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Electrophoresis in strong electric fields

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ABSTRACT

Two kinds of non-linear electrophoresis (ef) that can be detected in strong electric fields (several hundred V/cm) are considered. The first ("classical" non-linear ef) is due to the interaction of the outer field with field-induced ionic charges in the electric double layer (EDL) under conditions, when field-induced variations of electrolyte concentration remain to be small comparatively to its equilibrium value. According to the Shilov theory, the non-linear component of the electrophoretic velocity for dielectric particles is proportional to the cubic power of the applied field strength (cubic electrophoresis) and to the second power of the particles radius; it is independent of the zeta-potential but is determined by the surface conductivity of particles. The second one, the so-called "superfast electrophoresis" is connected with the interaction of a strong outer field with a secondary diffuse layer of counterions (space charge) that is induced outside the primary (classical) diffuse EDL by the external field itself because of concentration polarization. The Dukhin–Mishchuk theory of "superfast electrophoresis" predicts quadratic dependence of the electrophoretic velocity of unipolar (ionically or electronically) conducting particles on the external field gradient and linear dependence on the particle's size in strong electric fields. These are in sharp contrast to the laws of classical electrophoresis (no dependence of V_{ef} on the particle's size and linear dependence on the electric field gradient). A new method to measure the ef velocity of particles in strong electric fields is developed that is based on separation of the effects of sedimentation and electrophoresis using videoimaging and a new flowcell and use of short electric pulses. To test the "classical" non-linear electrophoresis, we have measured the ef velocity of non-conducting polystyrene, aluminium-oxide and (semiconductor) graphite particles as well as *Saccharomice cerevisiae* yeast cells as a function of the electric field strength, particle size, electrolyte concentration and the adsorbed polymer amount. It has been shown that the electrophoretic velocity of the particles/cells increases with field strength linearly up to about 100 and 200 V/cm (for cells) without and with adsorbed polymers both in pure water and in electrolyte solutions. In line with the theoretical predictions, in stronger fields substantial non-linear effects were recorded ($V_{ef}{\sim}E^3$). The ef velocity of unipolar ion-type conducting (ion-exchanger particles and fibres), electron-type conducting (magnesium and Mg/Al alloy) and semiconductor particles (graphite, activated carbon, pyrite, molybdenite) increases significantly with the electric field ($V_{ef}{\sim}E^2$) and the particle's size but is almost independent of the ionic strength. These trends are inconsistent with Smoluchowski's equation for dielectric particles, but are consistent with the Dukhin–Mishchuk theory of superfast electrophoresis.

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1. Introduction

Electrophoresis arises when charged colloidal particles or macromolecules are subjected to an outer electric field, and under the effect of this field the particles/molecules begin to move in respect to the liquid. It is widely used in colloid chemistry as a method for characterization of the surface of particles, for removal of dispersed particles from liquids, in biology and medicine to separate different biocolloids, macromolecules of proteins, in technology of coating, etc. Electrophoresis was discovered in 1808 by Prof. F. Reuss at the Moscow University. The classical theory of electrophoresis was developed by Smoluchowsky, it is based on the analogy between the hydrodynamic and electric fields. He derived a formula for calculation of the electrokinetic potential (ζ) of particles from the velocity of electrophoretic movement of particles or velocity of electroosmotic flow a liquid through a granulated (dispersed) media [1]:

$$\nu_{\mathrm{eph}} = \varepsilon\zeta E/4\pi\eta, \tag{1}$$

where ν_{eph} is the velocity of electrophoresis/electroosmosis, E is the external field gradient (V/cm), ε is the permittivity of the medium, η is the viscosity of the medium and ζ is the value of the electrokinetic potential (mV) which is in fact the coefficient of proportionality in the $\nu_{\mathrm{eph}}=f(E)$ dependence. This expression is valid for non-conducting particles or particles with lower conductivity than the medium and having thin electrical double layers ($\kappa a >> 1$, here κ is the reciprocal Debye length and a is the radius of particles). The proportionality between ν_{eph} and E is held for small electrical field gradients, typically several V/cm. It should be noted that according to the classical theory, the ef velocity does not depend on the particles shape and size.

2. Brief theoretical considerations

Electrophoresis is linear when the velocity of electrophoretic movement of particles is proportional to the strength of the applied field:

$$\nu_{\mathrm{eph}} = \mu_{\mathrm{eph}}E \tag{2}$$

As mentioned, this relationship is valid for sufficiently small field strengths only. The field-independent electrophoretic mobility μ_{eph} depends on the characteristics of the electric double layer (EDL) of the particle, mainly on its zeta-potential and surface conductivity, and on the concentration and viscosity of the electrolyte surrounding the particle. The calculation of μ_{eph} is the most common goal of the theory of electrophoresis. Dukhin and Semenikhin [2] derived an analytical expression of the electrophoretic mobility for the case of thin double layers. Their theory, which takes into account all the processes related to the concentration polarization of the EDL, uses a model that considers that all the kinetic parameters of the EDL, including the surface conductivity, are only related to the diffuse part of the EDL. This theory was later modified [3,4], introducing a “model-less” parameter for the surface conductivity K^{σ}, reflecting the contributions of any structures of the thin double layer besides its diffuse part: “stagnant layer”, Stern layer, etc. This modification was attained at the expense of neglecting the relatively small capillary osmotic contribution to the surface current.

We distinguish two kinds of non-linear electrokinetic phenomena. The first is due to the interaction of the outer field with field-induced ionic charges under conditions, when field-induced variations of electrolyte concentration remain to be small comparatively to its equilibrium value [5]. The second one, the “electrophoresis of the second kind” or “superfast electrophoresis” is connected with the interaction of a strong outer field with a secondary diffuse layer of counterions (space charge) that is induced outside the primary (classical) diffuse EDL by the external field itself because of concentration polarization [6,7].

Below the main theoretical considerations describing this phenomena and our resent data on non-linear electrophoresis of dielectric dispersed particles and superfast electrophoresis of unipolar conducting particles are described. So, our review is not a review of the literature at large but of our own pioneer results on electrophoresis of conducting and non-conducting particles of different nature and size in strong electric fields. It should be mentioned that other approaches can be used for studying the non-linear electrophoresis. For example, aperiodic electrophoresis allows us to study non-linear effects only, cutting off the linear parts [8,9]. New possibilities for elaboration of the phenomenon provide the investigation of electrophoresis at large Pecklet numbers [10].

2.1. “Classical” non-linear electrophoresis

It is due to the interaction of strong electric fields with the charges of the “classical” diffuse double layer of non-conducting dispersed particles. As soon as the strength of the applied field increases, the processes that are non-linear with respect to E start playing an even important role, determining a noticeable non-linearity of the dependence $v_{\mathrm{eph}}(E)$. The influence of non-linearity appears in higher than first order terms in the expansion of v_{eph} in powers of E. Electrophoretic mobility v_{eph} is an odd function of E and, correspondingly, even powers of E are absent in the expansion of v_{eph}. It follows from the fact, that a change in the sign (direction) of applied field without changing its absolute value gives rise to a change in the sign of the electrophoretic velocity, without changing its absolute value. Hence, the term that follows the linear electrophoretic term in the expansion of electrophoretic velocity, is cubic with respect to applied field:

$$v_{\mathrm{eph}} = \mu_{\mathrm{eph}}E + \mu_{\mathrm{eph}}^{(3)}E^3, \tag{3}$$

where the coefficients μ_{eph} and $\mu_{\mathrm{eph}}^{(3)}$ are field-independent.

An expression for $\mu_{\mathrm{eph}}^{(3)}$, which characterizes the cubic electrophoresis, for spherical particle with thin double layer for the case of symmetrical electrolyte $z^+=z^-=1$ has been derived (see in detail [5]). This problem was solved following the procedure of successive approximations in powers of the small parameter E [11,12]. The first step of this procedure consists in considering the action of an external field and of the fields, corresponding to system's linear response on the equilibrium distribution of ions. It leads to the well-known result of linear polarization of the EDL: field-induced deviations of the distributions of the electric potential and electrolyte concentration, both proportional to the first power of the external field. The second step consists in considering the interactions between these field-induced deviations of the electric potential and electrolyte concentration with each other, leading to the appearance of potential and ion concentration distributions that are proportional to the second power