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Colloidal systems — Methods for zeta-potential determination —

Part 1:
Electroacoustic and electrokinetic phenomena

Systèmes colloïdaux — Méthodes de détermination du potentiel zêta —
Partie 1: Phénomènes électroacoustiques et électrocinétiques

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13099 was prepared by Technical Committee ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

ISO 13099 consists of the following parts, under the general title *Colloidal systems — Methods for zeta-potential determination*:

— *Part 1: Electroacoustic and electrokinetic phenomena*

— *Part 2: Optical methods*

The following part is under preparation

— *Part 3: Acoustic methods*

Introduction

The basic theories and understanding of the electrokinetic and electroacoustic phenomena in a liquid suspension, an emulsion, or a porous body are presented within this part of ISO 13099 as an introduction to the subsequent parts, which are devoted to specific measurement techniques.

Many processes, from cleaning water, after either human or industrial fouling, to the creation of stable pharmaceutical suspensions, benefit from an understanding of the charged surfaces of particles. Also, causing the particles of a targeted mineral to have an affinity with respect to air bubbles, is a mechanism employed in the recovery of some minerals.

It should be noted that there are a number of situations where electrokinetic and electroacoustic measurements, without further interpretation, provide extremely useful and unequivocal information for technological purposes. The most important of these situations are:

a) identification of the isoelectric point (or point of zero zeta-potential) by electrokinetic titrations with a potential determining ion (e.g. pH titration);

b) identification of the isoelectric point by titrations with other reagents such as surfactants or polyelectrolytes;

c) identification of a saturation plateau in the adsorption indicating optimum dosage for a dispersing agent;

d) relative comparison of various systems with regard to their electric surface properties.

The determination of zeta-potential, which is not a directly measurable quantity, but one that is established by the use of an appropriate theory, can be interpreted to establish the region of stability for some suspensions. By determining the isoelectric point, conditions for the optimum coagulation of particles prior to either capture in a filter bed or settling out in a lagoon can be set to facilitate the clean-up of fouled water.

This document follows the IUPAC Technical Report on measurement and interpretation of electrokinetic phenomena (Reference [1]) and general References [2]–[5].

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Colloidal systems — Methods for zeta-potential determination —

Part 1:
Electroacoustic and electrokinetic phenomena

1 Scope

This part of ISO 13099 describes methods of zeta-potential determination, both electric and acoustic, in heterogeneous systems, such as dispersions, emulsions, porous bodies with liquid dispersion medium.

There is no restriction on the value of zeta-potential or the mass fraction of the dispersed phase; both diluted and concentrated systems are included. Particle size and pore size is assumed to be on the micrometre scale or smaller, without restriction on particle shape or pore geometry. The characterization of zeta-potential on flat surfaces is discussed separately.

The liquid of the dispersion medium can be either aqueous or non-aqueous with any liquid conductivity, electric permittivity or chemical composition. The material of particles can be electrically conducting or non-conducting. Double layers can be either isolated or overlapped with any thickness or other properties.

This part of ISO 13099 is restricted to linear effects on electric field strength phenomena. Surface charge is assumed to be homogeneously spread along the interfaces. Effects associated with the soft surface layers containing space distributed surface charge are beyond the scope.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1 Electric double layer

NOTE   The electric double layer (EDL) is a spatial distribution of electric charges that appears on and at the vicinity of the surface of an object when it is placed in contact with a liquid.

2.1.1
Debye–Hückel approximation
model assuming small electric potentials in the electric double layer

2.1.2
Debye length
κ^{-1}
characteristic length of the electric double layer in an electrolyte solution

NOTE   The Debye length is expressed in nanometres.

2.1.3
diffusion coefficient
D
mean squared displacement of a particle per unit time

2.1.4
Dukhin number
Du
dimensionless number which characterizes contribution of the surface conductivity in electrokinetic and electroacoustic phenomena, as well as in conductivity and dielectric permittivity of heterogeneous systems

2.1.5
dynamic viscosity

η

ratio between the applied shear stress and the rate of shear of a liquid

NOTE 1   For the purposes of this part of ISO 13099, dynamic viscosity is used as a measure of the resistance of a fluid which is being deformed by shear stress.

NOTE 2   Dynamic viscosity determines the dynamics of an incompressible newtonian fluid.

NOTE 3   Dynamic viscosity is expressed in pascal seconds.

2.1.6
electric surface charge density

σ

charges on an interface per area due to specific adsorption of ions from the liquid bulk, or due to dissociation of the surface groups

NOTE   Electric surface charge density is expressed in coulombs per square metre.

2.1.7
electric surface potential

ψ^s

difference in electric potential between the surface and the bulk liquid

NOTE   Electric surface potential is expressed in volts.

2.1.8
electrokinetic potential
zeta-potential
ζ-potential

ζ

difference in electric potential between that at the slipping plane and that of the bulk liquid

NOTE   Electrokinetic potential is expressed in volts.

2.1.9
Gouy–Chapman–Stern model
model describing the electric double layer

2.1.10
isoelectric point
condition of liquid medium, usually the value of pH, that corresponds to zero zeta-potential of dispersed particles

2.1.11
slipping plane
shear plane
abstract plane in the vicinity of the liquid/solid interface where liquid starts to slide relative to the surface under influence of a shear stress

2.1.12
Stern potential

ψ^d

electric potential on the external boundary of the layer of specifically adsorbed ions

NOTE   Stern potential is expressed in volts.

2.2   Electrokinetic phenomena

NOTE   Electrokinetic phenomena are associated with tangential liquid motion adjacent to a charged surface.

2.2.1
electroosmosis
motion of liquid through or past a charged surface, e.g. an immobilized set of particles, a porous plug, a capillary or a membrane, in response to an applied electric field, which is the result of the force exerted by the applied field on the countercharge ions in the liquid

2.2.2
electroosmotic counter-pressure
Δp_{eo}
pressure difference that is applied across the system to stop the electroosmotic flow

NOTE 1   The electroosmotic counter-pressure value is positive if the high pressure is on the higher electric potential side

NOTE 2   Electroosmotic counter-pressure is expressed in pascals.

2.2.3
electroosmotic velocity
$\boldsymbol{v}_{eo}$
uniform velocity of the liquid far from the charged interface

NOTE   Electroosmotic velocity is expressed in metres per second.

2.2.4
electrophoresis
movement of charged colloidal particles or polyelectrolytes, immersed in a liquid, under the influence of an external electric field

2.2.5
electrophoretic mobility
μ
electrophoretic velocity per electric field strength

NOTE 1   Electrophoretic mobility is positive if the particles move toward lower potential (negative electrode) and negative in the opposite case.

NOTE 2   Electrophoretic mobility is expressed in metres squared per volt second.

2.2.6
electrophoretic velocity
v_e
particle velocity during electrophoresis

NOTE   Electrophoretic velocity is expressed in metres per second.

2.2.7
sedimentation potential
U_{sed}
potential difference sensed by two electrodes placed some vertical distance apart in a suspension in which particles are sedimenting under the effect of gravity

NOTE 1   When the sedimentation is produced by a centrifugal field, the phenomenon is called centrifugation potential.

NOTE 2   Sedimentation potential is expressed in volts.

2.2.8
streaming current
I_{str}
current through a porous body resulting from the motion of fluid under an applied pressure gradient

NOTE   Streaming current is expressed in amperes.

2.2.9
streaming current density
J_{str}
streaming current per area

NOTE   Streaming current density is expressed in coulombs per square metre.

2.2.10
streaming potential
U_{str}
potential difference at zero electric current, caused by the flow of liquid under a pressure gradient through a capillary, plug, diaphragm or membrane

NOTE 1   Streaming potentials are created by charge accumulation caused by the flow of countercharges inside capillaries or pores.

NOTE 2   Streaming potential is expressed in volts.

2.2.11
surface conductivity
K^{σ}
excess electrical conduction tangential to a charged surface

NOTE   Surface conductivity is expressed in siemens.

2.3   Electroacoustic phenomena

NOTE   Electroacoustic phenomena arise from the coupling between the ultrasound field and electric field in a liquid that contains ions. Either of these fields can be primary driving force. Liquid might be a simple newtonian liquid or complex heterogeneous dispersion, emulsion or even a porous body. There are several different electroacoustic effects, depending on the nature of the liquid and type of the driving force.

2.3.1
colloid vibration current
CVI
I_{CVI}
a.c. current generated between two electrodes, placed in a dispersion, if the latter is subjected to an ultrasonic field

NOTE   Colloid vibration current is expressed in amperes.

2.3.2
colloid vibration potential
CVU
a.c. potential difference generated between two electrodes, placed in a dispersion, if the latter is subjected to an ultrasonic field

NOTE   Colloid vibration potential is expressed in volts.

2.3.3
electrokinetic sonic amplitude
ESA
A_{ESA}
amplitude is created by an a.c. electric field in a dispersion with electric field strength, E; it is the counterpart of the colloid vibration potential method

NOTE 1   See Reference [6].

NOTE 2   Electrokinetic sonic amplitude is expressed in pascals.

2.3.4
ion vibration current
IVI

a.c. electric current created from different displacement amplitudes in an ultrasound wave due to the difference in the effective mass or friction coefficient between anion and cation

NOTE 1   See References [7][8].

NOTE 2   Ion vibration current is expressed in amperes.

2.3.5
streaming vibration current
SVI

streaming current that arises in a porous body when ultrasound wave propagates through it

NOTE 1   See References [9][10].

NOTE 2   A similar effect can be observed at a non-porous surface, when sound is bounced off at an oblique angle, see Reference [11].

NOTE 3   Streaming vibration current is expressed in amperes.

3   Symbols

a particle radius

c electrolyte concentration in the bulk

C_{dl} double layer capacitance

c_i concentration of the ith ion species

D_+ diffusion coefficient of cations

D_{eff} effective diffusion coefficient of the electrolyte

Du Dukhin number

D_- diffusion coefficient of anions

e elementary electric charge

F Faraday constant

K^σ surface conductivity

k_B Boltzmann constant

K_m conductivity of the dispersion medium

K_p conductivity of the dispersed particle

K_s conductivity of the dispersion

m parameter characterizing electroosmotic flow contribution to surface conductivity

N_A Avogadro's number

p pressure

q_{eo} electroosmotic flow rate per current

R ideal gas constant

r radial distance from the particle centre

R_c radius of cell in electrokinetic cell model

T absolute temperature

U_{str} streaming potential

x distance from the particle surface

Z acoustic impedance

$z_\pm$ valencies of the cations and anions

z_i valency of the ith ion species

ε_0 vacuum permittivity

ε_m relative permittivity of the medium

ε_p relative permittivity of the particle

ζ electrokinetic potential, zeta-potential

η dynamic viscosity

κ reciprocal Debye length

μ electrophoretic mobility

μ_d dynamic electrophoretic mobility

ρ_m medium density

ρ_p particle density

ρ_s density of the dispersion

σ electric surface charge density

σ^d electric charge density of the diffuse layer

φ volume fraction

φ_{over} critical volume fraction

ψ^d Stern potential

$\psi(x)$ electric potential in the double layer

Ω drag coefficient

ω rotational frequency

ω_{hd} critical frequency of hydrodynamic relaxation

ω_{MW} Maxwell–Wagner relaxation frequency

4   Theory: general comments

Theory is an essential element in calculating zeta-potential from the measured data. However, there is no theory which is valid for all real systems. Instead, there is a multitude of different theories that are each valid for a certain subset of real dispersions and conditions. It is convenient to organize the theories into two groups: elementary theories and advanced theories.