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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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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].

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

$\boldsymbol{v}_{\mathrm{eo}}$

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

$U_{\mathbf{sed}}$

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

$I_{\mathbf{str}}$

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.

The elementary theories encompass several theories for non-conducting solids having a common basis for all electrokinetic and electroacoustic phenomena. These were originally established and applied to electrophoresis in Reference [12] and subsequently developed for other electrokinetic and electroacoustic effects. These theories have the remarkable features that they are valid for any shape, concentration of particles and any geometry of pores in porous body.

An important feature of the elementary theories is that there is only one EDL parameter, the zeta-potential. These theories allow direct calculation of zeta-potential from experimental data. All instruments that report zeta-potential values apply one or another version of the elementary theories, which are appropriate for the corresponding measurement.

Elementary theories have restricted validity range. Application of these theories beyond their validity range leads to substantial errors in absolute values of the zeta-potential. These errors can be tolerated for purposes of monitoring relative variations. However, there are many instances when accurate absolute values of zeta-potential are required. There are more sophisticated theories for such cases.

These more specific theories, referred to here as advanced theories, are described in Annexes C and D. These theories contain some other parameters of the EDL, such as Debye length, surface conductivity, Stern potential (References [2]–[4]). Applications of the advanced theories to zeta-potential calculation are not that direct. Additional assumptions or even measurement techniques are required.

5 Elementary theories, Smoluchowski's limit for electrokinetics

5.1 General

There are three restrictions that define the range of validity of the Smoluchowski theory for any electrokinetic and electroacoustic phenomena.

The first requirement is that the EDL be thin compared to the characteristic size of the heterogeneous system (see A.4):

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

Many aqueous dispersions satisfy this condition. This condition is not valid for nano-particles at low ionic strength in aqueous solutions and for many organic liquids.

The second requirement is a negligible contribution of the surface conductivity (Annex B):

$$Du << 1 \tag{2}$$

The third requirement is that the interface does not conduct normal electric current between phases. This condition is valid for non-conducting particles, ideally polarized metal particles, and porous bodies with a non-conducting matrix.

5.2 Electrophoresis

The Smoluchowski equation (Reference [12]) for the electrophoretic mobility, μ is:

$$\mu = \frac{\varepsilon_{\mathrm{m}}\varepsilon_0\zeta}{\eta} \tag{3}$$

The derivation of this equation requires no EDL model.

5.3 Electroosmosis

The electroosmotic flow rate of liquid per unit current, q_{eo}, can be derived from:

$$q_{\mathrm{eo}} = -\frac{\varepsilon_{\mathrm{m}}\varepsilon_0\zeta}{\eta K_{\mathrm{m}}} \tag{4}$$

where K_{m} is the conductivity, in siemens per metre, of the medium.

5.4 Streaming current or potential

In general, it is impossible to quantify the distribution of the electric field and the velocity in pores with unknown or complex geometry. However, this fundamental difficulty is avoided at the Smoluchowski limit, when hydrodynamic and electrodynamic fields have the same space distribution.

The value of the streaming potential U_{str} is obtained by the condition of equality of the conduction and streaming currents (the net current vanishes). According to Kruyt (Reference [5]) this leads to the simple Formula (5):

$$\frac{U_{\mathrm{str}}}{\Delta p} = \frac{\varepsilon_{\mathrm{m}}\varepsilon_0\zeta}{\eta K_{\mathrm{m}}} \tag{5}$$

Formula (5) does not contain geometric parameters, which makes it very convenient for determining zeta-potential.

5.5 Sedimentation potential or current

There is an analogue of the Smoluchowski equation [Formula (5)] for sedimentation potential, U_{sed}:

$$U_{\mathrm{sed}} = \frac{\varepsilon_{\mathrm{m}}\varepsilon_0\zeta(\rho_{\mathrm{p}}-\rho_{\mathrm{m}})gd\varphi}{\eta K_{\mathrm{m}}} \tag{6}$$

where d is the distance between the points where the potential is measured and g is the acceleration due to gravity.

6 Elementary theories, Smoluchowski's limit for electroacoustics

6.1 General

Electroacoustic theory, following electrokinetic theory, operates with a notion that it is closely related to electrophoretic mobility. This so-called dynamic electrophoretic mobility, μ_{d}, is the generalization of the electrophoretic mobility concept for high-frequency oscillating particle motion.

The relationship between dynamic electrophoretic mobility and experimental electroacoustic data is not as trivial as that in the case of electrokinetics. The additional theoretical step has been made through the O'Brien electroacoustic theory (Reference [14]), which is valid for concentrated systems as well as dilute ones.

According to the O'Brien relationship, the average dynamic electrophoretic mobility, μ_{d}, is defined as:

$$\left.\begin{aligned} \mu_{\mathrm{d}} &= A_{\mathrm{ESA}}\frac{\rho_{\mathrm{m}}}{\varphi(\rho_{\mathrm{p}}-\rho_{\mathrm{m}})}\frac{1}{A(\omega)F(Z)} \\ \mu_{\mathrm{d}} &= I_{\mathrm{CVI}}\frac{\rho_{\mathrm{m}}}{\varphi(\rho_{\mathrm{p}}-\rho_{\mathrm{m}})}\frac{1}{A(\omega)F(Z)} \end{aligned}\right\} \tag{7}$$

where A_{ESA} or I_{CVI} are normalized with respect to corresponding driving forces. $A(\omega)$ is an instrument constant found by calibration, and $F(Z)$ is a function of the acoustic impedances of the transducer and the dispersion under investigation. The densities of 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 cases considered, the coefficient of proportionality between electroacoustic signal and dynamic electrophoretic mobility is independent of particle size and zeta-potential. This feature makes the dynamic electrophoretic mobility an important and central parameter of the electroacoustic theory.

There are two versions of the dynamic electrophoretic mobility theory at the Smoluchowski limit: when EDL is thin and when surface conductivity is negligible. This is expressed with the same two conditions as in the electrokinetic theory [Formulae (1) and (2)].

The first one is for dilute systems with negligible particle–particle interaction (Reference [14]), valid for spherical particles only, but with no restriction on the particle size except that the size be small compared to the sound wavelength. This is called “O'Brien theory for dynamic electrophoretic mobility”. It is more limited than Smoluchowski theory for electrophoresis, which is valid for any particle shape and concentration.

The other version of the electroacoustic theory is almost as general as Smoluchowski theory for electrophoresis. This can be achieved by restricting the frequency range. If the frequency is sufficiently low, dynamic electrophoretic mobility becomes identical to the static electrophoretic mobility. Currently, this theory is available for CVI only (References [15][16]). It is referred to as “Smoluchowski limit theory for dynamic electrophoretic mobility”.

6.2 O'Brien's theory for dynamic electrophoretic mobility

This theory does not take into account particle–particle interactions, and is thus valid only in dilute dispersions.

$$\mu_{\mathrm{d}} = \frac{2\varepsilon_{\mathrm{m}}\varepsilon_0\zeta}{3\eta} G(s)\left[1 + F(\omega')\right] \tag{8}$$

where

$$G(s) = \frac{1+(1+\mathrm{j})s}{1+(1+\mathrm{j})s+\mathrm{j}\left(2s^2/9\right)\left\{\left[3+2\left[\left(\rho_{\mathrm{p}}-\rho_{\mathrm{m}}\right)/\rho_{\mathrm{m}}\right]\right]\right\}} \tag{9}$$

$$F(\omega') = \frac{1+\mathrm{j}\omega'\left[1-\left(\varepsilon_{\mathrm{p}}/\varepsilon_{\mathrm{m}}\right)\right]}{2+\mathrm{j}\omega'\left[2+\left(\varepsilon_{\mathrm{p}}/\varepsilon_{\mathrm{m}}\right)\right]} \tag{10}$$

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

The frequency dependence of dynamic electrophoretic mobility is determined by the two factors s^2 and ω' 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 (References [17]–[19]).

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 1 and 0,5, respectively. This means that at sufficiently low frequency, dynamic electrophoretic mobility depends only on those factors that are taken into account by the Smoluchowski theory for electrophoresis.

6.3 Smoluchowski limit theory for dynamic electrophoretic mobility

This version of the theory (References [15][16]) is important because it is as general as Smoluchowski theory, within its range of validity — sufficiently low frequency. It is adequate for particles of any size, any shape and, most importantly, any concentration including highly concentrated systems.

There are two critical frequencies that determine the valid range of this theory, together with the Smoluchowski restrictions, Formulae 1 and 2.

The critical frequency of hydrodynamic relaxation (ω_{hd}) determines the range of the particle inertia and that of the influence of the factor $G(s)$. This factor becomes negligible when frequency ω satisfies the condition:

$$\omega << \omega_{\mathrm{hd}} = \frac{\eta}{\rho_{\mathrm{m}} a^2} \tag{11}$$

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

$$\omega << \omega_{\mathrm{MW}} = \frac{K_{\mathrm{m}}}{\varepsilon_{\mathrm{m}} \varepsilon_0} \tag{12}$$

The expression for dynamic electrophoretic mobility at this limit was derived only for colloid vibration current (References [15][16]):

$$\mu_{\mathrm{d}} = \frac{\varepsilon_{\mathrm{m}} \varepsilon_0 \zeta}{\eta} \frac{K_{\mathrm{s}}}{K_{\mathrm{m}}} \frac{(\rho_{\mathrm{p}} - \rho_{\mathrm{s}})\rho_{\mathrm{m}}}{(\rho_{\mathrm{p}} - \rho_{\mathrm{m}})\rho_{\mathrm{s}}} \tag{13}$$

7 Advanced theories

Application of the advanced theories is much more complicated, because other parameters of the EDL are involved. On the other hand, application of these theories allows much more detailed description of the electric surface properties. The two most important parameters are the Debye length and Dukhin number. There are several ways of characterizing these parameters for the proper use of the advanced theories. They are described in Annex C. Increasing complexity of the measuring procedure yields more detailed determination of these additional parameters, which in turn leads to the more accurate zeta-potential value. There are several distinctive steps in this balance between complexity of the measuring procedure and accuracy of the zeta-potential.

Estimation of the Debye length using conductivity is simpler than measuring Dukhin number. On the other hand, information on the Debye length allows us only limited modelling of the surface conductivity (Annex B). This approach requires the assumption that surface conductivity is only associated with the diffuse layer. It is so-called “standard Debye length model” where according to Lyklema (Reference [2]) the Dukhin number becomes dependent only upon Debye length and zeta-potential (Formula B.4). There are two analytical theories of electrophoresis that can be applied in this case: simplified Dukhin–Semenikhin theory (Formula D.10) and O’Brien theory (Formula D.11).

The next level of complexity requires direct measurement of the Dukhin number, which takes into account surface conductivity not only in the diffuse layer, but under it and even in the Stern layer. There are a number of studies indicating the importance of this stagnant layer surface conductivity (Reference [2]). Direct measurement of the Du can be achieved using several different experimental procedures (Reference [2]). One of the most suitable is based on the conductivity measurement, as presented in Annex C. Calculation of zeta-potential can be based on the numerical procedure by O’Brien and White (D.2), or general Dukhin–Semenikhin analytical theory (D.5).

The overlap of EDL is another factor that complicates theoretical interpretation. It becomes important for concentrated nano-particles and non-polar dispersions. In the latter case, it can appear even at rather low volume fractions, as discussed in A.4. There are two theories that take into account this factor for both electrophoresis (D.6) and electroacoustics (E.4).

Each particular study of zeta-potential requires a certain level of accuracy. This accuracy determines the complexity of the theoretical interpretation procedure and the choice between either elementary or appropriate advanced theory.

8 Equilibrium dilution and other sample modifications

A comparison of different methods is complicated by the fact that the zeta-potential is not only a property of particles alone, but also depends on the chemical equilibrium between particle surface and the liquid. Any variation of the liquid chemical and ionic composition affects this equilibrium and, consequently, affects zeta-potential.

This presents a problem for methods that require extreme dilution of the sample. Dilution can change the chemical composition of the liquid, if special measures are not taken. The sample preparation shall follow a procedure so that zeta-potential is not changed from the original system to the diluted sample.

This procedure requires, upon dilution, not only that particles and their surfaces remain identical between the original and diluted systems, but also that liquids remain identical. 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.

The sample preparation shall use the so-called equilibrium dilution procedure, which employs the same liquid as in the original system as a diluent. After dilution, the only parameter that has changed is the particle concentration. Only sample preparation based on equilibrium dilution provides zeta-potential values that are identical between the original system and the diluted sample.

There are two approaches to the collection of the liquid used for dilution. The first consists of extracting a supernatant using sedimentation or centrifugation. This supernatant can be used for diluting the initial sample to the degree that is optimal for the particular measuring technique. This method is suitable for large particles with sufficient density contrast. It is not very convenient for nano-particles and soft biological systems.

The other approach, more suitable for nano- and bio-colloids is to employ dialysis. Dialysis membranes are required that are penetrable for ions and molecules, but not for colloidal particles (Reference [15]).

In some rare cases, there can be a need to prepare more concentrated samples from the dilute ones. This can be achieved by initially separating particles from the liquid and the re-dispersing them in the same liquid but at a higher volume fraction.

Annex A
(informative)

Electric double layer models

A.1 General

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. This object might be a solid particle, gas bubble, liquid droplet, or porous body. The structure consists of two parallel layers of electric charges. One layer (either positive or negative) coincides with the surface of the object. It is the electric surface charge. The other layer is in the fluid. It electrically screens the first one. It is diffuse, because it forms under the influence of electric attraction and thermal motion of free ions in fluid. It is called the diffuse layer.

Interfacial EDL is usually most apparent for dispersions and emulsions with sizes on the micrometre or even nanometre scale or porous bodies with pore sizes on the same scale.

EDL plays a very important role in real world systems. For instance, milk exists only because fat droplets are covered with an EDL that prevents their coagulation into butter. EDLs exist in practically all heterogeneous liquid based systems, such as blood, paint, inks, ceramic slurries, cement slurries, etc.

The earliest model of the electrical EDL is usually attributed to Helmholtz (Reference [13]) who treated the EDL mathematically as a simple capacitor, based on a physical model in which a single layer of ions is adsorbed at the surface with compensating countercharges in the solution. Later Gouy and Chapman (References [20][21]) made significant improvements by introducing a diffuse model of the EDL, in which the electric potential decays exponentially away from the surface into the bulk liquid. The Gouy–Chapman model fails for highly charged EDLs. In order to resolve this problem, Stern (Reference [22]) suggested the introduction of an additional layer adjacent to the surface that is now called the Stern layer. The combined Gouy–Chapman–Stern model is the one most commonly used.

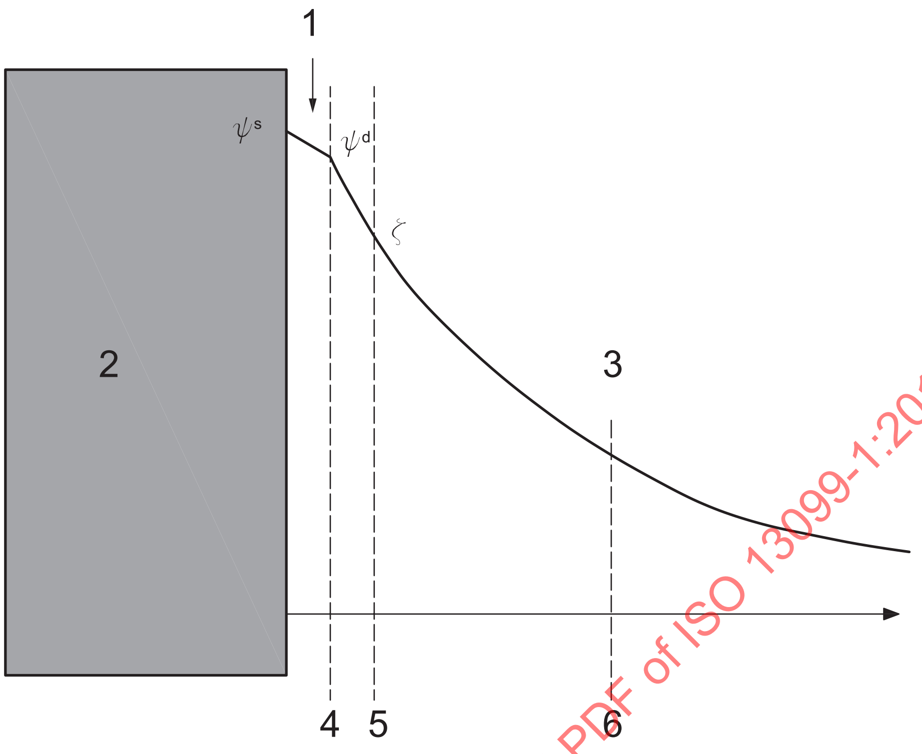
There are some limitations in the Gouy–Chapman–Stern model:

- ions are effectively point charges;
- the only significant interactions in the diffuse layer are coulombic;
- electric permittivity is constant throughout the electric double layer;
- dynamic viscosity of fluid is constant beyond the slipping plane.

There are more recent theoretical developments studying these limitations of the Gouy–Chapman–Stern model, which have been reviewed in References [1]–[4].

Figure A.1 illustrates an interfacial EDL in more detail (Reference [2]). The reason for the formation of a relaxed (equilibrium) double layer is the non-electric affinity of charge-determining ions for a surface. This process leads to the build-up of an electric surface charge. This surface charge creates an electrostatic field that then affects the ions in the bulk of the liquid. This electrostatic field, in combination with the thermal motion of the ions, creates a countercharge, and thus screens the electric surface charge. The net electric charge in this screening diffuse layer is equal in magnitude to the net surface charge, but has the opposite sign. As a result, the complete structure is electrically neutral. Some of the counterions might specifically adsorb near the surface and contribute to the Stern layer. The outer part of the screening layer is usually called the diffuse layer.

The diffuse layer, or at least part of it, can move under the influence of tangential stress. There is a conventionally introduced slipping plane that separates mobile fluid from fluid that remains attached to the surface. The electric potential at this plane is called the electrokinetic potential or zeta-potential.



Key

1 Stern layer
2 Positively charged particle
3 Negatively charged diffuse layer
4 Stern plane
5 Slipping plane
6 Debye length

Figure A.1 — Illustration of the double layer structure according to the Gouy–Chapman–Stern model

The electric potential on the external boundary of the Stern layer versus the bulk electrolyte is referred to as the Stern potential, ψ^d. The electric potential difference between the bulk of the fluid and the surface is called the electric surface potential, ψ^s .

General experience indicates that the plane of shear (slipping plane) is located very close to the outer Helmholtz plane that determines the Stern potential. The layer between this plane and the interface is usually called the "stagnant layer". Both planes are abstractions of reality. This means that, in practice, the zeta-potential is equal to or lower in magnitude than the Stern potential, ψ^d.

A characteristic value of the electric potentials in the EDL at the slipping plane is 25 mV with a maximum value around 100 mV for aqueous systems. The chemical composition of the sample that brings zeta-potential to zero is called the point of zero zeta-potential or isoelectric point. It is usually determined by the pH value of the solution.

There are useful mathematical relationships between EDL parameters that can be found in the literature. Several geometric configurations of the EDL are presented here.

A.2 Flat surfaces

The EDL thickness is characterized by the so-called Debye length, κ^{-1}, defined by:

$$\kappa^2 = F^2 \sum_i \frac{c_i z_i}{\varepsilon_\mathrm{m} \varepsilon_0 RT} \qquad \text{(A.1)}$$

where

F is the Faraday constant;

R is the gas constant;

T is the absolute temperature;

ε_o is the dielectric permittivity of vacuum;

ε_m is the relative permittivity of the liquid;

c_i is the molar concentration of the ith ion species.

z_i is the absolute valency of the ith ion species.

For a symmetrical electrolyte $z_+ = -z_- = z$.

For a flat surface and a symmetrical electrolyte of concentration c, there is a straightforward relationship between the electric charge density in the diffuse layer, σ^d, and the Stern potential, ψ^d, namely:

$$\sigma^\mathrm{d} = -\sqrt{8\varepsilon_\mathrm{m}\varepsilon_0 cRT}\,\sinh\frac{F\psi^\mathrm{d}}{2RT} \qquad \text{(A.2)}$$

If the diffuse layer extends to the surface, Formula A.2 can then be used to relate the surface charge to the surface potential.

Sometimes it is helpful to use the concept of a differential EDL capacitance. For a flat surface and a symmetrical electrolyte, this capacitance per area is given by:

$$C_\mathrm{dl} = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\psi}\right|_{\psi=\psi^\mathrm{d}} = \varepsilon_\mathrm{m}\varepsilon_0\kappa\cosh\frac{F\psi^\mathrm{d}}{2RT} \qquad \text{(A.3)}$$

For a symmetrical electrolyte, the electric potential, ψ, at a distance, x, from the flat surface into the EDL, is given by:

$$\exp(-\kappa x) = \frac{\tanh\left[zF\psi(x)/4RT\right]}{\tanh\left(zF\psi^\mathrm{d}/4RT\right)} \qquad \text{(A.4)}$$

The relationship between the electric charge density and the potential over the diffuse layer for an asymmetric electrolyte is given by:

$$\sigma^\mathrm{d} = -\left(\mathrm{sgn}\,\psi^\mathrm{d}\right)\sqrt{2\varepsilon_\mathrm{m}\varepsilon_0 cRT}\left[\nu_+\exp\left(-z_+\bar{\psi}^\mathrm{d}\right) + \nu_-\exp\left(-z_-\bar{\psi}^\mathrm{d}\right) - \nu_+ - \nu_-\right]^{1/2} \qquad \text{(A.5)}$$

where $\nu_\pm$ is the number of cations and anions produced by dissociation of a single electrolyte molecule, and $\bar{\psi}^\mathrm{d}$ is a dimensionless potential given by:

$$\bar{\psi}^\mathrm{d} = \frac{F\psi^\mathrm{d}}{RT} \qquad \text{(A.6)}$$

For the general case of an arbitrary electrolyte mixture, there is no analytical solution.

A.3 Spherical isolated electric double layers

There is only one geometric parameter in the case of a flat EDL, namely the Debye length $1/\kappa$. In the case of a spherical EDL, there is an additional geometric parameter, namely the radius of the particle, a. The ratio of these two parameters, κa, is a dimensionless parameter that plays an important role in colloid science. Depending on the value of κa, two asymptotic models of the EDL exist.

The thin EDL model corresponds to colloids in which the EDL is much thinner than particle radius, or simply:

$$\kappa a \gg 1 \tag{A.7}$$

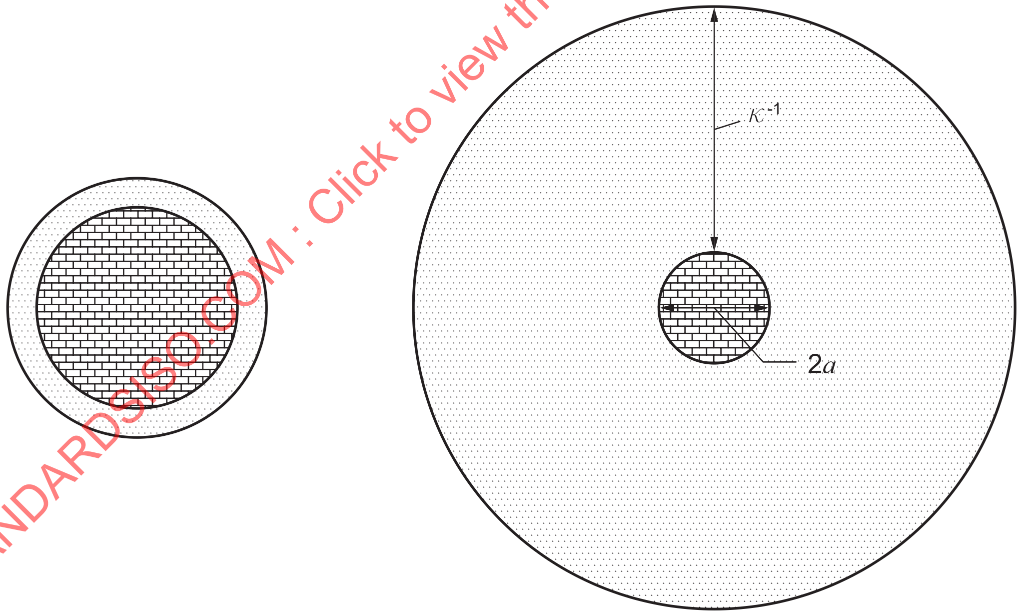
The vast majority of aqueous dispersions satisfy this condition, except for very small nano-particles in low ionic strength media. If it is assumed that for an ionic strength greater than 10^{-3} mol/l, corresponding to the majority of natural aqueous systems, the condition $\kappa a \gg 1$ is satisfied for virtually all particles having a size above 100 nm.

The opposite case of a thick EDL corresponds to systems where the EDL is much larger than the particle radius, or simply:

$$\kappa a \ll 1 \tag{A.8}$$

Many aqueous nano-dispersions at low ionic strength and the vast majority of dispersions in hydrocarbon media, having inherently very low ionic strength, satisfy this condition.

These two asymptotic cases allow one to picture, at least approximately, the EDL structure around spherical particles as shown in Figure A.2:



a) thin double layer b) thick double layer

Key

κ^{-1} Debye length

2a particle diameter

Figure A.2 — Illustration of the "thin" and "thick" double layer models

A general analytical solution exists only for low potential:

$$\psi^{\mathrm{d}} << \frac{RT}{F} \tag{A.9}$$

At 25 °C, the value for the right hand side is approximately 25,8 mV.

This so-called Debye–Hückel approximation yields the following expression for the electric potential in a spherical EDL, $\psi(r)$, at a distance, r, from the particle centre:

$$\psi(r) = \psi^{\mathrm{d}} \frac{a}{r} \exp\left[-\kappa(r-a)\right] \tag{A.10}$$

The relationship between diffuse charge density and the Stern potential is then:

$$\sigma^{\mathrm{d}} = -\varepsilon_{\mathrm{m}}\varepsilon_0 \kappa \psi^{\mathrm{d}} \left(1 + \frac{1}{\kappa a}\right) \tag{A.11}$$

This Debye–Hückel approximation is valid for any value of κa, but this is somewhat misleading, since it covers only isolated double layers.

There is also one important approximate relationship derived independently by several authors in References [23]–[25]:

$$\sigma^{\mathrm{d}} = -\frac{2Fcz}{\kappa}\left[2\sinh\frac{z\tilde{\psi}^{\mathrm{d}}}{2} + \frac{4\tanh\left(z\tilde{\psi}^{\mathrm{d}}/4\right)}{\kappa a}\right] \tag{A.12}$$

It is approximately valid for values of κa above 2.

A.4 Overlapping double layers

The Debye–Hückel approximation does not take into account the probability of an overlap of double layers as in a concentrated dispersion, i.e. high volume fraction. A simple estimate of this critical volume fraction, φ_{over}, the volume fraction for which the Debye length is equal to the shortest distance between the particles, is given by Formula (A.13) (Reference [16]):

$$\varphi_{\mathrm{over}} \approx \frac{0{,}52}{\left[1 + (1/\kappa a)\right]^3} \tag{A.13}$$

This dependence is illustrated in Figure A.3.

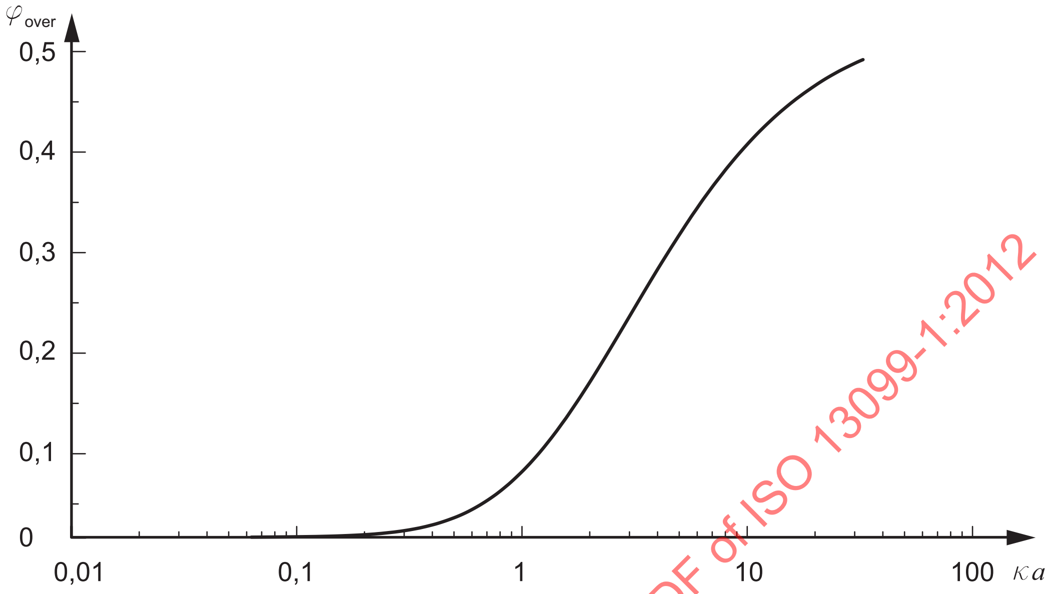
It is clear that for $\kappa a >> 10$ (thin EDL) we can consider the EDLs as isolated entities even up to volume fractions of 0,4. However, the model for an isolated EDL becomes somewhat meaningless for small κa (thick EDL), because EDL overlap then occurs even in very dilute suspensions.

There is one extreme case that offers a significant simplification of the theory. When EDLs overlap strongly, they lose their original exponential diffuse structure. The overlapping area becomes more and more homogeneous. At the extreme, it can be imagined that charged particles are simply screened with a homogeneous cloud of counter-ions. This is the so-called "homogeneous" model (Reference [26]).

This model yields a very simple relationship between surface charge density and zeta-potential, especially for a monodisperse, dispersion of spherical particles:

$$\sigma^{\mathrm{d}} = \frac{1}{3}\frac{RT}{F}\frac{1-\varphi}{\varphi}\varepsilon_{\mathrm{m}} a \kappa^2 \sinh\frac{F\zeta}{RT} \tag{A.14}$$

Formula (A.14) reflects a very important distinction between "thin EDL" and "overlapping EDLs". In the case of the traditional "thin EDL" theory, both surface charge and zeta-potential are surface properties, independent of the volume fraction. In the case of "overlapping EDLs", surface charge is a true parameter of the surface properties. The electrokinetic zeta-potential can lead to erroneous conclusions, because it depends on the volume fraction, not simply on the surface charge. This all indicates that both zeta-potential and surface charge shall be reported when dealing with concentrated dispersions with thick EDL.



Key

κa	reciprocal Debye length times particle radius
φ_{over}	critical volume fraction

Figure A.3 — Estimate of the volume fraction of the overlap of the electric double layer

Annex B
(informative)

Surface conductivity

B.1 General

Surface conduction is the name given to the excess electric conduction that takes place in dispersed systems due to the presence of the electric double layers. Excess charges in them may move under the influence of electric fields applied tangentially to the surface. The phenomenon is quantified in terms of the surface conductivity K^σ, which is the surface equivalent to the bulk conductivity, K_m. K^σ is a surface excess quantity, just like the surface concentration of a certain species.

The motion of the diffuse layer charges located outside the shear plane always contributes to the surface conductivity. This is the "Bikerman surface conductivity" (Reference [28]). In addition, there is a possible contribution due to conductivity of the stagnant layer. This can include one contribution due to the specifically adsorbed charge and another due to the part of the diffuse layer charge that can reside behind the plane of shear. The charge on the solid surface is generally assumed to be immobile.

B.2 Calculation of the Dukhin number

The formulae in this clause apply to systems where the double layer is thin compared to the particle radius, i.e. $\kappa a >> 1$. The conductivity in the diffuse double layer outside the shear plane consists of two parts (Reference [28]): a migration contribution, caused by the movement of charges with respect to the liquid; and a convective contribution, due to the electroosmotic liquid flow beyond the shear plane, which gives rise to an additional mobility of the charges and hence leads to an extra contribution to K^σ. For the calculation of K^σ the Bikerman equation can be used, which expresses K^σ as a function of the electrolyte and double layer parameters. For a symmetrical electrolyte, a convenient expression is:

$$K^\sigma = \frac{2e^2 N_A z^2 c}{k_\mathrm{B} T}\left\{D_+\left[\exp\left(-\frac{\tilde{\zeta}}{2}\right)-1\right]\left(1+\frac{3m_+}{z^2}\right)+D_-\left[\exp\left(-\frac{\tilde{\zeta}}{2}\right)-1\right]\left(1+\frac{3m_-}{z^2}\right)\right\} \tag{B.1}$$

where

$$\tilde{\zeta} = \frac{zF\zeta}{RT}$$

The parameters $m_\pm$ reflect the relative contribution of electroosmosis to the surface conductivity:

$$m_\pm = \frac{2}{3}\left(\frac{kT}{e}\right)^2 \frac{\varepsilon_\mathrm{m}\varepsilon_0}{\eta D_\pm} \tag{B.2}$$

A measure of the relative importance of surface conductivity is given by the dimensionless Dukhin number, Du, which relates surface and bulk conductivities:

$$Du = \frac{K^\sigma}{K_\mathrm{m} a} \tag{B.3}$$

where a is the local radius of curvature of the surface.

For the Bikerman part of the conductivity, Du can be written explicitly. For a symmetrical electrolyte, cation and anion diffusion coefficients are identical, so that $m_+ = m_- = m$:

$$Du = \frac{2}{\kappa a}\left(1 + \frac{3m}{z^2}\right)\left(\cosh\frac{\tilde{\zeta}}{2} - 1\right) \tag{B.4}$$

where

$$m = \frac{2}{3}\left(\frac{kT}{e}\right)^2 \frac{\varepsilon_\mathrm{m}\varepsilon_0}{\eta D_\mathrm{eff}}$$

Formula (B.4) for the Dukhin number reflects only the surface conductivity in the diffuse layer outside of the shear plane.

B.3 Measurement of Dukhin number using conductivity

Surface conductivity through the stagnant layer increases the Dukhin number, in some cases substantially. This requires direct measurement of the Dukhin number, because there is no explicit equation that would link the Dukhin number with the double layer properties in this case.

Measurement of the conductivity is the simplest way to obtain the additional experimental information required for calculation of Dukhin number. Maxwell–Wagner–O'Konski theory (References [17]–[19]) yields Formula (B.5) for the conductivity of dispersion with non-conducting spherical particles, K_s:

$$\frac{K_\mathrm{s}}{K_\mathrm{m}} = \frac{1 + Du - \varphi(1 - 2Du)}{1 + Du + 0{,}5\varphi(1 - 2Du)} \tag{B.5}$$

Parameter K_s can be readily measured. The volume fraction φ is usually known, or easily measured with a pycnometer. The measurement of the equilibrium conductivity of the dispersion medium K_m can be determined from the supernatant.

Annex C
(informative)

Debye length

C.1 General

This parameter is an estimate of the EDL thickness according to Annex A. It is important for understanding aggregative stability and particles interaction. It estimates an average distance of particles approaching each other in liquid before electrostatic interaction becomes significant.

There are two ways to establish information on Debye length: calculation using Formula (A.1) or by measurement.

C.2 Calculation of Debye length

The calculation of Debye length using Formula (A.1) only requires that the concentration of the sample and the valencies of the ion species be known.

This method works when the dispersion medium is prepared following a defined recipe.

In addition, it is imperative to take special measures to remove impurities by washing the powder. Powders usually contain some chemical substances that can dissolve and substantially affect the chemical composition of the dispersion medium.

This method of estimating Debye length has very limited application. It does not work with liquids of unknown ionic composition. It does not work in cases when particles interact with liquid. It can be strongly affected by impurities.

Conductivity and pH measurement can assist in assessing the impact of impurities. This can be achieved by comparing the conductivity and pH of the initial liquid and the final dispersion.

Conductivity measurement also provides experimental data for the direct estimation of the Debye length.

C.3 Measurement of Debye length using conductivity

This method was suggested by Dukhin and Goetz (Reference [16]):

$$\kappa^{-1} \approx \sqrt{\frac{\varepsilon_{\mathrm{m}}\varepsilon_0 D_{\mathrm{eff}}}{K_{\mathrm{m}}}} \tag{C.1}$$

The main uncertainty in Formula (C.1) arises from the unknown effective diffusion coefficient D_{eff}. However, this parameter varies over a limited range. For instance, the diffusion coefficients of most ions in aqueous solutions are similar and have values that at room temperature are in the range of 0,6 $\times 10^{-9}$ m^2/s to 2 $\times 10^{-9}$ m^2/s. The square root of this variation yields uncertainty of the order of only tens of percentage points.

With regard to non-aqueous systems, the Fuoss theory (Reference [27]) can be used for relating diffusion coefficient to the electric permittivity of the liquid.

Annex D
(informative)

Advanced electrophoretic theories

D.1 General

The elementary theories of electrophoresis presented in the main body of this part of ISO 13099 assume thin EDL, negligible surface conductivity and non-conducting particle bulk, which is reflected through the following mathematical expressions:

$$\kappa a >> 1 \tag{D.1}$$

$$Du << 1 \tag{D.2}$$

$$K_\mathrm{p} = 0 \tag{D.3}$$

There are several theoretical developments that allow relaxation of some of these restrictions and yield more general expressions for electrophoretic mobility.

D.2 O'Brien and White numerical theory

See Reference [29].

This is the most general approach, which allows the calculation of the electrophoretic mobility for any dilute dispersion of non-interacting spherical particles. All restrictions in Formulae (D.1) to (D.3) are relaxed.

D.3 Henry–Ohshima theory for conducting and non-conducting particles

See References [30][31].

This theory relaxes restrictions in Formulae (D.1) and (D.3). The restriction in Formula (D.2) remains.

For a non-conducting sphere, Henry derived the following expression (Reference [30]):

$$\mu = \frac{2\varepsilon_\mathrm{m}\varepsilon_0}{3\eta}\zeta f_1(\kappa a) \tag{D.4}$$

where the function f_1 varies smoothly from 1,0, for low values of κa, to 1,5 as κa approaches infinity. Reference [30] gives two series expansions for the function f_1, one for small κa and one for large κa. Reference [31] provides an approximate analytical expression which duplicates the expansion in Reference [30] almost exactly:

$$f_1(\kappa a) = 1 + \frac{1}{2}\left[\!\left[1 + \left\{\frac{2,5}{\kappa a\left[1 + 2\exp(-\kappa a)\right]}\right\}\right]\!\right]^{-3} . \tag{D.5}$$

Formula D.4 can be used in the calculation of the electrophoretic mobility of particles with non-zero bulk conductivity, K_p. With that aim, it can be rearranged as in Formula (D.6) (Reference [1]):

$$\mu = \frac{2\varepsilon_\mathrm{m}\varepsilon_0}{3\eta}\zeta F_1\left(\kappa a, K_\mathrm{p}\right) \tag{D.6}$$