



Non-dilute Systems

Abstract

One of the principal advantages of the electroacoustic method is its ability to provide direct characterization of colloidal dispersions, at moderate to high particle concentrations, without the need for dilution. This note discusses the value of such measurements compared to the alternative techniques that require the sample to be extensively diluted.

Dilution Procedures

Preparing a colloid sample of the appropriate dilution for, say, a light scattering measurement, is not simply a matter of adding some solvent. This dilution is time consuming, but worse, it can lead to large errors in the zeta potential due to changes in the concentration of the background electrolyte.

The suspension has to be diluted with an electrolyte that is exactly the same as the electrolyte beyond the double layers. But in some cases even this careful dilution is not enough. Experienced workers in the field know that there are dynamic equilibria set up between the surfaces of the particles and the bulk solution, and that these must not be disturbed if one is to obtain meaningful data.

This is a particular problem for systems in which particles are partially soluble in the solvent and in emulsion systems, where the ion concentration can be altered during dilution by the release of ions which are soluble in both phases.

What is less well known is that even the usual preferred dilution method, involving centrifugation, has its limitations.

Problems with the Centrifugation Technique

Apart from being tedious and time-consuming, the centrifugation procedure must be done very carefully to be at all successful.

The normal procedure is to centrifuge the sample sufficiently strongly to produce a clear supernatant and then to make up the final dispersion by adding a little of the undiluted material to this clear solution. The initial centrifugation must be done completely, since otherwise the final sample will over-represent the smaller particles, which will be the last to clear from the supernatant.

The main problem with this procedure is that, if one has to spin the particles down hard, the lower part of the sediment will be compressed to the point where the particle double layers begin to overlap. If overlap is sufficiently strong, it causes a

shift in the equilibrium of the surface ions. Some of them are desorbed and move up into the supernatant. The composition of the supernatant is then no longer the same as the initial interparticle fluid.

This sort of problem is compounded if the system is a complex one, involving both surfactant and polymer adsorbates. The complex interactions that occur in such systems are significantly affected by the closeness of approach of the particles. That interaction will be greatly altered by the compression that occurs when the particles are forced together at the base of the centrifuge tube. Again that will mean the composition of the supernatant prepared by centrifugation is not the same as the original interparticle fluid. That means the dilute system is no longer a correct representation of the more concentrated one. This problem is particularly true when the original system is very concentrated.

In cases where the disperse material is fluid (as in an emulsion) there is the further problem alluded to earlier: there may be components in the system which are able to dissolve in both the oil and the water phase. Any change in the ratio of the two phases will effect that solution equilibrium and necessarily alter the surface properties of the system.

There are other problems in working at very low particle concentration. The most important one is that of contamination. At high pH, sufficient silica can dissolve from the surface of a glass container to drastically alter the surface properties of mineral oxides by adsorption onto those surfaces. Attempts to get over the problem by moving to plastic containers can be counter-productive, if the plasticizer exuded from the walls is surface active, as is usually the case.

Advantages of Working at Higher Concentration

The AcoustoSizerII and ZetaProbe are designed to work in concentrated colloids. Such colloids are much less sensitive to contamination than their diluted counterparts because of their very large particle surface area. Any contaminant will be spread over this large area and so its effect will usually be negligible. Thus it is not necessary to use ultra clean systems when working with such colloids.

Another advantage is the remarkable reproducibility of the data which is obtained, especially for complex systems, for which such data has not previously been available. Figure 1 shows some zeta potential data for a sample of a commercial skim milk[1] using the AcoustoSizer. The solids concentration here is 9% but the salt concentration is very high (about 0.1M). Prior to this study, zeta potentials had only been measured on very dilute samples and values from -8 [2] to about -48 mV [3] were quoted at the natural pH (6.8) with little or no consistency. A skim milk suspension is a very complex mixture but the predominant component is casein in the form of 'micelles', which are made up of the various casein proteins linked together with calcium ions associated with phosphate groups.

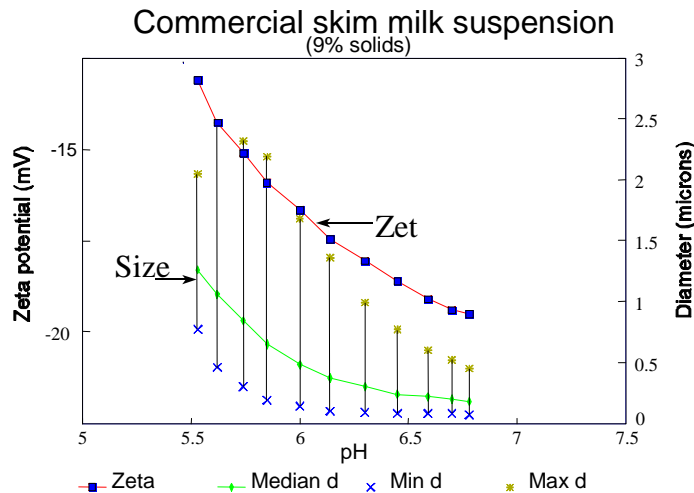


FIGURE 1: SIZE AND ZETA POTENTIAL OF CASEIN MICELLES IN SKIM MILK. THE VERTICAL LINES ON THE SIZE GRAPH REPRESENT THE RANGE OF THE SIZES FROM THE MEDIAN VALUES (SHOWN BY THE GREEN LINE).

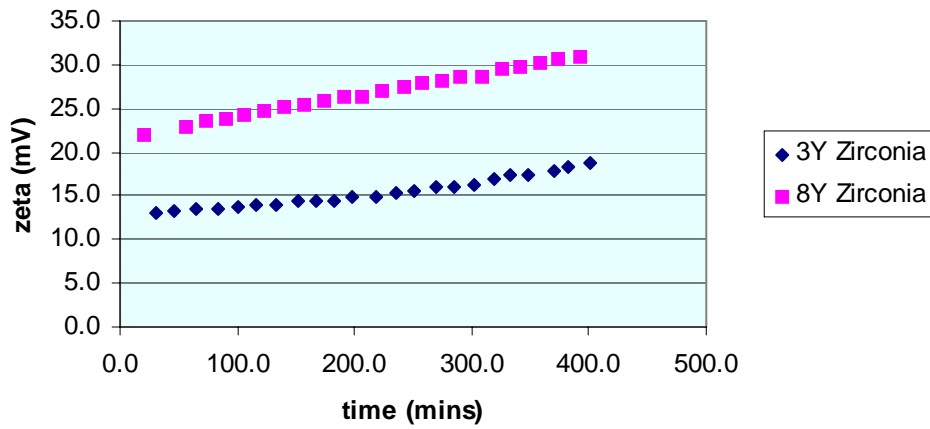
The smooth variation of the zeta data at different pHs suggests that these results are definitive. The fact that one can repeat such studies and obtain not merely similar *but essentially identical* results places the AcoustoSizer and ZetaProbe in a class of their own where complex systems are concerned.

The result is in some cases due to the reduced effect of contaminants, and sometimes a matter of having a better sample of the material, but in this case it is almost certainly because of the avoidance of artifacts induced by the dilution process.

It is also a consequence of the very high stability of the measuring system used in the AcoustoSizer. Each data point corresponds to the collection of over 100 repeat measurements, at each of the thirteen measuring frequencies in the range of the instrument, to minimize the effects of random noise on the signal.

Another type of suspension that cannot be diluted for zeta measurement is one in which the particles are partially soluble in the solvent. An example is the yttria doped zirconias used in the ceramics industry. In the figure below we show AcoustoSizer II measurements of the zeta potential of two such suspensions over time [3]. The 3Y and 8Y samples have 3 and 8 mole% yttria respectively. Clearly the zeta is increasing more rapidly in the higher yttria content. According to Greenwood [3], this increase in time is caused by the dissolution of yttria from the particles followed by readsorption on the surface. Thus the surface composition is changing with time and this is the reason for the change in zeta. Greenwood points out that measurements such as these should be one of the routine initial tests in the characterisation of a powder, to see if there is dissolution that can alter the surface chemistry. Note that change in zeta with time depends on the particle concentration, and such changes would not be picked up in a very dilute sample because the dissolved ions do not alter the background electrolyte.

Dissolution of zirconia



References

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