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Colloidal systems — Methods for zeta potential determination —

Part 3:
Acoustic methods

Systèmes colloïdaux — Méthodes de détermination du potentiel zêta —

Partie 3: Méthodes acoustiques

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Foreword

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The committee responsible for this document is 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*

— *Part 3: Acoustic methods*

Introduction

Zeta potential is a parameter that can be used to predict the long term stability of suspensions and emulsions, and to study surface morphology and surface adsorption of particles and other surfaces in contact with a liquid. Zeta potential is not a directly measurable parameter. It can be determined using appropriate theoretical models from experimentally determined parameters, which depend on electric charge separation at interfaces. "Electrokinetic phenomena" encompass such experimentally observed effects. A group of electrokinetic phenomena at high frequency on MHz scale is referred to as "electroacoustics".[1] Each classical electrokinetic phenomenon at DC or low AC conditions has electroacoustic analogue. These electroacoustic phenomena have been widely used to determine electrophoretic mobility of various concentrated particulates without sample dilution. The purpose of this part of ISO 13099 in methods for Zeta potential determination is description of general features of such electroacoustic methods that should be common for all instrumental implementation for measuring electrophoretic mobility using electroacoustics and following calculation of zeta potential of particulates.

Colloidal systems — Methods for zeta potential determination —

Part 3:
Acoustic methods

1   Scope

This part of ISO 13099 describes in general electroacoustic effects that can be defined as high frequency electrokinetic phenomena.

Particular attention is given to two methods of measurement of electrophoretic mobility of particles suspended in a liquid at high concentration above 1 % v/v, colloid vibration current (CVI)[2] and electric sonic amplitude (ESA),[3] [4] respectively.

Estimation of surface charge and determination of zeta potential can be achieved from measured electrophoretic mobility using proper theoretical models, which are described in detail in ISO 13099-1.

2   Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 13099-1, *Colloidal systems — Methods for zeta-potential determination — Part 1: Electroacoustic and electrokinetic phenomena*

ISO 13099-2, *Colloidal systems — Methods for zeta-potential determination — Part 2: Optical methods*

3   Terms, definitions and symbols

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

3.1   Electric double layer (EDL)

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.

3.1.1
Debye-Hückel approximation
model assuming small electric potentials in the electric double layer

3.1.2
Debye length
κ^{-1}
characteristic length of the electric double layer in an electrolyte solution

Note 1 to entry: The Debye length is expressed in nanometres.

3.1.3
diffusion coefficient
D
mean squared displacement of a particle per unit time

Note 1 to entry: The diffusion coefficient is expressed in metre squared per second.

3.1.4
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

3.1.5
dynamic viscosity
η
ratio of the applied shear stress and the rate of shear of a liquid

Note 1 to entry: For the purpose of this part of ISO 13099, dynamic viscosity is used as a measure of resistance of a fluid which is being deformed by shear stress.

Note 2 to entry: Dynamic viscosity determines the dynamics of an incompressible Newtonian fluid.

Note 3 to entry: Dynamic viscosity is expressed in pascal seconds.

3.1.6
electric surface charge density
σ
charges on interface per area due to specific adsorption of ions from the liquid bulk, or due to dissociation of the surface groups

Note 1 to entry: Electric surface charge density is expressed in coulombs per square metre.

3.1.7
electric surface potential
ψ^s
difference in electric potential between the surface and the bulk liquid

Note 1 to entry: Electric surface potential is expressed in volts.

3.1.8
ζ - potential
electrokinetic potential
zeta potential
ζ
difference in electric potential between that at the slipping plane and that of the bulk liquid

Note 1 to entry: Electrokinetic potential is expressed in volts.

3.1.9
Gouy-Chapman-Stern model
model describing the electric double layer

3.1.10
isoelectric point
condition of liquid medium, usually the value of pH, that corresponds to zero zeta-potential of dispersed particles

3.1.11
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

3.1.12
Stern potential
Ψd
electric potential on the external boundary of the layer of specifically adsorbed ions

Note 1 to entry: Stern potential is expressed in volts.

3.2   Electrokinetic phenomena

Note 1 to entry   Electrokinetic phenomena are associated with tangential liquid motion adjacent to a charged surface.

3.2.1
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

3.2.2
electroosmotic counter-pressure
Δp_{eo}
pressure difference that is applied across the system to stop the electroosmotic flow

Note 1 to entry: The electroosmotic counter-pressure value is positive if the high pressure is on the higher electric potential side.

Note 2 to entry: Electroosmotic counter-pressure is expressed in pascals.

3.2.3
electroosmotic velocity
v_{eo}
uniform velocity of the liquid far from the charged interface

Note 1 to entry: Electroosmotic velocity is expressed in metres per second.

3.2.4
electrophoresis
movement of charged colloidal particles or polyelectrolytes, immersed in a liquid, under the influence of an external electric field

3.2.5
electrophoretic mobility
μ
electrophoretic velocity per unit electric field strength

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

Note 2 to entry: Electrophoretic mobility is expressed in metres squared per volt second.

3.2.6
electrophoretic velocity
v_e
particle velocity during electrophoresis

Note 1 to entry: Electrophoretic velocity is expressed in metres per second.

3.2.7
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 to entry: When the sedimentation is produced by a centrifugal field, the phenomenon is called centrifugation potential.

Note 2 to entry: Sedimentation potential is expressed in volts.

3.2.8
streaming current

I_{str}

current through a porous body resulting from the motion of fluid under an applied pressure gradient

Note 1 to entry: Streaming current is expressed in amperes.

3.2.9
streaming current density

J_{str}

streaming current per area

Note 1 to entry: Streaming current density is expressed in coulombs per square metre.

3.2.10
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 to entry: Streaming potentials are created by charge accumulation caused by the flow of countercharges inside capillaries or pores.

Note 2 to entry: Streaming potential is expressed in volts.

3.2.11
surface conductivity

K^{σ}

excess electrical conduction tangential to a charged surface

Note 1 to entry: Surface conductivity is expressed in siemens.

3.3   Electroacoustic phenomena

Electroacoustic phenomena arise due to the coupling between the ultrasound field and electric field in a liquid that contains ions. Either of these fields can be primary driving forces. 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.

3.3.1
colloid vibration current

CVI

a.c. current generated between two electrodes, placed in a dispersion, if the latter is subjected to an ultrasonic field

Note 1 to entry: Colloid vibration current is expressed in amperes.

3.3.2
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 1 to entry: Colloid vibration potential is expressed in volts.

3.3.3
electrokinetic sonic amplitude
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 to entry: See References [3] and [4].

Note 2 to entry: Electrokinetic sonic amplitude is expressed in pascals.

3.3.4
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 to entry: See Reference [5].

Note 2 to entry: Ion vibration current is expressed in amperes.

3.3.5
seismoelectric effect
SEI

non-isochoric streaming current that arises in a porous body when an ultrasound wave propagates through

Note 1 to entry: See References [6] and [7].

Note 2 to entry: A similar effect can be observed at a non-porous surface, when sound is bounced off at an oblique angle.[11]

Note 3 to entry: Seismoelectric effect is expressed in amperes.

3.3.6
electroseismic effect
ESI

non-isochoric electroosmotic pressure wave that arises in a porous body under influence of high frequency electric field

Note 1 to entry: See References [6] and [7].

Note 2 to entry: Electroseismic effect is expressed in pascals.

3.3.7
dynamic electrophoretic mobility
μ_d

electrophoretic velocity per unit electric field strength in high frequency (MHz) electric field

Note 1 to entry: Traditional electrophoretic mobility is low frequency asymptotic of the dynamic electrophoretic mobility.

Note 2 to entry: Electrophoretic mobility is expressed in metres squared per volt second.

4 Symbols

a	particle radius
c	electrolyte concentration in the bulk
D_+	diffusion coefficient of cations
D_-	diffusion coefficient of anions
D_{eff}	effective diffusion coefficient of the electrolyte
Du	Dukhin number
e	elementary electric charge
F	Faraday constant
K_m	conductivity of the dispersion medium
K_p	conductivity of the dispersed particle
K_s	conductivity of the dispersion
K^σ	surface conductivity
k_B	Boltzmann constant
m	parameter characterizing electroosmotic flow contribution to surface conductivity
N_A	Avogadro's number
P	pressure
R	ideal gas constant
r	radial distance from the particle centre
T	absolute temperature
U_{st}	streaming potential
μ	electrophoretic mobility
μ_d	dynamic electrophoretic mobility
X	distance from the particle surface
Z	acoustic impedance
z_i	valence of the ith ion species
$z_\pm$	valences of the cations and anions
ε_m	relative permittivity of the medium
ε_p	relative permittivity of the particle
ε_0	vacuum permittivity
η	dynamic viscosity

φ	volume fraction
κ	reciprocal Debye length
ρ_m	medium density
ρ_p	particle density
ρ_s	density of the dispersion
σ^d	electric charge density of the diffuse layer
σ	electric surface charge density
ω	rotational frequency
ω_MW	Maxwell-Wagner relaxation frequency
ω_hd	critical frequency of hydrodynamic relaxation
ζ	electrokinetic potential, zeta potential
$\Psi(x)$	electric potential in the double layer
Ψ_d	Stern potential
Ω	drag coefficient

5   Principle

Any instrument designed for characterizing ζ-potential should contain three essential components for achieving three distinctive purposes.

— means for generating motion of the liquid phase relative to the dispersed phase (either solid or liquid);

— means for monitoring response induced by such motion;

— means for calculating ζ-potential from the measured response.

The first purpose is usually achieved by manipulating one of the two fields that are responsible for electrokinetic phenomena (electrical and mechanical). For instance, in optical electrophoretic methods (see ISO 13099-2) an electric field generates mechanical motion of particles relative to the liquid. This field is usually constant in time or oscillates with low frequency up to KHz range.

Similarly, one can go to a higher frequency electric field (MHz range) for generating relative motion of phases. There is a special term for such high frequency electrophoresis (electric sonic amplitude reflecting the fact that the wave nature of the mechanical motion at such high frequency becomes dominant). This mechanic effect is an ultrasound wave. There is also a reversible effect: propagation of an ultrasound wave though the concentrated particulate system generates an oscillating electric field and related current (colloid vibration current). These effects are symmetrical according to the Onsager principle.[8] Both of them can be used for generating a relative motion of phases. The field used for such purposes is called "driving force".

The second purpose of monitoring relative phase motion is often achieved by optical means as described in ISO 3099-2.

It turns out that at a high frequency range, there is no need to use an additional "monitoring" field. Instead, the field complimentary to the driving force can be measured. If the electric field is the driving force,

then the ultrasound response can be measured using the ESA method. Alternatively, if an ultrasound wave is the driving force then electric current can be measured using the CVI mode.

Both these methods yield raw experimental data for calculating electrophoretic mobility from the magnitude of the response field and sign of the surface charge from its phase. This electrophoretic mobility becomes frequency-dependent due to a number of factors. There are well verified theories for extracting ζ-potential from such "dynamic electrophoretic mobility" described in ISO 13099-1. The simplest one is practically identical to the well-known Smoluchowski theory that usually serves as the basis for optical methods.[9]

There are no known advantages of one electroacoustic method over the other.

Electroacoustic phenomena exist not only in particulates systems but in porous materials saturated with liquid as well. There are two known electroacoustic effects in porous media introduced by Frenkel.[6] [7] Seismoelectric effect is a high frequency analogy of the streaming current/potential. Electroseismic effect is a high frequency analogy of electroosmosis. Annex A presents the relationship between classical electrokinetic effects and high frequency electroacoustics.

Electroacoustics effects in porous materials can be measured with modern devices,[10] [11] [12] but it is still at the stage of research. This part of ISO 3099 is dedicated to the electroacoustic methods in particulates only.

All electroacoustic instruments that have been designed to date are built as a probe. Such probe design includes elements for generating (measuring) ultrasound and elements for generating (measuring) electric field (current). There are common features for all existing instruments, presented in the next section.

6 Zeta potential probe design elements

An electroacoustic instrument contains an electronic block that generates electric pulses of certain frequency. A pulse technique is an essential feature of all electroacoustic instruments. The frequency range of these pulses is from 1 MHz to 20 MHz.

The same block is used for analysing either electric (CVI mode) or ultrasound (ESA mode) pulses generated by a sample in response to the initial driving pulse.

The electronic block is supplied with a probe that contains elements required for transmitting pulses to the sample and receiving generated response. Such a sensing probe contains piezo-electric devices which are able to convert electric energy into ultrasound and vice versa. All piezo-electric devices shall contain a delay rod that separates pulses in time. There shall be also an additional insert that provides for matching of acoustic impedances between the probe and a sample.

There is also a system of two electrodes used either for launching electric pulse in the sample or measuring electric response.

An initial electric pulse can be applied directly to the dispersed system for generating relative phase motion by the electrode system. This motion generates ultrasound that is measured with the piezo-electric device. This approach is used in the ESA mode.

The CVI approach uses a piezo-electric device first, converting the initial electric pulses into ultrasound that then are launched into the dispersed system. This ultrasound generates a relative phase motion and electric current that is then measured with the electrode system.

7 Determination of the dynamic electrophoretic mobility

Electroacoustic devices measure the magnitude and phase of the electroacoustic signal, which might be either ESA or CVI depending on the nature of the driving force. This is the raw experimental data that might vary for different instruments. It shall be converted to some other parameters that would be universal for all instruments and methods. Such a parameter was suggested by O'Brien[4] and is

currently in use in all electroacoustic devices ("dynamic electrophoretic mobility"). This parameter (μ_d) is the generalization of the electrophoretic mobility concept for high frequency oscillating particle motion.

According to the O'Brien relationship, the average dynamic electrophoretic mobility, μ_d, is defined as:

$$\mu_d = \left(A_{ESA} \text{ or } A_{CVI}\right)\left[\frac{\rho_m}{\phi\left(\rho_p - \rho_m\right)}\right]\left[\frac{1}{A(\omega)F(Z)}\right]$$ (1)

where

A_{ESA} and A_{CVI}	are the magnitudes of ESA and CVI electroacoustic signals normalized with corresponding driving forces;
$A(\omega)$	is an instrument constant found by calibration;
$F(Z)$	is a function of the acoustic impedances of the transducer and the dispersion under investigation describing reflection of ultrasound on the surface of the electroacoustic probe.

The densities of the medium and particles, ρ_m and ρ_p, are required, as well as the volume fraction of particles φ.

According to O'Brien, a complete functional dependence of electroacoustics on key parameters, such as zeta potential, particle size and frequency, is incorporated into the dynamic electrophoretic mobility. For all considered cases, the coefficient of proportionality between electroacoustic signal and dynamic electrophoretic mobility is frequency independent and independent of particle size and zeta potential. This feature makes the dynamic electrophoretic mobility an important and central parameter of the electroacoustic theory. It can be used for comparing results produced by different instruments.

7.1 Subtracting background electroacoustic signal generated by ions

Electroacoustic probes measure the total electroacoustic signal, which is the sum of the signal produced by particles and signal produced by ions. Historically, the electroacoustic signal from ions was the first electroacoustic effect predicted theoretically by Debye in 1933.[5]

The electroacoustic signal from ions is normally much smaller than the signal produced by particles and can be neglected. Its role increases with increasing ionic strength due to a larger number of ions. Increasing ionic strength causes a decay in ζ-potential, which also enhances the relative contribution of ionic background.

Another factor that controls relative contribution of ions and particles in the measured electroacoustic signal is the volume fraction of particles. The contribution from ions becomes more important in dilute systems due to the smaller particles contribution.

The next factor is particle size. Increasing particle size leads to a reduction of the particles contribution which, in turn, amplifies the role of the ionic background.

The last factor is density contrast that also affects particles contribution.

It is impossible to provide exact thresholds for individual parameters because the total effect depends on multiplicative contributions of individual factors. It is possible to provide approximate values for individual parameters causing sufficient reduction of the particles contribution for making ionic background important. These empirical thresholds are: ionic strength exceeding 0,1 M, volume fraction below 1 %, particle size above 10 microns, and density contrast below 0,1.

The electroacoustic signal generated by equilibrium supernate should be measured if one of the mentioned above parameters is below the specified threshold. It is quite possible that large values of

some parameters would compensate for low value of others and the particles contribution would still be much larger than the ionic background.

If the ionic background signal becomes comparable with total measured electroacoustic signal for a particular sample, then it shall be subtracted. This subtraction is not trivial due to the fact that both electroacoustic signals (total and ionic background) are vectors, which is the usual presentation of AC electric effects.

8 Calculation of zeta potential

8.1 General

Dynamic electrophoretic mobility, same as classical electrophoretic mobility, depends first of all on the degree of the individual particles or pores double layers interaction. This interaction is usually negligible in aqueous solutions due to a very small Debye length, κ^{-1}, as compared to the particle size dimension a. That is why double layers in aqueous solutions are usually assumed to be isolated and not interacting, even at rather high volume fraction of particles φ. ISO 13099-1 contains the following formula for critical volume fraction, φ_{over}, that limits the range of isolated double layers model.

$$\phi_{over} \approx \frac{0,52}{\left[1+(1/\kappa a)\right]^3} \tag{2}$$

Parameter, κa, is usually quite large in aqueous solutions. As a result, critical volume fraction that limits applicability of the isolated double layers model is also high and this limitation is not very important.

Nevertheless, this factor might become more important for nano-dispersions due to the small particle size that leads to κa decay. In fact, this is valid for classical electrokinetics as well.

Overlap of the particle double layer becomes much more important in non-aqueous systems, especially in non-polar ones where Debye length becomes much large due to the low ionic strength.

There are dynamic electrophoretic mobility theories for both isolated and overlapped double layers.

Overlap of double layers is just one of the mechanisms that affect particle dynamic electrophoretic mobility due to their interaction. Particles generate hydrodynamic and electric fields when they participate in electroacoustic phenomena, as well as in the classical electrokinetic one. These fields could affect motion of neighbouring particles. Electroacoustic theory shall take into account this interaction. Otherwise, it would be valid only for dilute systems, where such interactions are negligible.

8.2 Isolated double layers

Where there are isolated double layers, dynamic electrophoretic mobility is proportional to the ζ-potential, similarly to the classical electrophoretic mobility. There are several theories allowing calculation of the ζ-potential from the dynamic electrophoretic mobility. They are valid for different ranges of several parameters, such as κa, surface conductivity, volume fraction, particle conductivity. Some of them take into account particles interaction (others do not), which would limit the volume fraction range of applicability.

8.2.1 O'Brien theory for dilute systems

The electroacoustic theory for dilute systems with negligible particle-particle interaction is valid for spherical particles only but with no restriction on the particle size. It is called the "O'Brien theory for

dynamic electrophoretic mobility"[4]. It yields the following expression for the dynamic electrophoretic mobility:

$$\mu_d = \frac{2\varepsilon_0 \varepsilon \zeta}{3\eta} G(s) \left[1 + F(\omega') \right] \tag{3}$$

where

$$G(s) = \frac{1 + (1+j)s}{1 + (1+j)s + j \dfrac{2s^2}{9} \left(3 + 2 \dfrac{\rho_p - \rho_m}{\rho_m} \right)} \tag{4}$$

$$F(\omega') = \frac{1 + j\omega' \left(1 - \dfrac{\varepsilon_p}{\eta} \right)}{2 + j\omega' \left(2 + \dfrac{\varepsilon_p}{\varepsilon} \right)} \tag{5}$$

$$s^2 = \frac{a^2 \omega \rho_m}{2\eta} \; ; \; \omega' = \frac{\omega}{\omega_{MW}}$$

s^2 and ω' are two factors that determine the frequency dependence of dynamic electrophoretic mobility and j is the square root of –1. The factor $G(s)$, reflects the frequency dependence related with the inertia effects, whereas the factor $F(\omega')$, represents the influence of the Maxwell-Wagner polarization of the EDL.[13] [14]

For aqueous colloids, the inertia factor, $G(s)$, plays a more important role than the EDL polarization factor, $F(\omega')$. The inertia factor dramatically reduces the magnitude of the dynamic mobility of larger particles at high frequencies. In addition to reducing the amplitude, the inertia factor also causes a lag in the particle motion relative to the external driving force, and this interposes a phase shift on the dynamic electrophoretic mobility. This phase shift reaches a maximum value of 45° at the high frequency limit.

Neither of these two factors is important at low frequency when the $G(s)$ and $F(\omega')$ factors approach to 1 and 0,5 respectively. This means that at sufficiently low frequency, dynamic electrophoretic mobility would depend only on those factors that are taken into account by Smoluchowski theory for electrophoresis. It is known that Smoluchowski theory for electrophoresis is valid for any volume fraction, any shape of the particles. That is why Smoluchowski theory is so popular.

8.2.2 Smoluchowski theory for CVI in concentrates, including particles interaction

It is important to have Smoluchowski theory for electroacoustics as well. Such theory was developed for CVI mode.[2] This theory effectively takes into account particles hydrodynamic and electrodynamic interaction. It yields the following expression for the dynamic electrophoretic mobility measured in CVI mode:

$$\mu_d = \left(\frac{\varepsilon \varepsilon_0 \zeta}{\eta} \right) \left[\frac{K_s}{K_m} \frac{(\rho_p - \rho_s)\rho_m}{(\rho_p - \rho_m)\rho_s} \right] \tag{6}$$

This theory was verified with the equilibrium dilution experiment, see Annex B.

It is more limited than Smoluchowski theory for electrophoresis. There are two critical frequencies that determine the valid range of this theory. The critical frequency of hydrodynamic relaxation (ω_{hd})

determines the range of the particle inertia and that of the factor $G(s)$ influence. This factor becomes negligible when frequency ω satisfies the following condition:

$$\omega << \omega_{hd} = \frac{\eta}{\rho_m a^2} \tag{7}$$

This condition is valid for particles with sizes under 300 nm assuming that the frequency is 1 MHz. This critical size increases with decreasing density contrast and becomes much higher for emulsions and soft particles.

The critical frequency of EDL electric polarization ω_{MW} presents a frequency range where the second factor, function $F(\omega')$, becomes negligible:

$$\omega << \omega_{MW} = \frac{K_m}{\varepsilon_0 \varepsilon} \tag{8}$$

Both theories presented above have been derived assuming a thin double layer:

$$\kappa a >> 1 , \tag{9}$$

and a negligible contribution of the surface conductivity, expressed in terms of small Dukhin number:[1] [2] [3] [4] [5] [6] [7] [8]

$$Du << 1 \tag{10}$$

The theory given in 8.2.3 eliminates restriction specified with Formula (10).

8.2.3 CVI theory in polydisperse concentrates with surface conductivity and particles interaction

There is also version of CVI theory that takes into account particles interaction and eliminates restriction on the Dukhin number, see Reference [15].

$$\mu_d = \frac{2\varepsilon_m \varepsilon_0 \zeta (\rho_s - \rho_m)\rho_s}{3\eta(\rho_p - \rho_m)\rho_m} \frac{\sum\limits_{i=1}^{N} \frac{9\rho_s \phi_i h(s_i)}{4j\phi(1-\phi)s_i I(s_i)\left\{\rho_p - \rho_m\left[\frac{3H_i}{2I(s_i)}+1\right]\right\}} \frac{3}{2+\phi+2Du_i(1-\phi)}}{1-\frac{\rho_p}{1-\phi}\sum\limits_{i=1}^{N}\frac{\left[\frac{3H_i}{2I(s_i)}+1\right]\phi_i}{\rho_p - \rho_m\left[\frac{3H_i}{2I(s_i)}+1\right]}} \tag{11}$$

where

Index i corresponds to fraction with size a in polydisperse system with N fractions.

$Du_i = \kappa^\sigma / K_m \, a_i$ is the Dukhin number for the ith fraction of the polydisperse colloid.

$s_i = \alpha_i \sqrt{\omega \rho_m / 2\eta}$, and special functions h, H, and I are given in Section 2.5.2 of Reference [2].

It is assumed that all fractions have the same ζ-potential .

This theory was verified with the equilibrium dilution experiment, see Annex B.

8.2.4 ESA theories for concentrates with particles interaction

There are several papers of the same type and about the same range of parameters[17] [18] [19] dedicated to the ESA effect in concentrated dispersions.

8.3 Overlapped double layers

Both theories mentioned above assume isolated non-overlapped DLs. This condition might not be valid in concentrated systems, especially with nano-size range and/or low ionic strength. There is a theory developed for overlapped DLs.[16] It exists so far only for the CVI mode:

$$\mu_d = \frac{2\sigma a}{3\eta\Omega} \frac{\rho_m}{\rho_s + i\omega(1-\phi)\dfrac{\phi}{\gamma}\rho_p\rho_m} \tag{12}$$

where

$$\gamma = \frac{9\eta\phi\Omega}{2a^2} \tag{13}$$

Ω is a drag coefficient introduced according to the Stokes law, $F = 6\pi\eta a\Omega v$, and reflecting hydrodynamic particles interaction.

It is important to stress that this approximation of the electroacoustic method makes possible direct measurement of the electrokinetic charge in nano-colloids and non-polar dispersions without the need to know the Debye length.

9 Operational procedures

9.1 Requirements

9.1.1 Instrument location

The instrument should be located in a clean environment that is free from excessive electrical noise.

Mechanical vibrations are not important.

Temperature fluctuations are important. It is desirable to prevent temperature variations over 1 °C during measurement period for maintaining specified precision level.

9.1.2 Sample handling

Samples can be stirred, mixed, or pumped for eliminating the possible sedimentation influence and ensure stability of results. Otherwise, there is not general requirement for sample being agitated.

Bubbles do not affect results unless they are attached to electrodes.

The electrophoretic mobility measured in a sample is only valid for a batch of material if the test sample is representative for that batch.

9.1.3 Preparation

Sample can be measured without dilution.

Samples exhibiting sedimentation and deposit formation shall be homogenized before the measurement.

9.1.4 Sample volume fraction requirement

Sample volume fraction should be above 1 % v/v. Contribution of particles exceeds contribution of ions and precision of the measurement.

9.2 Verification

9.2.1 Reference materials

Electroacoustic instruments perform better for systems with higher density contrast. That is why traditional latex standards are not appropriate for verifying and calibrating electroacoustic instruments. Reference materials are used in two different stages of the measurement process:

Calibration: Reference materials used for calibration should meet the requirements specified for certified reference materials, namely being homogeneous and stable and having value assigned according to a metrologically valid procedure. These materials shall be used to either calibrate the instrument or to verify trueness of the measured results.

Daily quality control: Reference materials shall be used with every measurement series to ensure correct performance of the instrument system. This control is most suitably done using quality control charts. Reference materials for this purpose need to be homogeneous and stable, but do not have to have a metrologically valid assigned value.

Different reference materials shall be used for calibration and for daily quality control.

NOTE   At the time of the publication of this standard, no certified reference materials for zeta potential existed. Non-certified reference materials with assigned values are available from several suppliers. Another currently frequently used option is using Ludox®[1) This is a 50 % silica suspension and is usually diluted with a 0,01 KCl solution to a mass fraction of 10 %. There is reported value of ζ-potential for these particles calculated using Smoluchwski approximation as −38 mV, which corresponds to electrophoretic mobility −4 (µm/s) (cm/V). [2] This value of the electrophoretic mobility measured with CVI methods agrees within 10 % with independent measurement of the same material conducted using ESA method (paper).[24] These materials are well suited for the daily quality control, but are insufficient for calibration and/or instrument verification. However, in the absence of certified reference materials, these have to be used. Priority should be given to materials with clearly stated values by the producers.

9.2.2 Repeatability

To achieve the desired repeatability of electrophoretic mobility measurement, the following steps need to be followed:

a)   Set up the instrument adequately, select the proper settings for operating conditions and allow all parts sufficient warm-up time.

b)   Follow the measurement protocol given for the material.

c)   Perform at least six consecutive measurements with the same aliquot.

An instrument is considered as meeting the requirement of this standard if the CV for the mean electrophoretic mobility value of six measurements for a reference material is less than 3 % if the absolute value of the reference material mobility is higher than 1 μm·cm/V·s.

9.2.3 Intermediate precision

The test of intermediate precision shall follow the procedure set out in 9.2.2 except that six different sample aliquots at an appropriate concentration shall be used.

NOTE   Care must be taken that the material used is stable after opening.

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1)   Ludox® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

An instrument is considered as meeting the requirement of this standard if the CV for the mean electrophoretic mobility value of six measurements for a reference material is less than 4 % if the absolute value of the reference material mobility is higher than 1 μm·cm/V·s.

9.2.4 Trueness

The accuracy of operation of instruments shall be determined using certified reference materials meeting the definition of ISO Guide 30 and having been produced in compliance with ISO Guide 34. In the absence of certified reference materials, non-certified reference materials meeting the definitions of ISO Guide 30, of hard spheres from a reliable source, homogenous and stable having a defined electrophoretic mobility determined by optical means at specified conditions can be used, bearing in mind that the use of non-certified reference materials precludes absolute demonstration of accuracy. The test of accuracy shall follow the procedure set out in 9.2.3.

An instrument is considered to meet this standard if the mean electrophoretic mobility value for the six measurements is in agreement with the assigned value of the reference material. For checking the agreement both the uncertainty of the reference material and an uncertainty of the six results shall be taken into consideration.

9.3 Sources of measurement error

The main source of the errors in the reported values of ζ-potential are errors in input parameters, such as volume fraction of solids, densities, viscosity of liquid, dielectric permittivity of the liquid.

Usually, high values of ζ–potential exceeding 100 mV occur due to

— lower input volume fraction values than in reality,

— lower input density contrast, than in reality,

— lower input dielectric permittivity, than in reality, or

— higher viscosity, than in reality.

Wrong particle size calculated from the electroacoustic phase can be also a source of the error in the ζ-potential. The phase of the electroacoustic signal depends on several parameters, not only particle size. For instance, particles and particle aggregates porosity affect the phase. Particles shape is another factor. If these and contributions from others factors are attributed to the influence of the particles size, then it would be wrong and calculated ζ-potential would be wrong as well.

Sedimentation of particles on the surface of the electroacoustic probe leads to increasing volume fraction in the vicinity of sensing elements. This effect would be reported as increasing ζ-potential, instead of increasing volume fraction, unless recognized by the user.

Annex A
(informative)

Electroacoustics: high frequency electrokinetics

Electroacoustics is a family of electrokinetic effects that occur at high frequency oscillating either electric or acoustic fields. Both, electroacoustics and electrokinetic phenomena arise due to the spatial distribution of electric charges at the vicinity of the object interface when it is placed in contact with a liquid. Both electroacoustics and electrokinetics are result of the electric and mechanical fields coupling.

Every traditional electrokinetic effect has its electroacoustic analogue as shown in Table A.1.

Table A.1 — Electroacoustic analogues of electrokinetic phenomena

Electrokinetics	Electroacoustics
Electrophoresis: Motion of particles in electric field DC, AC KHz	**Electric sonic amplitude:** Ultrasound generated by particles motion in the electric field, AC MHZ
Sedimentation potential, Dorn effect: Electric field generated by particle sedimentation, DC conditions	**Colloid vibration current:** Electric field generated by particle motion in ultrasound wave, AC conditions
Electroosmosis: Liquid motion through a porous material induced by electric field, DC, AC KHz	**Electroseismic effect:** Liquid motion through a porous material induced by electric field, AC MHz
Streaming current/potential: Electric field/current generated by gradient of pressure applied to the porous material, DC, AC KHz	**Seismoelectric effect:** Electric field/current generated by gradient of pressure applied to the porous material, AC MHz

There are number of differences between electroacoustic and traditional electrokinetic phenomena that justify introduction of electroacoustics as a separate group of experimental phenomena.

First of all, a wavelength of mechanical (sound) field becomes comparable with system-sample dimensions at MHz range. It is 1,5 mm at 1 MHz in water. That is why mechanical force needs to be described in wave terminology at MHz range, in contrast to traditional electrokinetic phenomena. At the same time, wavelength is still much longer than particle size. This "long wavelength limit" leads to tremendous theory simplifications, which allow introduction of Smoluchowski theory analogues for all electroacoustic effects.

Secondly, a liquid behaves as compressible on macroscopic scale, which opens up completely new avenues for instrument design.

Annex B
(informative)

Verification of electroacoustic theories

There are two approaches to the experimental verification of particular electroacoustic theory. The first one is a comparison with independent results obtained with classical electrokinetic methods, such as electrophoresis. The second is a test of the volume fraction dependence. In both cases one shall be very careful how dilution of initial concentrated dispersion would be performed. ISO 13099-1 contains a section on "equilibrium dilution" as the only method of maintaining the same interfacial properties at various volume fractions.

There are numerous papers published on this subject (a detailed bibliography is given in Dukhin, AS and Goetz, PJ[2]). A few of these are mentioned here.

The most vigorous test of O'Brien's theory for dilute systems has been carried out by O'Brien's own group, using monodisperse cobalt phosphate and titanium dioxide dispersions.[23] They observed very good correlation with microelectrophoresis data for different chemical compositions of the suspensions. They also observed a linear dependence of CVP for monodisperse latex of particle size 88 nm. Electroacoustic measurements were conducted in ESA mode.

There are several very detailed studies conducted in CVI mode by independent scientists, on manufacturers of the instruments.

The first one was performed by Van Tassel and Randall,[20] who studied the ζ-potential of both concentrated and dilute dispersions of alumina in ethanol. For the concentrated slurries, they used the CVI measurements. For the dilute samples, they used the microelectrophoretic measurements. They observed almost perfect correlation between the CVI-based data and microelectrophoretic measurements.

The second one was performed by group of Japanese scientists[21] with several latex dispersions. They report very close agreement in ζ-potential values measured with CVI device in concentrates and electrophoresis in dilute state.

Third study was conducted by the US, German and Japanese national standardization bodies on subject of iso-electric point determination with electroacoustic devices.[22] Both, ESA and CVI electroacoustic devices were used. Results of electroacoustics were compared with independent data generated with streaming current method. Very good agreement was reported.

With regard to the volume fraction dependence test, the equilibrium dilution described in ISO 13099-1 is again the logical experimental protocol. Equilibrium dilution maintains the same chemical composition of the dispersion medium for all volume fractions, which means that the ζ-potential calculated from the CVI should remain constant for all volume fractions. Any variation of the ζ-potential with volume fraction is an indicator that a particular theory does not correctly reflect the particle-particle interactions that occur at high volume fraction.

Tests that confirm the theories presented in 8.2.2 and 8.2.3 are presented here.

Colloidal silica [Ludox®1) TM-50] is ideal for verification of Smoluchowski theory.[6] The small particle size allows us to eliminate the particle size dependence caused by inertia. Using small particles gives another simplifying advantage; it eliminates any contribution to the overall attenuation because small particles do not attenuate sound at low frequency. Thus the choice of small particles allows us to test only .the volume fraction dependence.

Gravimetric separation does not work well for the very small silica Ludox®1) particles; for this, dialysis was employed. Original dispersion of Ludox®1) at 50 % w/w was placed inside of the tube formed by

membrane with pore sizes that are much less than 30 nm – size of silica Ludox®[1] particles. The outside solution was 0,1 KCl in water. Ions can penetrate through the membrane and establish equilibrium between the inside and outside solutions. Then the outside solution was used for diluting the inside solution in steps from an initial 35 % v/v down to 1 % v/v. The electroacoustic device measured the CVI signal for every volume fraction, and then the zeta potential was calculated using Smoluchowski type theory for CVI. The results are shown in Figure B.1.

Key
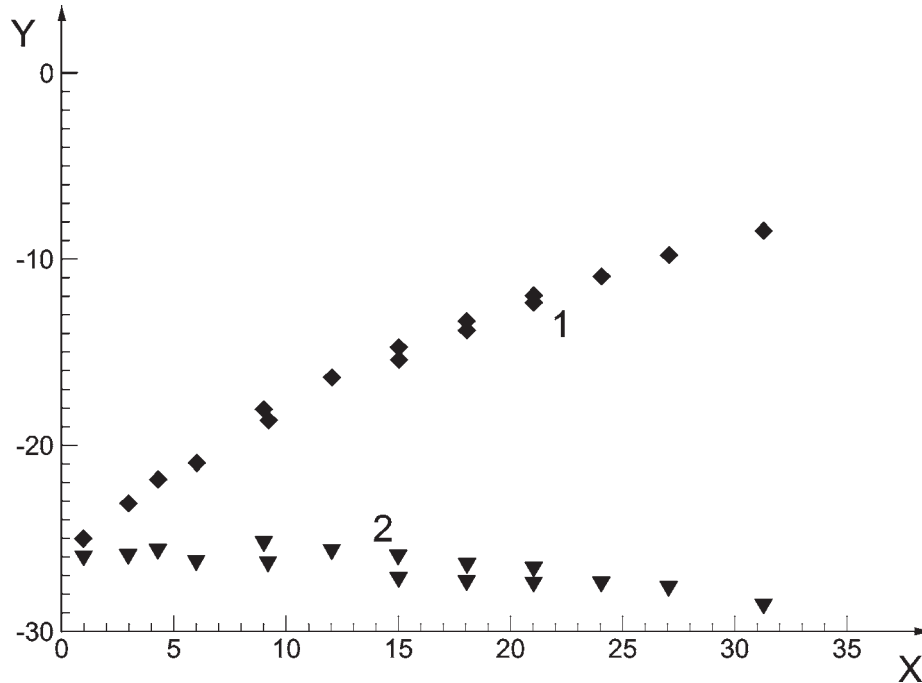
1   dilute system theory
2   new CVI theory
X   volume fraction in %
Y   zeta potential [mV]

**Figure B.1 — Comparison of the zeta potential of colloidal silica calculated using
the dilute case theory and the new CVI theory**

It is seen that the zeta potential calculated using Smoluchowski type theory for CVI (marked as "new CVI theory") remains practically constant within the complete range of the tested volume fractions.

Another test was conducted using rutile dispersion with median size around 300 nm. The selection of rutile as the second dispersion gives an opportunity to test the particle size dependence, and enhance the density contrast contribution. This test would also verify the more general theory presented in 8.2.3 that takes into account hydrodynamic and electrodynamic interaction of particles with larger sizes.

An equilibrium solution required for a proper dilution test was generated using sedimentation. Dilution was performed from an initial 46 % v/v down to 1 % v/v. The results are shown on Figure B.2.

Key

1   dilute system theory

2   new CVI theory

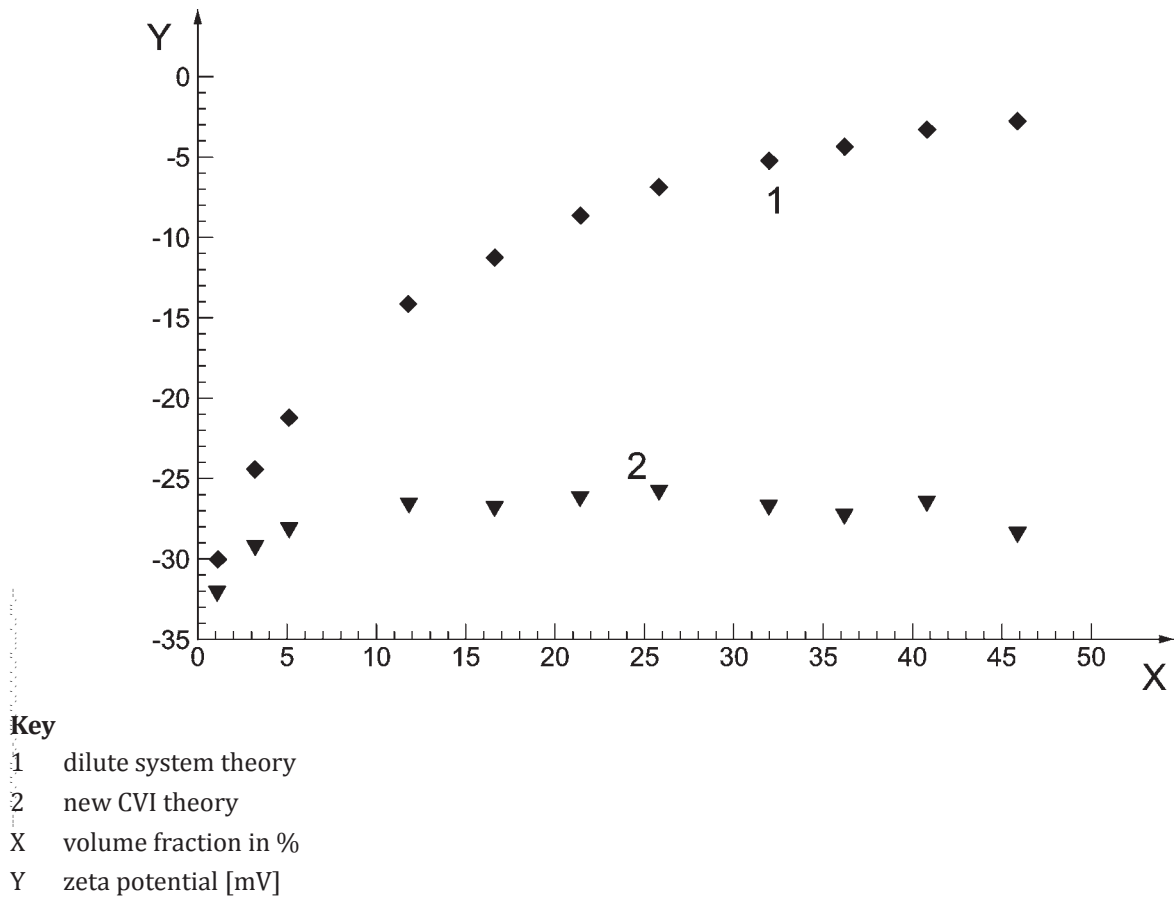X   volume fraction in %

Y   zeta potential [mV]

Figure B.2 — Comparison of the zeta potential of rutile using the dilute case theory and the new CVI theory

It is seen that zeta potential remains constant within the full range of tested volume fractions.

Figures B.1 and B.2 also show results using the dilute case theory. For the rutile the error exceeds 1000 %. This illustrates the importance of particle-particle interaction.

Bibliography

[1] Measurement and Interpretation of Electrokinetic Phenomena, International Union of Pure and Applied Chemistry, Technical Report, *Pure Appl. Chem.*, 77(10), 1753-1805, 2005 or *J. of Colloid and Interface Science*, 309, 194-224, 2007

[2] DUKHIN A.S., & GOETZ P.J. *Characterization of liquids, Nano- and microparticulates, and porous bodies using ultrasound*. Elsevier, Second Edition, 2010

[3] OJA T., PETERSEN G., CANNON D. Measurement of Electric-Kinetic Properties of a Solution, *US Patent 4,497,208*, 1985

[4] O'BRIEN R.W. Electro-Acoustic Effects in a Dilute Suspension of Spherical Particles. *J. Fluid Mech.* 1988, **190** pp. 71–86

[5] DEBYE P. A Method for the Determination of the Mass of Electrolyte Ions. *J. Chem. Phys.* 1933, **1** pp. 13–16

[6] FRENKEL J. "On the Theory of Seismic and Seismoelectric Phenomena in a Moist Soil", J. of Physics, USSR, vol. 3, 5, pp. 230-241 (1944), re-published. *J. Eng. Mech.* 2005

[7] DUKHIN A.S., & SHILOV V.N. Seismoelectric effect: A non-isochoric streaming current. 2. Theory. *J. Colloid Interface Sci.* 2010, **346** pp. 248–253

[8] LYKLEMA J. *Fundamentals of Interface and Colloid Science*. Academic Press, **Vol. 2**, 1995, pp. 3–208.

[9] SMOLUCHOWSKI M. *Handbuch der Electrizitat und des Magnetismus*. Barth, Leipzig, **Vol. 2**, 1921

[10] DUKHIN A.S., GOETZ P.J., THOMMES M. Seismoelectric effect.: A non-isochoric streaming current. 1. Experiment. *J. Colloid Interface Sci.* 2010, **345** pp. 547–553

[11] DUKHIN A.S., & PARLIA S. Studying homogeneity and zeta potential of membranes using electroacoustics. *J. Membr. Sci.* 2012

[12] DJERDJEV A.M., BEATTIE J.K., O'BRIEN R.W. The electrokinetic sonic amplitude effect in filtration membranes: Part 1 Experiment", J.Membrane Science, vol. 402-401, pp. 13-24, (2012)

[13] MAXWELL J.C. *Electricity and Magnetism*. Clarendon Press, Oxford, **Vol. 1**, 1892

[14] WAGNER K.W. *Arch. Elektrotech.* 1914, **2** p. 371

[15] DUKHIN A.S., SHILOV V.N., OHSHIMA H., GOETZ P.J. Electroacoustics Phenomena in Concentrated Dispersions. New Theory and CVI Experiment. *Langmuir.* 1999, **15** (20) pp. 6692–6706

[16] SHILOV V.N., BORKOVSKAYA Y.B., DUKHIN A.S. Electroacoustic Theory for Concentrated Colloids with overlapped DLs at Arbitrary ka. Application to Nanocolloids and Nonaqueous Colloids. *J. Colloid Interface Sci.* 2004, **277** pp. 347–358

[17] RIDER P.F., & O'BRIEN R.W. The Dynamic Mobility of Particles in a Non-Dilute Suspension. *J. Fluid Mech.* 1993, **257** pp. 607–636

[18] ENNIS J.P., SHUGAI A.A., CARNIE S.L. Dynamic Mobility of Two Spherical Particles with Thick Double Layers. *J. Colloid Interface Sci.* 2000, **223** pp. 21–36

[19] ENNIS J.P., SHUGAI A.A., CARNIE S.L. Dynamic Mobility of Particles with Thick Double Layers in a Non-Dilute Suspension. *J. Colloid Interface Sci.* 2000, **223** pp. 37–53

[20] TASSEL VAN J.. Randall, C.A. "Surface chemistry and surface charge formation for an alumina powder in ethanol with addition of HCl and KOH. *JCIS.* 2001, **241** pp. 302–316

[21] Ishikawa Y., Aoki N., Ohshima H. Characterization of latex particles for aqueous polymeric coating by electroacoustic method. *Colloids and Surfaces B*. 2005, **46** pp. 147–151

[22] Hackley V., Patton J., Lum L., Wasche R.J., Naito M., Abe H. et al. Analysis of the isoelectric point in moderately concentrated alumina suspensions using electroacoustic and streaming potential methods. *J. of Dispersion Science and Technology*. 2002, **23** (5) pp. 601–617

[23] O'Brien R.W., Midmore B.R., Lamb A., Hunter R.J. Electroacoustic studies of Moderately concentrated colloidal suspensions. *Faraday Discuss. Chem. Soc.* 1990, **90** pp. 1–11

[24] James R.O., Texter J., Scales P.J. Frequency dependence of electroacoustic (electrophoretic) mobilities. *Langmuir*. 1991, **7** pp. 1993–1997

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