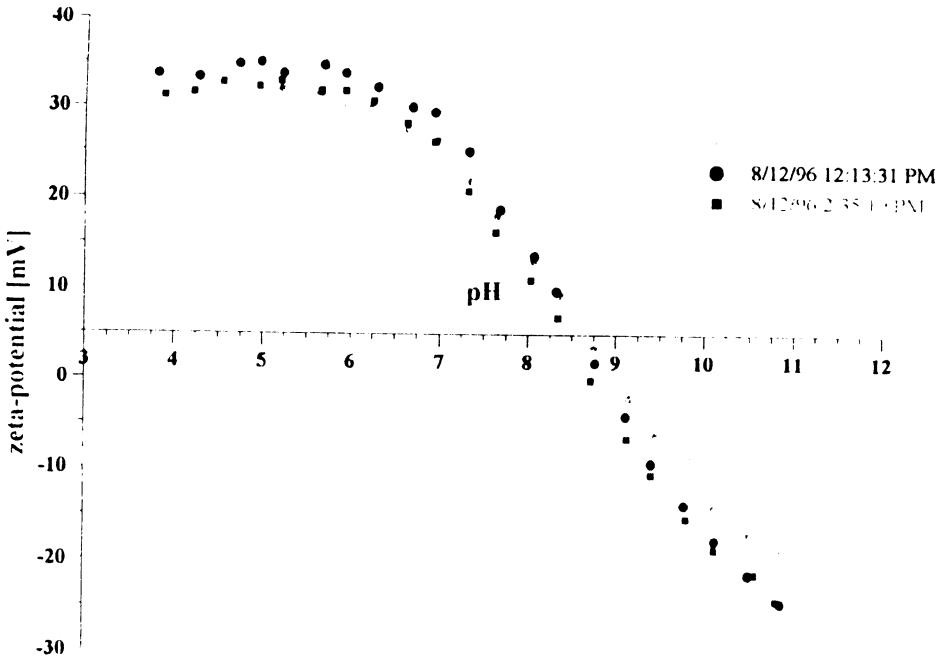

Fig. 3. Titration of three samples of the same 6 wt.% alumina.

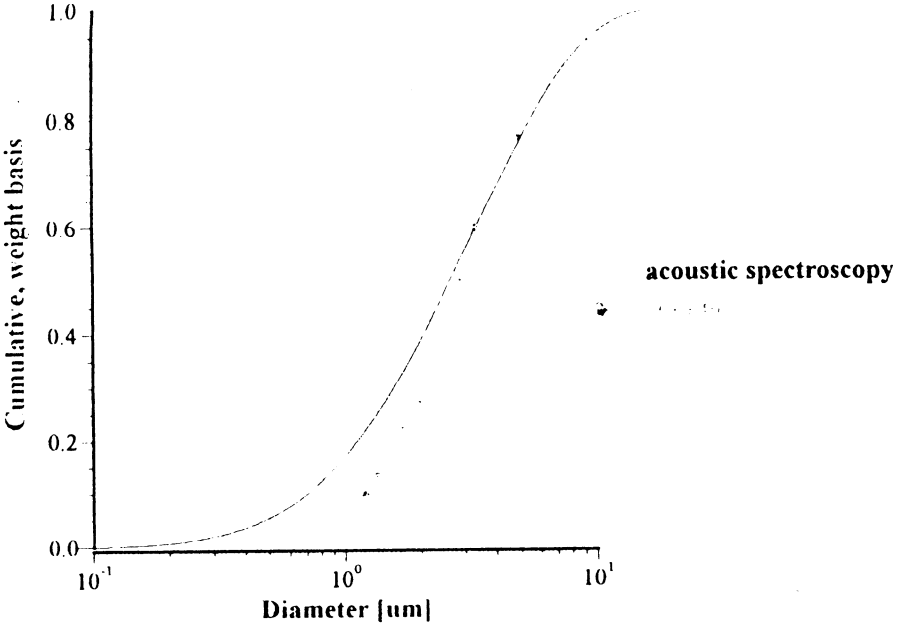

Fig. 4. Particle-size distribution of the silica quartz BCR. The acoustic measurement was performed with 11 wt.% particles in ethanol.

Testing the accuracy of ζ-potential measurements is much more complicated because there is no ζ-potential standard for concentrated systems. The lack of an electroacoustic theory for concentrated systems creates additional complexity. Our experience is that CVI makes it possible to measure ζ with the almost same accuracy as microelectrophoresis.

3. Titration experiment

3.1. Materials

Titration experiments have been performed with the two different materials: alumina and rutile. We chose these materials because of the different expected values of their isoelectric points. The isoelectric point of rutile is at about pH = 4, whereas that for alumina is around pH = 9.

A concentrated aqueous rutile slurry was obtained from E.I. Du Pont de Nemours. It is referred to commercially as R746 and is normally supplied at a weight content of 76.5% (44.5% by volume). The density of the particles was 4.06 g cm^{-3}, which is slightly less than for regular rutile because of the various surface modifiers used to stabilize the slurry. A pH titration was performed with a relatively concentrated sample, 7 vol.%. The sample was diluted with distilled water and adjusted to pH 8.5 with potassium hydroxide. The median particle size of this rutile slurry is about 0.3 μm according to the manufacturer's data.

The alumina slurry was 11.6 wt.% or 4 vol.%; the initial pH was 4. This sample was used in titrations without additional dilution. The median particle size of the alumina particles was unknown.

3.2. Results and discussion

Electroacoustic measurements of ζ potential confirmed the expected values of isoelectric points for both alumina and rutile. Corresponding titration curves are shown in Fig. 5.

According to general colloid chemical principles, dispersed systems lose stability at a pH close to the isoelectric point. Particle aggregation changes the particle-size distribution. This in turn will affect the attenuation spectra. The experiment

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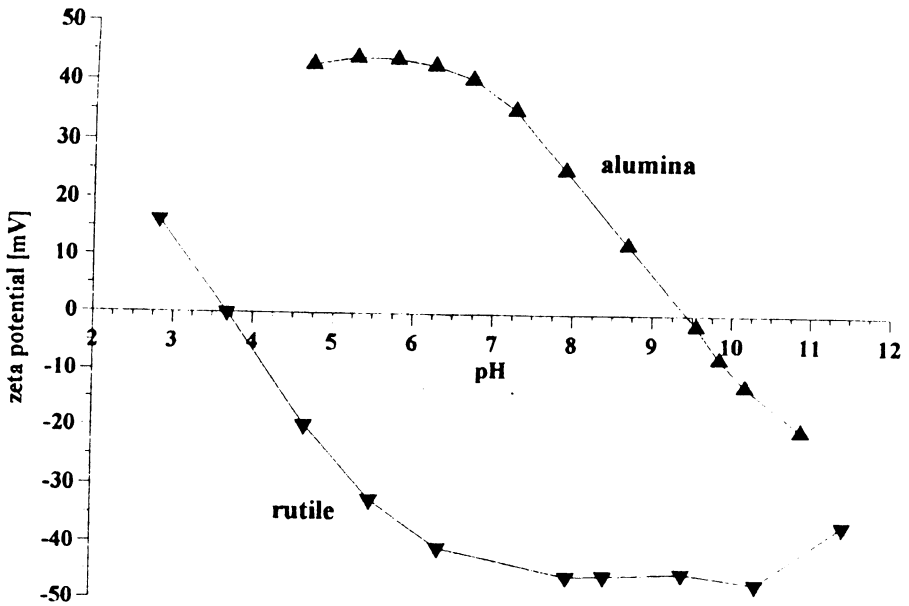


Fig. 5. Titration ζ-potential curves for 7 vol.% rutile and 4 vol.% alumina.

shows, indeed, that the attenuation spectra changes with pH for both alumina and rutile (Fig. 6).

It is interesting that in both cases the attenuation spectra remain unchanged up to a certain pH. In the case of alumina it is stable up to pH = 7.3; in the case of rutile, this critical pH is 5.9. The attenuation spectra change beyond this critical pH.

This critical pH marks a range of aggregation stability. Alumina is stable for pH below 7.3 whereas rutile is stable for pH above 5.9. In both cases this critical pH corresponds to the same value of ζ potential, about 30 mV. Both dispersed systems lose their stability when the ζ potential drops to the level of 30 mV.

A continuous change of pH beyond the critical point causes a fast change of the attenuation spectrum. It reaches another stable level in both cases. The existence of this other, pH-independent attenuation spectrum is a very interesting peculiar feature that is common for both systems.

In the case of alumina, the attenuation spectrum remains the same over a wide pH range from 8.2 to 11. The attenuation spectrum of rutile at pH below at least 4 does not change either. This means that, for some reason, particle-size distribution does not change in the vicinity of the isoelectric point. The systems are certainly unstable at these pH values; however, there is a factor which prevents particles from collapsing into large aggregates.

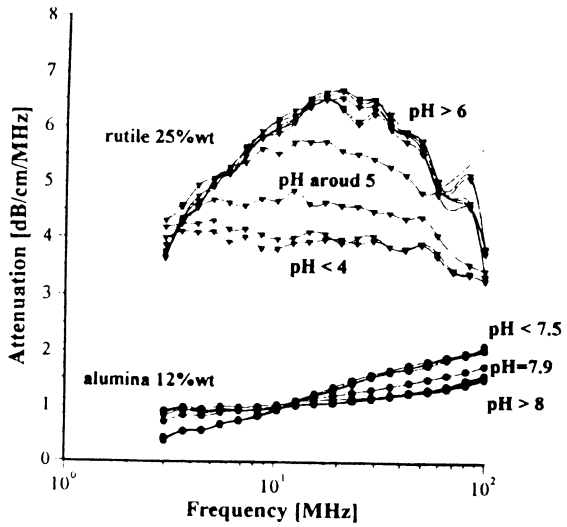
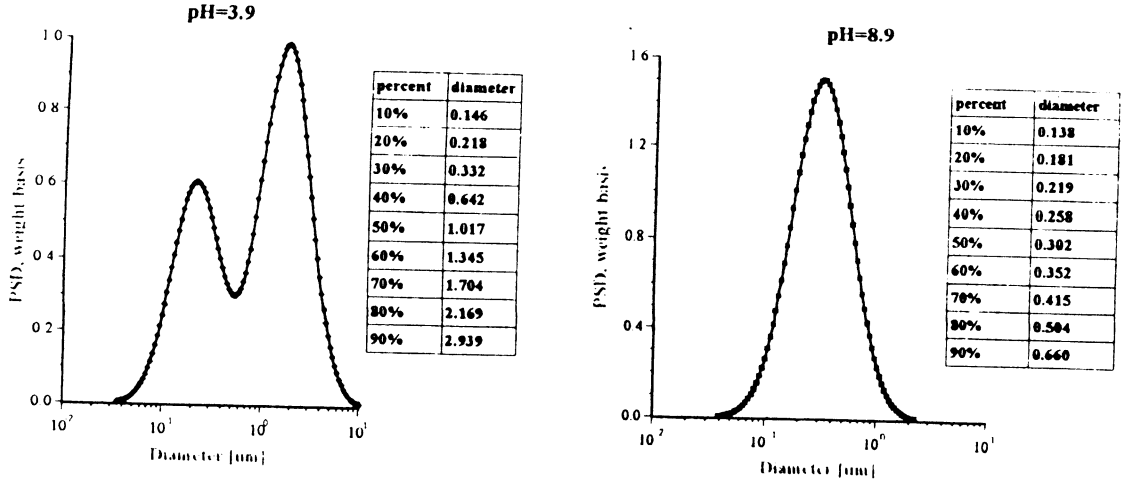


Fig. 6. Attenuation spectra for 7 vol.% rutile and 4 vol.% alumina at different pH values.

Particle-size distributions are shown in Figs. 7 and 8 for various pH values. The error analysis presented in the following section proves that the distribution becomes bimodal beyond the critical pH. However, the size of the aggregates does not exceed several μm.

We believe that the bimodal particle-size distributions are stable in time because of the stirring. The titration experiment requires samples to be stirred to achieve quick and homogeneous mixing of the added chemicals. Shear stresses caused by this stirring might break up large aggregates. This shear can be a factor which restricts the size of the aggregate. This idea can be tested experimentally in the future by making measurements at different stirring rates.

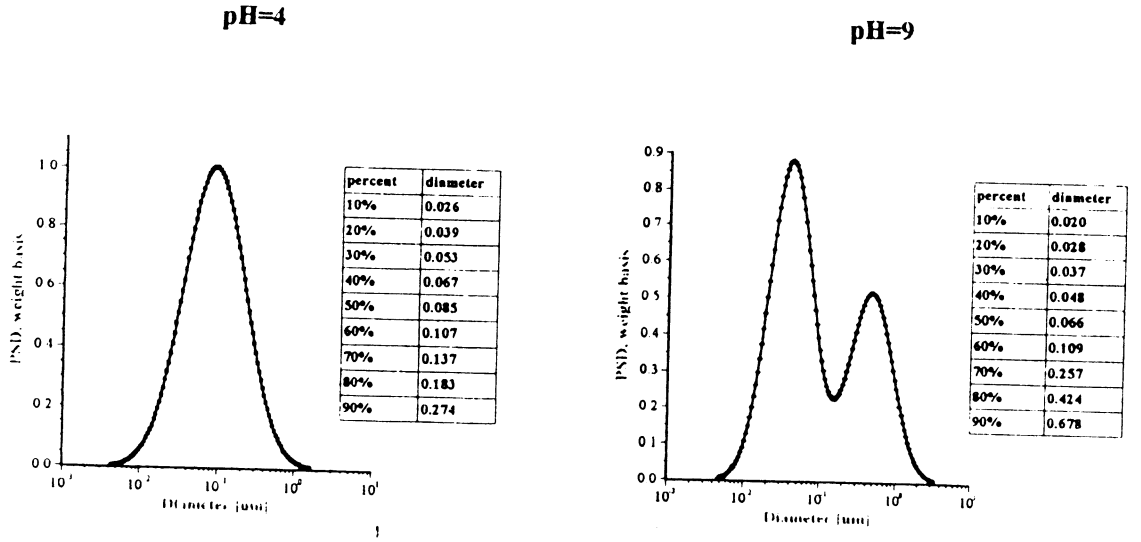
There is another unsolved question, however. We do not know whether the aggregation observed is reversible. Both systems used did not allow us to reach the ζ potential above the critical value



percent	diameter
10%	0.146
20%	0.218
30%	0.332
40%	0.642
50%	1.017
60%	1.345
70%	1.704
80%	2.169
90%	2.939

percent	diameter
10%	0.138
20%	0.181
30%	0.219
40%	0.258
50%	0.302
60%	0.352
70%	0.415
80%	0.504
90%	0.660

Fig. 7. Particle-size distribution of stable and unstable 7 vol.% rutile.



percent	diameter
10%	0.026
20%	0.039
30%	0.053
40%	0.067
50%	0.085
60%	0.107
70%	0.137
80%	0.183
90%	0.274

percent	diameter
10%	0.020
20%	0.028
30%	0.037
40%	0.048
50%	0.066
60%	0.109
70%	0.257
80%	0.424
90%	0.678

Fig. 8. Particle-size distribution of stable and unstable 4 vol.% alumina.

(30 mV) after crossing the isoelectric point. The ζ-potential value is restricted by increasing ionic strength at high pH for the alumina and at low pH for the rutile. We need another material with an isoelectric point at the middle pH range in order to answer this question.

3.3. Error analysis

When calculating PSD from the attenuation spectra, the DT-1200 analysis program searches for particle-size distributions with predefined shape. The five different shapes are used: monodisperse, lognormal, bimodal, modified lognormal [20] and modified bimodal. This approach makes it possible to increase the number of adjustable parameters in steps and also to implement a priori information. The number of adjustable parameters is equal to 1 for monodisperse PSD (size), 2 for lognormal (size and standard deviation) and 4 for bimodal (two mode sizes, standard deviation of the mode assumed to be the same for both of them and the relative weight of modes). Modified lognormal and bimodal PSDs give an opportunity to use a priori information about minimum and/or maximum size.

The analysis software searches for the best values of adjustable parameters by minimizing the deviation between experimental and theoretical attenuation spectra calculated for the various PSDs. The result of this search is five best distributions (best monodisperse, best lognormal, best bimodal, best modified lognormal and best modified bimodal).

There is a theoretical error corresponding to the best fit achieved with a distribution of particular shape. Comparison of these errors allows a decision to be made about which distribution is the most suitable: the smaller error, the better the PSD. The error value decreases with increasing number of adjustable parameters. However, this does not mean that a bimodal distribution is always better than a lognormal one because the reliability of the PSD is reciprocally proportional to the number of adjustable parameters. Although an increase in the number of adjustable parameters improves the theoretical fit, it reduces reliability.

It is obvious that there is some optimum number of adjustable parameters. Experimental error should be used in order to define this optimum number. According to Ocaam's principle, we should stop adding adjustable parameters when the theoretical error becomes smaller than the experimental error.

The values of theoretical and experimental errors are shown on Fig. 9 for both alumina and rutile. Errors of the lognormal and bimodal distributions are almost identical for pH values corresponding to the stable systems: >5.9 for rutile and <7.3 for alumina. The larger number of adjustable parameters for the bimodal PSD causes no improvements in theoretical fit. This means that there is no reason to claim a bimodal PSD for $pH>5.9$ for rutile and $pH<7.3$ for alumina.

The error of the theoretical fit for the lognormal distribution becomes much larger than that for the bimodal one at $pH<5.9$ for rutile and $pH>7.3$ for alumina. A lognormal distribution fails to fit experimental attenuation spectra in this pH range. The much smaller theoretical error is the reason to claim a bimodal PSD for these two pH points.

This error analysis yields the conclusion that a lognormal distribution is not suitable for characterizing unstable dispersed systems. This type of particle-size distribution does not reflect adequately the formation of aggregates.

4. Conclusions

Combined acoustic and electroacoustic spectroscopy provides independent characterization of particle-size distribution (PSD) and ζ potential. In essence, the acoustic spectra provide PSD information, whereas the electroacoustic signal (colloid vibration current, CVI) yields ζ potential.

Acoustic spectroscopy can characterize the median particle size with a precision and accuracy of about 1%. The width of the distribution can be characterized with a precision of about 1% and an accuracy of about 5%.

Values of ζ potential can be determined with a precision of a fraction of a mV and an accuracy about several mV, depending on the particle volume fraction.

Acoustic attenuation spectra and CVI measured

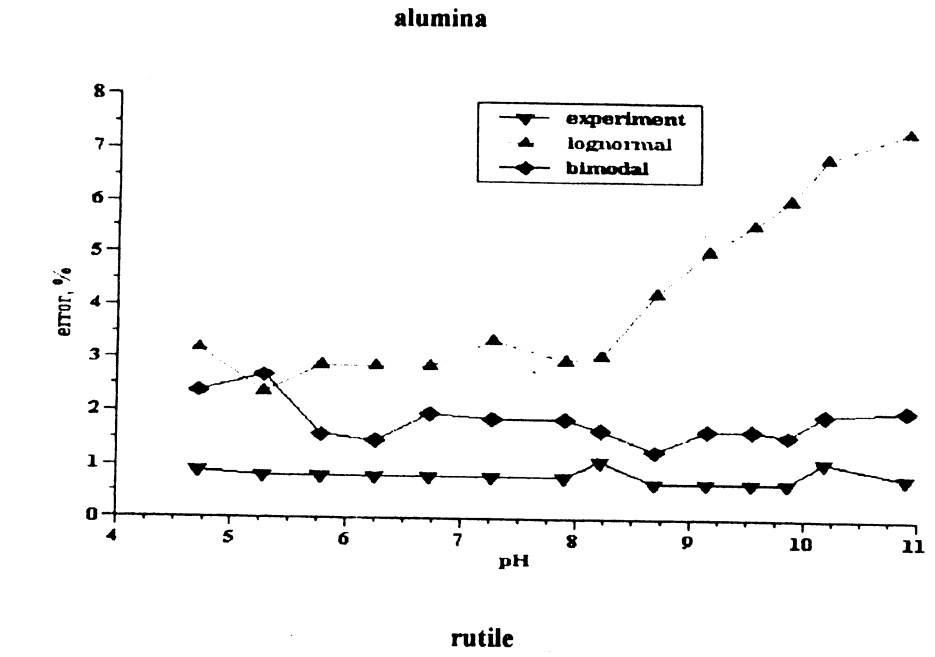


Fig. 9. Errors of theoretical fit achieved with lognormal and bimodal distributions for different pH values.

for concentrated 7 vol.% rutile and 4 vol.% alumina dispersions show pronounced changes caused by pH. These changes are associated with aggregative stability. Both dispersions lose stability within ± 2 pH units of the isoelectric point. Both dispersions become unstable when the absolute value of ζ potential drops below 30 mV.

The particle-size distribution for both dispersions becomes bimodal near the isoelectric point. This bimodal distribution remains quite stable

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within ±2 pH units in the vicinity of the isoelectric point.

A lognormal PSD is not very suitable for characterizing such unstable systems. The fitting error between the experimental spectra and the lognormal PSD is much larger than the error for a bimodal PSD. The lognormal PSD fails to reflect properly the formation of aggregates.

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