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Electroacoustic study of dispersions containing two types of colloidal particles

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ABSTRACT

The procedure of subtraction of electrolyte background electroacoustic signal, which is a standard feature in commercially available instruments, can be used to determine the ζ potentials of particular types of colloidal particles in multi-component dispersions. A preliminary study was carried out in a few two-component dispersions (dispersions containing two types of particles). One-component dispersion with the same mass fraction of component 1 and with the same solution composition as in the two-component dispersion of interest was prepared and the electroacoustic signal of that one-component dispersion was measured and saved as the “electrolyte background”. Then, the signal of the two-component dispersion was measured, and the saved background signal was subtracted from the signal of the two-component dispersion, thus producing the ζ potential of component 2. An analogous procedure was carried out to determine the ζ potential of component 1. Two opposite types of behavior were observed in various two-component dispersions. In certain dispersions (e.g., titania-alumina in dilute solutions of 1–1 electrolytes at various pH), the behavior of the both types particles was independent, that is, their ζ potentials at certain pH in one- and two-component dispersions were equal. In other dispersions (e.g., silica-alumina at neutral pH), the apparent behavior of particles in one- and two-component dispersions was completely different. The observed difference indicates an interaction between the particles, e.g., formation of aggregates containing both types of particles, adsorption of products of dissolution or formation of new phases.

1. Introduction

The ζ potential is an important parameter characterizing particles in dispersions. Many commercially important properties of dispersions, e.g., their stability against coagulation, rheological properties, their adhesion to various surfaces are directly related to the ζ potential. There is a substantial limitation in direct measurement of ζ potentials in dispersions, namely such measurements produce reliable results in one-component dispersions only, that is, in dispersions containing one type of colloidal particles. Technically, a measurement of the ζ potential can also be carried out in a multi-component dispersion, but the physical sense of such an “combined” (overall) ζ potential is not clear. The contributions of particular types of particles to the overall ζ potential depend on their mass fractions and on various properties including the refractive index, size and shape of colloidal particles; thus, the overall ζ potential is difficult to interpret. Moreover, interactions between particles of different types may lead to formation of aggregates containing both types of particles (of various compositions), adsorption of products of dissolution [1–5], and even formation of new phases, although the experimental evidence for the later is scarce. For example, adsorption of metal ions on silica is usually interpreted in terms of surface complexation, but adsorption of Co on silica has been re-interpreted in terms of formation of a trioctahedral clay [6]. Several publications report the overall ζ potential measured in naturally occurring or man-made multicomponent dispersions, e.g., clays and rocks [7–11].

The electroacoustic method of measurements of ζ potentials offers several possibilities, which are not available in classical electrokinetic techniques. Measurements in dispersions of fine particles, which are not stable against coagulation, are possible by means of electroacoustic method. Namely a dispersion is continuously stirred and/or pumped in course of electroacoustic measurements to prevent sedimentation. For example, dispersions in very concentrated electrolyte solutions are usually unstable thus not suitable for measurement by electrophoresis. The procedure of subtraction of background signal of the electrolyte, which is a standard feature in commercial electroacoustic instruments, can be used to determine the ζ potentials at ionic strengths on the order of 1 M, which are beyond the range of applicability of classical electrokinetic techniques [12]. In this present study, the procedure of subtraction of electrolyte background electroacoustic signal is applied to obtain ζ potentials of particular components in multi-component dispersions. A standard feature of a commercial

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apparatus is used, but so far such an option has been overlooked in the scientific literature. In contrast to electrophoresis, in which the overall signal of a multi-component dispersion is difficult to interpret, in the electroacoustic method, the overall signal is interpreted as a sum of signals of particular components of the system, that is, particles and ions.

This present study is limited to two-component dispersions. Component 2 is actually the studied component of a two-component dispersion (containing also component 1). One-component dispersion of component 1 is used as the background. The ζ potential of component 2 is obtained by subtraction of the background (dispersion of component 1) from the signal of two-component dispersion (containing components 1 and 2).

Multi-component dispersions are widely used, e.g., in the investment casting process. A typical slurry (used to produce the investment) contains colloidal silica (binder) and coarse grains of refractory material, e.g., alumina. The properties of those components in multi-component dispersions are relevant to the rheological properties of the slurry, its aging, etc.

2. Experimental

2.1. Materials

Ludox 50 TM (Aldrich, 50% suspension in water) and the following powders: fumed silica (Aldrich), and Alu C, and P-25 titania from Evonik-Degussa were used as received. The specific surface area of Ludox is 125 m^2/g. The specific surface areas of the powders are 380, 100, and 50 m^2/g, respectively. The other chemicals were reagent grade, and water was from PurelabPlus (Elga USF, Germany). The above powders were used as component 1 or component 2 (see Section 2.3) in various combinations. Certainly Ludox (dispersion) could only be used as component 1, but not as component 2.

2.2. Instrument

DT-1200 from Dispersion Technology (USA) was used. The instrument has a built-in pH-meter. No special efforts were undertaken to avoid atmospheric CO_2. The temperature was 25–27.5 °C. The instrument does not have a thermostat, and only, the temperature in the laboratory was controlled. The heat produced by a stirrer induced an increase in the temperature in course of the measurement from the initial 25 °C to a steady state at about 27.5 °C. The temperature in the measurement cell was measured but not adjusted.

2.3. Procedures

The mass fractions of particular components were 0.2–10%. These and all other data on the concentrations of the components reported in this paper refer to mass fractions. The mass fraction of component 2 (sample) was at least of the same order of magnitude as the mass fraction of component 1 (background). Thus, a calculation of a small number, as a difference of two large and almost equal numbers, was avoided. The experiments were carried out without addition of 1–1 salts. The only electrolytes added to the dispersions were concentrated (about 3 M) solutions of NaOH or HCl used to adjust the pH. The effective ionic strengths in the dispersions were in the range of 0.01 M. Such an ionic strength produces a weak electroacoustic signal, which does not substantially contribute to the overall signal. Most experiments were carried out at (approximately) constant pH. The experimental conditions were adjusted to avoid substantial changes in pH in course of the experiment. Unfortunately, the changes in pH could not be entirely avoided. Namely, the stability of pH in course of an experiment depends on the component 1/component 2 ratio. With a high component 1/component 2 ratio, the pH is very stable (insensitive to addition of component 2), but then the signal of two-component dispersion is not much different from the background, and the signal of component 2 is obtained as a difference between two large and almost equal numbers. Thus, the value and even the sign of the calculated ζ potential of component 2 are very uncertain. With lower component 1/component 2 ratio, the calculated ζ potential of component 2 is more certain, but the pH is less stable (more sensitive to addition of component 2).

The measurements of the ζ potentials in one-component dispersions were carried out for a freshly prepared dispersion (no titration, only one portion of acid or base added to adjust the pH). A series of consecutive measurements (no reagents added) was continued until the apparent ζ potential reached a constant value.

The measurements of the ζ potentials in two-component dispersions were preceded by measurements in one-component dispersions. Once the ζ potential of component 1 in one-component dispersion reached a constant value, the signal of that dispersion was stored as a background. Then, a two-component dispersion was prepared by addition of component 2 (as a powder) to the one-component dispersion.

The mass fraction of component 2 used in this study is a compromise between two contradictory postulates. Large mass fraction produces a desired affect, because it makes the signal of component 2 strong, thus insensitive to minor variations in the background (signals of the ions and of component 1). On the other hand, large mass fraction of component 2 produces an undesired affect, because it induces a shift in the pH of the dispersion, which in turn affects the ζ potential of component 1, and the background signal. Thus, stable sample signal and constant background signal cannot be achieved simultaneously. Obviously, acid or base can be added to adjust the pH back to the initial value (pH of the dispersion used as a background) after addition of component 2, but the added electrolyte contributes to the electroacoustic signal of the dispersion, and the required amount of acid or base (to bring the pH back to the initial value) is nearly proportional to the mass fraction of component 2.

The following types of experiments were carried out in two-component dispersions.

- Dummy experiment. Component 2 was actually not added, but addition of component 2 (the same mass fraction as in the planned real experiment) was recorded in the "sample definition" box, while the experiment was carried out in a dispersion containing only component 1. The expected result is that the signal of the sample and that of the background (which are identical) cancel out, and the apparent "background corrected" ζ potential of component 2 equals zero. The dummy experiment does not produce data points, but it confirms the validity of the method in a system of interest.
- Solid titration (of a dispersion of component 1 with component 2). Several portions of component 2 were consecutively added every 1–3 h. The actual mass fraction of component 2 (specific for certain titration step) was recorded in the "sample definition" box, and the same saved background (dispersion of component 1) was used for all two-component dispersions. The expected result is that the background corrected ζ potential of component 2 is independent of its mass fraction (at constant pH).
- Kinetic experiment. Apparent ζ potential of component 2 obtained by subtraction of the background from the signal of two-component dispersion was studied as the function of time for a period up to 4 d (usually 1 d). Longer equilibration times are not likely to produce valuable results because the ζ-probe calibration holds for a few days, and then, the ζ potential in a