TECHNICAL REPORT

ISO/TR 19997

Guidelines for good practices in zeta-potential measurement

Lignes directrices relatives aux bonnes pratiques pour la mesure du potentiel zéta

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Contents

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This document was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Zeta-potential is often used to investigate the isoelectric point (IEP) and surface adsorption for particles in liquid media, and as an indicator in comparing different samples regarding electrostatic-dependent dispersion stability. Zeta-potential is not a directly measurable quantity, but is established using an appropriate theory. Furthermore, zeta-potential is not an intrinsic property of suspended particles; it depends on both particle and medium properties, and how they interact at the interface. Any variation in the liquid chemical and ionic composition affects this interfacial equilibrium and, consequently, zeta-potential. Therefore, sample preparation and measurement procedures can both affect the measurement result. Incorrect conclusions often result from artefacts in sample preparation and issues arising from measurement procedures, or incorrect application of theoretical models for calculating zeta-potential from measurement results.

This document provides general guidelines for sample preparation and measurement procedures for the determination of zeta-potential by optically-based electrophoretic mobility or electroacoustic methods.

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ISO/TR 19997:2018
https://standards.iteh.ai/catalog/standards/sist/e0883b08-e57a-4ca4-be7d-
1949b81dba35/iso-tr-19997-2018

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Guidelines for good practices in zeta-potential measurement

1 Scope

This document addresses the zeta-potential measurement operation for applications such as new product design, optimization of existing products, quality control during processing and/or during usage of the product. It does not provide a complete procedure for zeta-potential measurements. The instructions and key points addressed in this document are considered useful for performing zeta-potential measurements as specified in ISO 13099-1 and ISO 13099-2.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Symbols

μ electrophoretic mobility

ε_m relative permittivity of the medium

ζ electrokinetic potential, zeta-potential

η_o medium viscosity

5 Principle

Zeta-potential (ζ) is the electric potential at a hypothetical shear plane that separates the mobile solvent from solvent molecules that associate with the particle surface. Zeta-potential is frequently used to predict the stability of a suspension or the adhesion of suspended particles onto macroscopic surfaces (e.g. cellulose fibres, membranes). This is because interaction between particles or between particles and surfaces or between particles and proteins is often governed by the ion distribution in the diffuse layer, which is closely related to zeta-potential. Whenever electrostatic forces dominate interactions between particles or between particles and surfaces, zeta-potential is the principal system parameter to evaluate these interactions[1]. Repulsion requires high surface charges of equal sign, whereas attraction occurs in the absence of surface charge or for oppositely charged or "patchy" surfaces containing both negative and positive domains. High zeta-potential absolute values cause strong repulsion between dispersed particles and, thus, favour the stabilization of colloidal suspensions. This effect is even more pronounced for thick double layers in low electrolyte content. In contrast, low zeta-potential absolute values (+ or −), zeta-potentials of opposite sign (polarity), or high electrolyte concentrations, can promote agglomeration. Hence, zeta-potential can be principally employed to predict the suspension stability, which is frequently determined as a function of the pH and/or the

concentration of indifferent electrolytes and surface active ionic species (e.g. ionic surfactants, multi-valent ions and polyelectrolytes)[2][3].

Zeta-potential can be probed by imposing a relative motion between bulk solvent and particle. Zeta-potential measurements on colloidal suspensions are frequently conducted via either electrophoresis or electroacoustics for applications under different sample conditions (e.g. diameter range from nanometre up to tens of micrometres with particle volume fraction from roughly 10^{-4} % to 40 %)[4].

Zeta-potential is not an intrinsic particle property; it depends on the chemical equilibrium between the particle surface and the liquid phase in which it is dispersed. Any variation of the liquid chemical and ionic composition may affect this equilibrium and, consequently, affects zeta-potential[5][6][7].

The perception that there is a universally valid critical zeta-potential value that defines the transition from unstable to stable suspensions has been proven only in limited applications. Zeta-potential values need to be used carefully when evaluating the suspension stability. It is recommended that in formulation work to predict stability, a second measurand (e.g. size distribution, turbidity, viscosity, etc.) can be monitored and correlated to verify the conclusion derived from zeta-potential measurement.

Information on Zeta-potential measurement for particles in non-polar media can be found in Annex A.

6   Sample preparation

6.1   General

As the particle zeta-potential depends on particles as well as the dispersion medium, simple dilution can change the chemical composition of the medium and then affect the particle zeta-potential. Therefore, in addition to general practice in sample preparation for particle systems[8], special measures need to be taken. Dilution can also induce dissolution, which alters both the surface and the medium. The sample preparation needs to follow a procedure such that zeta-potential is not changed from the original system to the diluted sample.

The sample preparation procedure requires that upon dilution not only do particles and their surfaces remain identical between the original system and the diluted system, but also that the medium remains electrochemically identical. Particle surface charge is wholly dependent upon the chemical characteristics of the dispersion medium. Both the pH and specific ion concentration of the dispersing medium are vital characteristics to be controlled if concentrated suspensions are to be diluted for measurement. The conditions that particles undergo within a concentrated suspension need to be entirely matched by the diluent.

This condition is not easy to satisfy if both dilution and surfactant stabilization of the sample are involved. The sample preparation procedures can affect liquid composition tremendously. It is rather difficult to adjust the particle concentration for electrokinetic measurements without impacting the physico-chemical properties of the dispersion medium and the interface. For instance, dispersing amorphous silica in KNO_3 solution results in a suspension that will be different from the same material in de-ionized water with respect to both pH and ionic strength. These differences have a considerable impact on the interfacial properties, such as the zeta-potential.

6.2   Sampling and sample inspection

The electrophoretic mobility (μ) measured in a sample is only valid for a batch of material if the test sample is representative of that batch and has been sampled adequately.

The material to be analysed should be inspected to ensure the particles have been dispersed adequately without any sedimentation occurring upon standing for a period relevant to the measurement time. If particles sediment during measurement, measurement using optical methods may not be appropriate since particles remaining in the laser beam may not represent the whole sample (e.g. with polydisperse samples, large particles will settle differentially resulting in a biased measurement of the smaller size particles).

Considerable care needs to be exercised during sample preparation to avoid changing the electrophoretic mobility[3] of the sample to be tested. Labware that comes into direct contact with the sample, such as a glass beaker or syringe, may adsorb specific ions from the medium or add residual contaminants to the sample that remain from a prior cleaning process or from production of the labware itself. Disposable plastic preparation beakers and pipettes are generally preferred, as long as they are chemically compatible with the sample.

A detailed report describing precisely how the sample was handled and how the diluent was prepared is to accompany the result. Several complete dilutions and measurements of the sample can be made to demonstrate that the method adopted is stable and reproducible.

6.3   Sample dilution procedures

In electroacoustic measurements, little or no sample preparation is typically required and instruments convert the raw measurement data to zeta-potential using a theory and calibration procedure that account for the finite particle concentration[9], as well as for the effect of particle size. In systems relying on electrophoresis with optical detection, particle-particle interactions are minimized by diluting the sample to an appropriate concentration. In this case, care needs to be taken that solvent shock or other dilution effects do not alter the electrokinetic properties of the sample.

Sample dilution can follow the so-called equilibrium dilution approach, wherein the same liquid as that in the original system is utilized as the diluent. When done properly, equilibrium dilution results in a sample where the only parameter modified is the particle concentration. Only sample preparation based on equilibrium dilution yields zeta-potential values that are theoretically identical between the original system and the diluted sample. Simple dilution using deionized water, for example, is a misleading and generally incorrect way to prepare samples for zeta-potential measurement.

There are two approaches to the collection of the liquid used for equilibrium dilution. The first consists of extracting a supernatant using gravitational sedimentation or centrifugation. This supernatant or "mother liquor" can then be used for diluting the initial sample to the degree that is optimal for the chosen measurement technique. This method is suitable for large particles with sufficient density contrast. It is not very convenient for nanoparticles and biological systems with low density contrast. For emulsions, where a third phase (an emulsifier) stabilizes the normally immiscible oil and aqueous phases, dilution into a matched ionic background is typical, due to the difficulty of using centrifugation in this case. Ideally, this preserves the same ionic background in both the concentrated and more dilute forms. This diluent can be obtained by knowledge of the ionic composition (ions, ionic surfactants) in the dispersant phase. However, this will not account for species released by the particle phase itself. A third approach, perhaps more suitable for nano- and bio-colloids is to employ dialysis. Dialysis membranes are required that are permeable for ions and molecules, but not for colloidal particles, and the process needs to be validated to avoid artefacts such as particle or surfactant loss to the membrane.

In some rare cases, there is a need to prepare samples at higher concentrations than the native material. This can be achieved by initially separating particles from the medium and then re-dispersing them into the same medium, but at a higher volume fraction. It may also be possible to gently centrifuge the particles to obtain a more concentrated fraction, after removal of the supernatant phase. This process needs to be optimized to mitigate particle loss or agglomeration effects.

Any medium utilized for dilution or for preparing samples is required to be initially free of particles (at least to the extent that residual particles can impact the zeta-potential measurement). For relatively "clean" media, one can use membrane filters (e.g. syringe filters) with a mean pore size smaller than the smallest particles to be analysed. The hydrophobicity or chemical resistivity of the membrane should also be considered. More complex media may prove more difficult to process. Centrifugation can also be used to achieve this objective.

6.4   Sample stability test

It is advisable to conduct a series of measurements, sequenced in time, to demonstrate that the sample is stable[8]. For example, the disassociation of ionic species from the particles in suspension may result in a change of pH or conductivity over time together with the mobility value. It is recommended that