Advances in Colloid and Interface Science 211 (2014) 77–92

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

# Electrophoresis and stability of nano-colloids: History, theory and experimental examples

C. Felix [a], A. Yaroshchuk [b], S. Pasupathi [a], B.G. Pollet [a], M.P. Bondarenko [c], V.I. Kovalchuk [c,*], E.K. Zholkovskiy [c]

[a] South African Institute for Advanced Materials Chemistry (SAIAMC), University of the Western Cape, Modderdam Road, Bellville 7535, Cape Town, South Africa
[b] ICREA and Department d'Enginyeria Química (EQ) Universitat Politècnica de Catalunya Av. Diagonal, 647, Edifici H, 4a planta, 08028, Barcelona, Spain
[c] Institute of Biocolloid Chemistry of Ukrainian Academy of Sciences, Vernadskogo, 42, 03142 Kiev, Ukraine

A R T I C L E  I N F O

Available online 20 June 2014

*Keywords:*
Electrophoresis
Coagulation dynamics
Nano-suspensions
Standard Electrokinetic Model
DLVO theory

A B S T R A C T

The paper contains an extended historical overview of research activities focused on determining interfacial potential and charge of dispersed particles from electrophoretic and coagulation dynamic measurements. Particular attention is paid to nano-suspensions for which application of Standard Electrokinetic Model (SEM) to analysis of experimental data encounters difficulties, especially, when the solutions contain more than two ions, the particle charge depends on the solution composition and zeta-potentials are high. Detailed statements of Standard Electrokinetic and DLVO Models are given in the forms that are capable of addressing electrophoresis and interaction of particles for arbitrary ratios of the particle to Debye radius, interfacial potentials and electrolyte compositions. The experimental part of the study consists of two groups of measurements conducted for Pt/C nano-suspensions, namely, the electrophoretic and coagulation dynamic studies, with various electrolyte compositions. The obtained experimental data are processed by using numerical algorithms based on the formulated models for obtaining interfacial potential and charge. While analyzing the dependencies of interfacial potential and charge on the electrolyte compositions, conclusions are made regarding the mechanisms of charge formation. It is established that the behavior of system stability is in a qualitative agreement with the results computed from the electrophoretic data. The verification of quantitative applicability of the employed models is conducted by calculating the Hamaker constant from experimental data. It is proposed how to explain the observed variations of predicted Hamaker constant and its unusually high value.

**Contents**

---

* Corresponding author. Tel./fax: +380 44 424 8078.
*E-mail address:* vladim@koval.kiev.ua (V.I. Kovalchuk).

http://dx.doi.org/10.1016/j.cis.2014.06.005
0001-8686/

## Nomenclature

*Latin letters*

| | |
|---|---|
| $a$ | radius of particle; |
| $C_k$ | concentration of the $k$th ion in the solution bulk; |
| $c_k$ | local concentration of the $k$th ion; |
| $D_k$ | the $k$th ion diffusion coefficient; |
| $\mathbf{E}$ | external electric field strength; |
| $\mathbf{e}_n$ | unity vector of Cartesian coordinate system; |
| $\mathbf{e}_r$, $\mathbf{e}_\theta$, $\mathbf{e}_\varphi$ | unit vectors of spherical coordinate system; |
| $\mathbf{e}_\beta$ and $\mathbf{e}_\nu$ | unit vectors of bispherical coordinate system; |
| $F$ | Faraday constant; |
| $G_{el}(h)$ | electrostatic free energy; |
| $G_W(h)$ | van der Waals free energy; |
| $H$ | Hamaker constant; |
| $h$ | minimum distance between particle surfaces; |
| $I$ | ionic strength; |
| $\mathbf{I}$ | unit tensor; |
| $\mathrm{n}$ | outward normal vector to a closed surface; |
| $p$ | local pressure; |
| $p_\infty$ | pressure in the solution bulk; |
| $q$ | surface charge density; |
| $R$ | gas constant; |
| $\mathbf{r}$ | vector coordinate; |
| $\mathbf{r}_{\mathbf{BA}}$ | vector whose origin and end coincide with the centers of particles B and A, respectively; |
| $r$ | polar radius in spherical coordinate system; |
| $T$ | absolute temperature; |
| $\mathbf{u}$ | local velocity of liquid; |
| $\mathbf{U}_{eph}$ | electrophoretic velocity; |
| $\mathbf{U}_{dph}$ | diffusiophoretic velocity; |
| $\mathrm{X}(h)$ | interaction force; |
| $x_n$ | Cartesian coordinate; |
| $Y(r)$ | radial part of the streaming function; |
| $Z_k$ | electric charge of the $k$th ion in Faraday units; |
| $\mathrm{z}$ | axial coordinate; |

*Greek letters*

| | |
|---|---|
| $(\beta, \nu)$ | bispherical coordinates; |
| $\xi_k = C_k^\infty z_k / \sum_n z_n^2 C_n^\infty$ | dimensionless coefficient; |
| $\eta$ | viscosity; |
| $\theta$ | spherical polar coordinate; |
| $\varepsilon$ | dielectric permittivity; |
| $\kappa$ | Debye parameter; |
| $\mu_k$ | the $k$th ion electrochemical potential; |
| $M_k(r)$ | the function describing radial dependency of perturbation of $k$th ion electrochemical potential; |
| $\Pi$ | effective pressure; |
| $\boldsymbol{\sigma}$ | stress tensor; |
| $\tau$ | coagulation time; |
| $\tau_{Sm}$ | Smoluchowski time scale parameter; |
| $\Psi$ | equilibrium electric potential; |
| $\psi = \Psi F/RT$ | normalized equilibrium electric potential; |
| $\zeta$ | electric potential at the interface in equilibrium state (zeta potential); |
| $\zeta_{\exp}$ | measured zeta potential; |

## 1. Introduction

Nano-particle systems have become one of the most important objects in modern science and technology because of highly specific and versatile properties of nano-particles, which are determined by their small, close to molecular and atomic, size. Moreover, their properties can be precisely tuned and functionalized by changing their size and composition and modifying their surface. In the recent less than two decades innumerable amount of various types of nano-particles were obtained having specific electronic, magnetic, optic, catalytic, biological and other properties [1–7]. This opens many opportunities for their use in numerous important applications in technology and biomedicine. The studies in this area are focused not only on the synthesis and tuning of nano-particles properties but also on their interactions and behavior in various media.

Liquid systems with dispersed nano-particles are particularly important. Nano-particle dispersions are widely used in technological processes, e.g. for obtaining substrates covered by nano-particles or nano-porous media. They are also very important for various biomedical applications. For most applications it is necessary to have stable nano-dispersions, which do not change their properties with time due to particle aggregation or chemical processes. The problem of aggregative stability of solid-in-liquid dispersions is widely studied in colloid science where it was shown that the stability is controlled by surface forces acting between the particles [8,9]. In particular, attractive (e.g. van der Waals) interactions facilitate aggregation of particles, whereas repulsive (e.g. electrostatic or steric) forces tend to prevent them from aggregation. Quantitative description of particle interactions and aggregation in liquids is usually based on the approach, pioneered by Derjaguin, Landau, Verwey and Overbeek (DLFO theory) [10,11]. After their foundational studies many efforts were devoted to the derivation of equations describing the dependence of attractive and repulsive forces on the distance between the particles under various conditions. However, the application of these equations to the case of nano-particle systems is not that straightforward. This is a consequence of commensurability of the particles size and the characteristic distances where the surface forces are acting, which makes inapplicable some common approximations.

The most important forces, stabilizing the dispersions, are repulsive electrostatic forces that arise because the particle surfaces are usually charged. The particle charge depends on the ionic composition of solution surrounding them, and near the so-called iso-electric point the dispersion loses its stability. Therefore, obtaining information on the particle charge under various conditions is very important for understanding and controlling the dispersion stability. A common approach to the relevant information about the particle charge is via electrokinetic measurements, in particular via the measurements of their electrophoretic mobility in solutions. However, the interpretation of such measurements for nano-sized particles is especially complicated.

Electrophoretic transport is driven by the electric forces acting on the interfacial charges. The role of interfacial charges in the suspension aggregative stability amounts to the electrostatic repulsion between the similarly charged particles, which decreases the frequency of “successful” collisions of particles participating in Brownian motion and thus the rate of coagulation. Thus, both electrophoretic transport and aggregative stability of suspensions are controlled by the interfacial electric charge.