



## Double layer electrical conductivity as a stability criterion for concentrated colloidal suspensions



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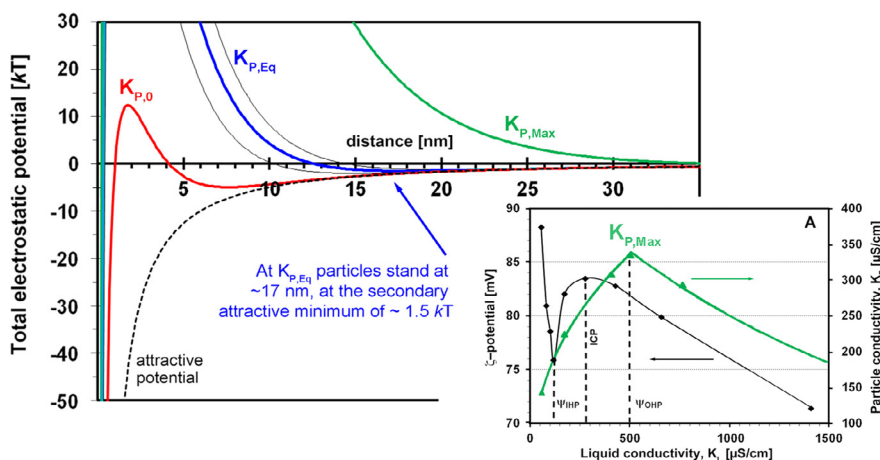
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### HIGHLIGHTS

- Relationship between particle electrical conductivity and DLVO colloidal stability.
- Identified processing window for the stability control of concentrated suspensions.
- DLVO secondary attractive minimum lies at 1.5 kT for the equilibrium conductivity.
- At the minimum reversible distance (~7 nm) particles conductivity is zero.
- More accurate measurement of static  $\zeta$ -potential at the isoconductivity point.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The slightly attractive inter-particle equilibrium potential associated with electrostatically stabilized suspensions of minimum viscosity is described by the DLVO theory and commonly gauged by static  $\zeta$ -potential measurements, plagued with experimental uncertainties. In this work, the electrokinetic mobility of alumina particles was measured in suspensions prepared with selected solids content and ionic strength, as well as was the electrical conductivity of each suspension and suspending liquid. Particles electrical conductivity was then calculated and related to the colloidal stability described by the DLVO theory, enabling the identification of a processing window for the stability control of concentrated suspensions. The maximum repulsive potential and distance between particles (~46 nm) corresponds to the particles maximum conductivity. When the particles conductivity is zero, the diffuse layer is fully collapsed and they stand at the minimum reversible distance (~7 nm). At the equilibrium conductivity, a potential curve is produced with a secondary attractive minimum of ~1.5 kT at an inter-particle distance of ~17 nm, as suggested by the DLVO theory and the Equipartition of Energy theorem. The condition for accurate measurement of static  $\zeta$ -potential occurs at the isoconductivity point between particles and suspending liquid.

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### 1. Introduction

The manipulation of nanoscale particles often requires the control of the mobility of suspended particles, which is the underlying

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feature of many processing methods in a variety of key applications. These range from catalysis and biosensing to remediation of surface and subsurface oceanic oil spills, through centuries old slip casting of ceramic suspensions [1–7].

The key challenge in such processing methods is the ability to prepare stable suspensions of the starting powders, so they all rely on the comprehension of colloidal interactions and stability of concentrated suspensions. Colloidal interactions are determined by inter-particle forces and can be manipulated by changes on the electrolyte (suspending liquid) or by surface functionalization, in order to promote specific characteristics (e.g. protein, cell or bacteria adsorption on surgical tools and medical implants, particle wettability by conflicting solvents, environmentally benign stable emulsions, electrophoretic deposition of films and coatings).

Particularly, it is important to know how the individual powder particles are spatially arranged within the suspension, for how long that arrangement is kept (i.e. colloidal stability) and how it propagates through the consolidation method into the green body, after removal of the suspending liquid. The need to remove the suspending liquid also explains why concentrated suspensions are generally preferred.

Colloidal electrostatic stability is characteristic of dispersed suspensions with comparatively low solids loads [1–4] and is usually explained by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory for the interactions between charged particle pairs [8,9]. Upon immersion in a polar liquid, adsorption or desorption of ionic species in solution, as dictated by the reaction constants of the corresponding dissociation equilibria, results in the development of electrical charges at the particles surface. As a consequence, ions of opposite charge are sequentially attracted to the particle surface, causing the development of a charged electrical double layer (internal Stern layer and outer diffuse layer) enveloping each particle. According to the DLVO theory, the total potential interaction energy between particle pairs results from the balance established between the repulsive potential, due to the electric charges present in the particles electrical double layer, and the attractive potential, due to the ever present long range London–van der Waals interactions (dispersion forces). When the repulsive potential is high, the total potential remains positive even for long separation distances and these suspensions are stable and unlikely to coagulate. If the repulsive potential decreases, a shallow attractive secondary minimum can be observed and particles tend to cluster at this distance (but strong short-range repulsive forces keep the particles from direct contact). By manipulating the ionic strength of the suspending liquid, hence, the thickness of the electrical double layer, the repulsive potential can be reduced enough as to destroy the repulsive energy barrier that opposes coagulation. This destabilizes the system and leads to flocculation (particles fall into a deep attractive primary minimum). The stability of dispersed suspensions was found to begin at the equilibrium inter-particle distance that corresponds to the net electrical potential within the DLVO shallow attractive secondary minimum and is usually associated with minimum viscosity.

In essence, the diffuse layer controls particle interactions and its electrical potential is estimated, in practice, in electrokinetic particle mobility tests carried out as function of varying pH. In these experiments the potential value at the “interface” between double layer and electrolyte, called zeta-potential ( $\zeta$ -potential), is measured. Suspensions stability is associated with high  $\zeta$ -potential, whereas flocculation is bound to occur at the isoelectric point (zero  $\zeta$ -potential) [10–17].

Commonly, static (electrophoresis)  $\zeta$ -potential is used but the values obtained are very sensitive to the experimental procedures. To overcome the experimental-related uncertainties encountered in static  $\zeta$ -potential measurements, different models, usually complex and with different limitations, and alternative measurement

techniques were proposed to describe and calculate the value of  $\zeta$ -potential. The measurement of particles mobility in Electrokinetic Sonic Amplitude (ESA)  $\zeta$ -potential tests offers the access to changes in the ionic envelope of the particles double layer and the choice of calculation model [12,15].

Generally, the Helmholtz–Smoluchowski model is used, the major assumption in which is that particles are non-conducting, electrical conduction being carried out only by the suspending liquid. The model requires that the ionic strength is high enough to ensure thin double layers and proposes a limiting value  $\kappa a > 100$  ( $a$  is the particle radius and  $\kappa^{-1}$ , the inverse Debye length, is its double layer thickness). In such cases, changes in the conductivity through the electrical double layer and the effects of the presence of added counter-ions and nonspecific adsorption become less important and might be neglected [10,11]. Other models were developed to describe  $\zeta$ -potential for dilute suspensions and thick double layers ( $\kappa a \approx 1$ ), to include the effects mentioned above and other observed deviations from the original DLVO model [18–24]. Among those, O'Brien's model, which considers both the electrical conductivity contribution of the diffuse layer and that of the suspending liquid, is frequently the preferred alternative [21]. Despite the different assumptions, both Helmholtz–Smoluchowski's model and O'Brien's propose a decrease of  $\zeta$ -potential with increasing  $\kappa a$  (increasing ionic strength in the suspending liquid) as the result of the compression of the diffuse layer.

Changes in ionic strength in the suspending liquid also result in changes in its electrical conductivity. Electrical conductivity phenomena are less affected by the measurement technique [25–27] and can be described by generally simpler models.

Previous work [28] carried out with aqueous suspensions of commercial  $\alpha$ -alumina (1–35 vol.% solids) showed that the change in the conductivity of the suspension  $K_S$  relative to that of the suspending liquid  $K_L$  (i.e. relative conductivity,  $K_S/K_L$ ) could be described by Maxwell's model for the conductivity of a mixture of two phases (such as suspensions, made of the continuous suspending liquid and the dispersed particles) as a function of the ratio  $\alpha$  between the particles conductivity  $K_P$  and that of the electrolyte  $K_L$  (i.e. conductivity ratio  $\alpha = K_P/K_L$ ) and the solids volume fraction  $\phi$ . More elaborate analytical models have been devised to theoretically predict the relationships between the relative conductivity and particle volume fraction and salt concentration [29] but Maxwell's approach, which remains essentially correct, offers the benefit of experimental simplicity.

In Maxwell's model, for a given  $\alpha$ , the relative conductivity varies according to  $K_S/K_L = 1 + \Delta K \cdot \phi$ , i.e. linearly with  $\phi$ . Three special cases can be considered for the line slope  $\Delta K$ , depending on  $\alpha$ : (1) when  $K_P \ll K_L$  (insulating particles,  $\alpha \rightarrow 0$ ), then  $\Delta K = -1.5$ ; (2) when the particles and the electrolyte have equal conductivities ( $\alpha = 1$ ),  $\Delta K = 0$ ; and (3) when  $K_P \gg K_L$ , (conductivity of the particles much higher than that of the electrolyte,  $\alpha \rightarrow \infty$ ),  $\Delta K = 3$ . Thus, an increase in the solids content might decrease, not affect, or increase the suspension conductivity, which can be lower than, equal to, or higher than that of the suspending liquid. In other words, Maxwell's model for the conductivity of suspensions shows that paradoxical effects can occur: the addition of dielectric particles can result in increased suspension conductivity.

The slope of the straight line in Maxwell's model for the relative conductivity,  $\Delta K = (K_S - K_L)/(K_L \cdot \phi)$ , which is called relative conductivity rate or electrical conductivity increment, was interpreted in terms of the DLVO theory and the particles double layer parameter  $\kappa a$ . As  $\kappa a$  changes in response to the changes in the ionic strength of the suspending liquid, so does the conducting to insulating character of the particles (expressed by  $\alpha$ ) and, as such, their contribution to the suspension conductivity (expressed by  $\Delta K$ ).

This work is aimed at throwing further light into the use of  $\Delta K$  as a suspension stability criterion and its interpretation in the light

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