Complete Concentration Dependence of the Electro-Phoretic Mobility of Charged Spheres in Realistically Salt Free Suspensions

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We considerably extended the accessible range of concentrations for optical investigations of colloidal electro-kinetics using super-heterodyne Doppler velocimetry with multiple scattering correction. We performed measurements of electro-phoretic mobility and DC conductivity of aqueous charged sphere suspensions under realistically salt free conditions covering more than three orders of magnitude in particle number densities, \(n\), and up to transmissions as low as 40\%. At low \(n\), the mobility shows an increase with \(n\), then plateaus at intermediate \(n\), and finally decreases at large \(n\). Our study reconciles previous experimental observations made on restricted concentration ranges, and thus demonstrates the existence of a generic density dependence of the electro-phoretic mobility. Comparison to state of the art electro-kinetic theory suggests its relation to a density dependent particle charge.
Introduction

Electro-kinetic effects are of a great importance for many physicochemical, biological and industrial issues, ranging from signaling in nervous fibers over suspension processing and stability to desalination of seawater. The concentrations of colloidal particles in such studies vary over several orders of magnitude, depending on the focus of interest. The density dependence of electro-kinetic effects is therefore of great fundamental and practical interest.

The theory of electro-kinetic effects, the so-called standard electro-kinetic model (SEM) is well established, and IUPAC recommendations give standard protocols for measurement procedures and conversion of measured mobilities to ζ-potentials or charges [1]. Few effects escaping mean field treatment (e.g. charge reversal observed in electrolytes with multi-valent ions [2, 3, 4]) can be approached by primitive level calculations and simulations including full hydrodynamics [5]. In general, the SEM set of coupled equations can be solved under given boundary conditions either analytically or numerically [6, 7, 8, 9]. Both requires the previous resolution of the Poisson–Boltzmann equation (PB) within some cell-model calculation [10, 11, 12]. If necessary, further account can be made for charge regulation [13] and/or the double layer storage capacity for electrolyte ions [14]. Recent developments of SEM also include realistically salt free conditions, i.e. they account for counter-ions released by the particles themselves, for solvent hydrolysis and the formation of carbonic acid from dissolved neutral CO₂ [15, 16].

An important unsolved problem, however is the particle concentration dependence of the electro-phoretic mobility. Very early, Dunstan, Rosen and Saville reported some indications for a maximum of the mobility at low volume fractions and low salt concentrations, but at the same time, they stressed the strong dependence of their observations on sample conditioning [17]. This necessitated the implementation of advanced conditioning methods [18] providing a flexible adjustment of particle and electrolyte concentration under precise in situ conductometric control. Subsequent studies on small, strongly interacting particles reported a mobility plateau followed by a decrease towards large concentrations [19, 20]. The decrease apparently started at the onset of counter-ion domination [21]. Other studies on more dilute suspensions of large particles, however, showed a slow increase followed by a plateau [22, 23]. This type of somewhat counter-intuitive number density dependence was also found in studies on silica particles at elevated salt concentrations [24]. The latter investigations are complemented by studies on isolated particles in either aqueous [25, 26, 27] or organic solvent [28] where very small mobilities were observed. Moreover, these studies also revealed that charge renormalization (compensating for neglecting finite ion sizes in mean field by a reduced renormalized charge \( Z_{\text{eff}} \) smaller than the bare charge \( Z \) [29, 30]) applies also under conditions approaching infinite dilution [31]. Low limiting mobility, increase and plateau have been observed in systems of different surface chemistry and various background electrolyte concentrations \( 10^{-6} \leq c_S \leq 10^{-2} \text{ mol L}^{-1} \) [32]. No clear correlation of experimental boundary conditions to the cross-over from increase to a constant value was observed, but several studies suggested a possible correlation to the onset of double layer overlap and/or of structure formation [21, 23, 33].
All these earlier studies were restricted in their range of accessible particle concentrations by the loss of signal at low concentrations and by multiple scattering at large concentrations. Another complication often arose from the freezing transition [34].

In the present paper we present the first systematic study over a sufficiently large range of volume fractions to catch both effects centered about a broad plateau maximum. This includes both highly dilute samples and the densely packed crystalline state. We employ a recently introduced novel variant of Super-Heterodyne Laser Doppler Velocimetry (SH-LDV) [35]. In integral small angle configuration, this instrument is capable to yield multiple scattering (MS) free electro-phoretic mobilities over several orders of magnitude in concentration (volume fraction $\Phi$ related to particle number density $n$ as $\Phi = n(4\pi/3)a^3$ with $a$ being the particle radius). Moreover it allows for simultaneous measurements of electro-osmotic mobilities [36]. In that study, we worked with initially deionized samples that were subsequently exposed to ambient air. The preliminary results supported the suggestion of a mobility maximum but no precise control of the electrolyte concentration was applied at that stage. In the present study, we therefore combine Super-Heterodyne Dynamic Light Scattering (SH-DLS) with advanced preparation techniques, and we complement our mobility experiments by simultaneous measurements of the DC conductivity and the suspension turbidity.

In what follows we shortly describe the experimental procedures and conditioning protocols. We present our results and compare them to previous findings. We then evaluate them using the standard electro-kinetic model (SEM) for realistically salt free conditions and constant surface charge density [16]. In the plateau region, we can give a consistent interpretation of our experimental mobilities assuming: i) a constant saturated CO$_2$ background, ii) a non-renormalized charge for the quartz cell wall, and iii) a renormalized charge for the carboxylate modified particles consistent with the one derived from conductivity. Off the plateau we find mobility values lower than expected for a constant surface charge and thus conclude an underlying density dependence of the bare particle charge $Z$. We close with some remarks on possible mechanisms for charge reduction and a short outlook to ongoing experiments.

**Experimental**

**Samples and sample conditioning**

We used commercial polystyrene latex spheres, stabilized by carboxyl surface groups (lab code PS260(mP), Lot PS-F-L2208, microParticles GmbH, Berlin, Germany). We obtained hydrodynamic particle diameters of $2a_h = (268\pm2)$ nm by standard DLS and geometric diameters of $2a_{SLS} = (254\pm4)$ nm from the static form factor measurements. The polydispersity index given by the manufacturer is $PI = 3.1\%$.

All measurements were conducted in a climatized lab at an ambient temperature $\vartheta = (25.2\pm0.2){\degree}\mathrm{C}$ Dispersions were conditioned in a closed circuit system [18] The sample is continuously deionized, while passing through a mixed bed ion-exchange resin filled column (IEX, Amberlite K306, Carl Roth GmbH Co. KG, Karlsruhe, Germany). The IEX column can be bypassed after attaining fully deionized conditions. An integrated DC conductometric cell (electrodes LR325/01 bridge LF340i, $f_M = 400$ Hz, WTW, Germany) allows
monitoring the residual ion concentration and detecting of impurity leaks. The leakage rates of the circuit were determined from measurements with pure water.

Deionizing for sufficiently long times (e.g. 15 min for 30 ml of suspension) yields the measured conductivity of $\sigma_{\text{min}} = (60-65) \text{nS cm}^{-1}$, corresponding to a concentration of carbonate ions of $1.5 \times 10^{-8} \text{ mol L}^{-1}$ or a residual concentration of dissolved $\text{CO}_2$ of $6.5 \times 10^{-8} \text{ mol L}^{-1}$. The typical duration of an electro-kinetic experiment is 15 min, during which leakage of the $\text{CO}_2$ from the ambient air into the circuit occurs. We further checked that the conductivity increase in a measuring cell isolated from the rest of the circuit by two-way valves is about one order of magnitude slower than in the complete circuit with its many tubing connections. In isolated cells, $\text{CO}_2$ leakage from external sources is therefore negligible as compared to the increase of the minimum conductivity by adding particles. However at finite $n$, we observe the conductivity rise to a significantly larger extend than in pure water. This shows that an additional source of $\text{CO}_2$ must be present. We attribute it to $\text{CO}_2$ stored by adsorption onto the particle surface [37]. To ensure well deionized conditions during the experiments, we therefore isolate the cells after circulating the suspensions a few minutes at constant minimal conductivity. The obtained minimal conductivities are displayed in Fig. 1a as a function of number density, $n$, as calibrated from the static light scattering on crystalline samples. Data show a linear increase at large $n$, but as expected level off towards low $n$. Data are not influenced by the freezing transition located at $n_f = (4.6 \pm 0.2) \times 10^{16} \text{ m}^{-3}$. For $n > 3 \times 10^{16} \text{ m}^{-3}$, and are well described by the linear dependence expected within Hessinger’s model of independent ion migration [38, 39], which returns an effective conductivity charge of $Z_{\sigma} = -2500 \pm 30$. We note in passing, that Hessinger’s model determines the effective number of freely moving counter-ions. For a comparison of these and other charge numbers using Alexander’s renormalized charge as a reference, see [29].

![Fig. 1: Suspension characterization. a) Number density dependence of the low frequency conductivity of realistically salt free PS260(mP). The data are corrected for the nominal contribution of water hydrolysis $\sigma_{\text{H}_2\text{O}} = 55 \text{nS cm}^{-1}$ at $\theta = (25.2 \pm 0.2)^\circ \text{C}$. The freezing density $n_f$ is indicated as vertical dashed line. Starting from $n = 3 \times 10^{16} \text{ m}^{-3}$, data show a linear $n$-dependence. The dashed line is a fit of the independent ion migration model [38] returning $Z_{\sigma} = -2500 \pm 30$. Inset: Laue pattern of an oriented bcc crystal forming at](image-url)
For turbidity measurements, a laser beam ($\lambda = 633$ nm) passes through a rectangular optical cell, and the light transmittance is measured by a power meter (PM, LabMax-TO, Coherent Inc., USA). Experiments were done at the background electrolyte concentration adjusted to $c = 6.3 \times 10^{-6}$ mol L$^{-1}$ to obtain fluid ordered samples. Results are displayed in Fig. 1b. The transmitted light obeys the Beer-Lambert attenuation law $-\ln(I/I_0) = 2d \sigma_n$ [40]. Here, $I$ and $I_0$ are the transmitted and the incident intensity, $d$ is the cell thickness, A fit using a refractive index of $\nu = 1.59$ returns an attenuation cross section $\sigma_{633} = (6.5 \pm 0.4) \times 10^{-3}$ $\mu$m$^2$ corresponding to a particle diameter of $2a = (247 \pm 16)$ nm in a good agreement with the optical radius from SLS.

**Electro-kinetic measurements**

Electro-kinetic experiments were conducted in the range of linear attenuation, corresponding to moderate MS, i.e. less than 5 scattering events per photon [35]. We used U-shaped quartz cells with rectangular optical cross-sections (EL10 by Rank Bros., Bottisham, Cambridge, UK or replica by Lightpath Optical Ltd., Milton Keynes, UK) and various thicknesses $2d$. The cells were cleaned by heating in a flame of a gas burner for some 15 min, letting to cool and successive sonication for 60 min at 35°C in 2% alkaline detergent solution (Hellmanex III, Hellma Analytics). They were further rinsed with milli-Q water and dried in a nitrogen stream. We used platinized platinum electrodes. For each cell, the effective electrode distance $l$ was calibrated using standard KCl solutions and is on the order of some 7 cm. To avoid accumulation of particles at electrodes, AC square-wave fields of $E = 10 – 45$ V cm$^{-1}$ and $f_{AC} = (0.02 – 0.1)$ Hz were utilized.

Super-heterodyne Dynamic Light Scattering (SH-DLS) is a novel variant of heterodyne Laser Doppler velocimetry. The detailed description and characterization of the experimental setup, together with the corresponding scattering theory has been given elsewhere [33, 35, 36]. It is based on a standard heterodyne light scattering or Doppler velocimetry [41], but uses a super-heterodyning approach of side band modulated spectroscopy [42] or Phase Analysis Light Scattering (PALS) [43, 44] allowing isolation of the desired heterodyne signal component from the homodyne part and low frequency noise. Operating in the integral mode [45], it averages over the complete cell cross section at mid-cell height. The super-heterodyne (shet) spectrum is then directly proportional to the particle velocity distribution. Thus the velocity distribution is measured in a single run, instead of tedious point-by-point measurements and both the electro-phoretic and the electro-osmotic velocities can be obtained simultaneously. Moreover, any deviations from the ideal parabolic flow profile are seen immediately. As a small angle scattering experiment, it delivers spectra of suspensions at rest or under electro-kinetic flow irrespective of particle concentration and suspension structure [33]. The most important advantage, however, is the possibility to identify and correct for multiple scattering contributions to the Doppler spectra [35].
Fig. 2: Selected spectra normalized to maximum intensity. Applied voltage $U = 151$ V. a) Evolution of spectral shape with increasing $n$ as indicated. The cell depth (field strength) was $2d = 2$ mm for the six lower spectra ($E = 13.1$ V cm$^{-1}$), it was $2d = 0.5$ mm ($E = 25.0$ V cm$^{-1}$) for the upper three. b) Disappearance of the signal in the MS background and spectral distortion due to flow instability. c) Stable stationary multiphase flow for smaller cell depth. For details see text.

Fig. 3: Correction and evaluation of spectra. a) Example raw time averaged spectrum taken at $n = 3.34 \times 10^{16}$ m$^{-3}$, $E = 12.5$ V cm$^{-1}$ and $2d = 2$ mm. b) The same after subtraction of the MS Lorentzian and the static background. The solid line is a fit to the corrected data returning $v_{eo} = 91.25$ µm s$^{-1}$; $v_{ep} = 45.0$ µm s$^{-1}$, and $D_{eff} = 5.96 \times 10^{-12}$ m$^2$s$^{-1}$.

In Fig. 2a we display power spectra for increasing $n$. A broad multiple scattering contribution appears for $n \geq 2\times10^{16}$ m$^{-3}$ and gains in strength. It swallows the signal for $n \geq 4.5\times10^{16}$ m$^{-3}$ (Fig. 2b). Accidentally, here $n = n_F$, and a shear induced flow instability occurs, which strongly distorts the spectral shape [46, 47]. Using a thinner cells of $2d = 0.5$ mm the flow instability gave way to stationary flow of counter-propagating crystals at the walls and in the cell center, separated by a broad fluid region [48]. Also the amount of MS is reduced considerably (Fig. 2c). With further increasing $n$ the fluid gap is reduced forming a thin shear band at the
largest investigated $n$ (upper three spectra in Fig. 2a), while application of larger fields widens the gap again (not shown).

All spectra shown were obtained averaging over some hundred time intervals restricted to one field direction, starting after the full development of electro-osmotic flow profile and ending shortly before the field reversal. Fig. 3a displays a raw spectrum of a fluid sample. In Fig. 3b, we subtracted the static background and the MS contribution as obtained by fitting a Lorentzian to the wings of the MS-signal [34]. We then fitted the remaining signal by standard procedures [35]. In crystalline samples, we followed [20] and varied the vertical location of the scattering plane ($y$-direction) during each measurement series at constant field strength. Then the electrophoretic mobilities derives as double average of velocities over the complete cross section of the cell. Note that this inhibits evaluation of electro-osmotic velocities. For each particle concentration, up to seven different field strengths were applied and velocities plotted versus $E$. The mobilities $\mu_{ep} = v_{ep}/E$ and $\mu_{eo} = v_{eo}/E$ were then obtained from linear fits to the data.

**Standard Electro-kinetic Model for realistically salt free conditions**

We performed calculations within SEM for realistically salt free concentrated suspensions. We have used a mean-field approach with a cell model scenario to account for the electro-hydrodynamic interactions between charged spherical particles in an average sense. This theoretical approach encompasses studies of many electro-kinetic phenomena in concentrated colloids as the electrophoresis [49, 50], electric permittivity [51], electro-viscous effect [52, 53] or electroacoustic phenomena [54, 55]. The cell model concept has been rigorously studied in the review by Zholkovskij et al. [56]. A spherical cell is composed by a particle of radius $a$ at its center surrounded by a fluid layer with an outer radius $b$. The particle volume fraction $\Phi$ of the suspension determines the outer radius $b$ of the cell, as it is obeyed that the particle volume fraction calculated in the ambit of the cell coincides with that of the whole suspension according to Happel boundary condition [57]: $\Phi = (a/b)^3$. It is admitted that the suspension properties can be obtained from appropriate averages of local properties in the cell where also appropriate boundary conditions at the outer cell surface are imposed to manage with electro-hydrodynamic interactions. The particle is characterized by a surface charge density $\sigma$, and the solution contains added counterions released by the particles by dissociation of surface groups responsible for the particle charging process. Apart from the added counterions species, that will be assumed in this work as $\text{H}^+$, if the particles are negatively charged, or $\text{OH}^-$ if positively charged, there are also ions from different sources as $\text{H}^+$ and $\text{OH}^-$ from water dissociation, and $\text{H}^+$, bicarbonate anions $\text{HCO}_3^-$ and neutral carbonic acid molecules $\text{H}_2\text{CO}_3$, from the atmospheric $\text{CO}_2$ contamination. According to the solubility and partial pressure of $\text{CO}_2$ in standard air at 25°C, the concentration of $\text{CO}_2$ in water is $1.18 \times 10^{-5}$ mol L$^{-1}$. The chemical reactions in the realistic salt-free aqueous solution are:
\[ H_2O \xrightleftharpoons[k_{i1}]{k_{-i1}} H^+ + OH^- \]
\[ H_2CO_3 \xrightleftharpoons[k_{i2}]{k_{-i2}} H^+ + HCO_3^- \]
\[ H_2CO_3 \xrightleftharpoons[k_{i3}]{k_{-i3}} CO_2 + H_2O \]  
\[ K_i \text{ and } K_{-i} \ (i=1, 2, 3) \] are the corresponding forward (s\(^{-1}\)) and backward (m\(^3\)s\(^{-1}\)) kinetic constants.

We will review here the main theoretical aspects of the electro-kinetic cell model for concentrated suspensions in realistically salt-free conditions in a static electric field \( E \), which is the DC limit of the general electro-kinetic model of the dynamic electrophoretic mobility and dielectric response in AC electric fields \[58\].

The fundamental equations connecting the electrical potential \( \Psi(r) \), the number density of each species, \( n_j(r) \), their drift velocity \( v_j(r) \), the fluid velocity \( v(r) \), and the pressure \( P(r) \) are:

\[ \nabla^2 \Psi(r) = -\frac{\rho_{el}(r)}{\varepsilon_n \varepsilon_0} \]  
(2)

\[ \rho_{el}(r) = \sum_{k=1}^{3} z_k e n_k(r) \]  
(3)

\[ \eta_s \nabla^2 v(r) - \nabla P(r) - \rho_{el}(r) \nabla \Psi(r) = 0 \]  
(4)

\[ \nabla \cdot v(r) = 0 \]  
(5)

\[ v_j(r) = v(r) - \frac{D_j}{k_BT} \nabla \mu_j(r) \quad (j=1,\ldots,4) \]  
(6)

\[ \mu_j(r) = \mu_j^\infty + z_j e \Psi(r) + k_BT \ln n_j(r) \quad (j=1,\ldots,4) \]  
(7)

\[ \nabla \cdot [n_j(r)v_j(r)] = \sigma_j(r) \quad (j=1,\ldots,4) \]  
(8)

Here, \( r \) is the position vector in a reference system fixed at the particle center. Also, \( j=1 \) stands for \( H^+ \), \( j=2 \) for \( OH^- \), \( j=3 \) for \( HCO_3^- \) and \( j=4 \) for the neutral species \( H_2CO_3 \). Eq. (2) is Poisson’s equation, where the electric charge density \( \rho_{el} \) is given by Eq. (3). \( \varepsilon_n \), \( \varepsilon_0 \) and \( e \) are the relative permittivity of the solution, the permittivity of a vacuum and the elementary electric charge, respectively, and \( z_k \) is the valence of the \( k \)-th ion.

Eqs. (4) and (5) are the Navier-Stokes equations for an incompressible fluid flow of viscosity \( \eta_s \) and mass density \( \rho_s \) at low Reynolds number in the presence of an electrical body force. Eq. (6) derives from the Nernst-Planck equation for the flow of each \( j \)-th species. Eq. (7) stands for the electro-chemical potential where \( \mu_j^\infty \) is its standard value, \( D_j \) its diffusion coefficient, \( k_B \) the Boltzmann constant and \( T \) the absolute temperature. Eq. (8) is the continuity equation that allows for the conservation of chemical species even if they are generated or annihilated by chemical reactions. The latter aspects are represented by the following generation-recombination functions \( \sigma_j(r), \ (j=1,\ldots,4) \), for ions and neutral molecules involved in chemical reactions:
\[ \sigma_i(r) = \sigma_{ri}(r) + \left[ K_i n_{ri0}(r) - K_i n_{ri}(r) n_{ri}(r) \right] + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] \]
\[ \sigma_i(r) = \sigma_{ri}(r) + \left[ K_i n_{ri0}(r) - K_i n_{ri}(r) n_{ri}(r) \right] + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] \]
\[ \sigma_i(r) = \sigma_{ri}(r) + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] \]
\[ \sigma_i(r) = \sigma_{ri}(r) + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] \]
\[ \sigma_i(r) = \sigma_{ri}(r) + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] + \left[ K_i n_{riC0}(r) - K_i n_{riK0}(r) n_{ri}(r) \right] \]

According to the procedure developed by Baygents and Saville for weak electrolytes [59].

The appropriate boundary conditions are:
\[ \Psi_p(r) = \Psi(r) \quad \text{at} \ |r|=a \]
\[ \varepsilon_0 \varepsilon \nabla \Psi(r) \cdot \hat{r} - \varepsilon_r \nabla \Psi_p(r) \cdot \hat{r} = -\sigma \quad \text{at} \ |r|=a \]
\[ v = 0 \quad \text{at} \ |r|=a \]
\[ v_j \hat{r} = 0 \quad (j = 1, \ldots, 4) \quad \text{at} \ |r|=a \]
\[ \langle (\rho_m v') \rangle = \frac{1}{V_{cell}} \int_{V_{cell}} (\rho_m v') (r') \, dV = 0 \]
\[ \omega = \nabla \times v = 0 \quad \text{at} \ |r|=b \]
\[ n_j(r) = n^0_j(r) \quad (j = 1, \ldots, 4) \quad \text{at} \ |r|=b \]
\[ \Psi(r) = \Psi^0(r) - \mathbf{E} \cdot \hat{r} \quad \text{at} \ |r|=b \]

At the particle surface \( |r|=r=a \), Eqs. (10) and (11) stand for the continuity of the electric potential and normal component of the displacement vector, \( \varepsilon_r \) being the relative permittivity of the particle (the sub-index \( p \) stands for the solid particle). Eq. (12) is the well-known non-slip condition for the fluid. Eq. (13) shows that the particle is impenetrable for ions and neutral molecules (\( \hat{r} \) is the radial unit vector pointing outwards to the particle surface). Eq. (14) states that the volume average of the macroscopic momentum per unit volume is zero [60], \( \rho_m \) standing for the local mass density, which equals \( \rho_s \) or \( \rho_p \) when the solution or the solid particle are called in the volume integral over the cell volume \( V_{cell} \), respectively, and being \( v' \) and \( r' \) the local velocity and position vector with respect to a fixed laboratory reference system. At the outer surface of the cell \( |r|=r=b \), Eq. (15) follows the Kuwabara null vorticity condition for the fluid velocity [61], and Eqs. (16) and (17) are Shilov-Zharkikh-Borkovskaya’s boundary conditions [62] for the concentrations of ions and neutral molecules, and of the electrical potential at the outer surface of the cell, respectively. An additional equation to close the problem comes from the equation of motion for the electro-neutral unit cell in the static case:
\[ \int_0^\theta [\sigma_{rr} \cos \theta - \sigma_{r\theta} \sin \theta] \cd \ 2\pi b^2 \sin \theta \ d\theta = 0 \]

Here, \( \sigma_{rr} \) and \( \sigma_{r\theta} \) are the normal and tangential components of the hydrodynamic stress tensor in spherical coordinates \( (r, \theta, \phi) \), with the polar axis \( (\theta = 0) \) parallel to the electric field.
The quantities with a superscript “0” in Eqs. (16) and (17) refer to equilibrium conditions (no applied electric field). The equilibrium electric potential and the equilibrium ionic concentrations are connected by the Poisson-Boltzmann equation (PB):

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\Psi^0}{dr} \right) + \frac{2}{r} \frac{d\Psi^0}{dr} = -\frac{\rho_{el}^0}{\varepsilon_r \varepsilon_0}
\]

\[
\rho_{el}^0(r) = \sum_{i=1}^{1} z_i e n_i^e(r) = \sum_{i=1}^{1} z_i e b_i \exp \left( -\frac{z_i e \Psi^0(r)}{k_B T} \right)
\]  

(19)

For each unknown coefficient \(b_k\), the local concentration of the \(k\)-th ionic species at the outer surface of the cell where the equilibrium electric potential is chosen to be zero: \(\Psi^0(b) = 0\). The equilibrium boundary conditions to solve the PB equation are:

\[
\left. \frac{d\Psi^0(r)}{dr} \right|_{r=b} = 0
\]

\[
\left. \frac{d\Psi^0(r)}{dr} \right|_{r=a} = -\frac{\sigma}{\varepsilon_r \varepsilon_0}
\]

(20)

To obtain the unknown coefficients \(b_k\), an iterative procedure must be used in connection with the equilibrium chemical equations and the electro-neutrality condition of the cell. A detailed study about the resolution method can be found in ref. [63, 64],

In addition, the electrophoretic mobility \(\mu_{ep}\) can be obtained from the boundary condition in Eq. (14) for the velocity, as the velocity \(v'\) in the cell is the particle velocity \(\mu_{ep}E\) when it refers to the solid particle [65]. The electro-kinetic equations with the mentioned boundary conditions have been numerically solved by using ODE Solver routines implemented in MATLAB©.

**Results**

We present the obtained \(n\)-dependence of the electro-kinetic mobilities for 19 different \(n\) in Fig. 4. Displayed data are averages over several independent conditioning runs for each particle concentration. The electrophoretic mobility increases from \(\mu_{ep} = 3.0 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}\) at \(n = 3 \times 10^{15} \text{ m}^{-3}\) to \(\mu_{ep} = 5.3 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}\) at \(n = 2 \times 10^{16} \text{ m}^{-3}\), then it plateaus up to \(n = 8.3 \times 10^{16} \text{ m}^{-3}\) from where it decreases again. In fluid samples, we also obtained the electro-osmotic mobility. Practically independent of the particle concentration, it stays constant at values close to \(\mu_{eo} = 7.2 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}\). Neither mobility is affected by the volume phase transition from fluid to bcc, similar to the behavior of the conductivity. One observes a small, but non-systematic scatter in the osmotic mobilities, which we attribute to the adsorption of colloids on the cell walls. We support this point by additional measurements with different freshly burned and cleaned quartz cells. In this case, the mobility reaches a limiting value of \(\mu_{eo} = 8.5 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}\) (dashed line in Fig. 4) independent of the cell thickness.
Fig. 4: Electro-kinetic mobilities as a function of $n$. The vertical dashed line indicates the fluid/crystal phase transition (F/C). The plateau value of electro-phoretic mobilities (yellow triangles) is $\mu_{ep} = 5.3 \times 10^{-8} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ (thick dashed line). The electro-osmotic mobility at the quartz cell (blue squares) wall is independent of particle concentration at a value of $\mu_{eo} = 7.2 \times 10^{-8} \text{m}^2\text{V}^{-1}\text{s}^{-1}$. Freshly burnt cells show slightly larger values independent of cell thickness (coloured symbols). The limiting electro-osmotic mobility is of $\mu_{eo} = 8.5 \times 10^{-8} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ (thin dotted line).

**Discussion**

We first compare to selected previous results obtained under similarly well controlled realistically salt free conditions. In fact, the electro-phoretic behavior of charged spheres, shown in Fig. 4, was partially described before in several studies. Indications of a maximum were obtained early [17]. Indirect evidence of an increase with $n$ was first reported by Deggelmann et al. [66]. The lack of detail as to both the latex cleaning and the interpretation of the mobility makes it difficult to discuss these data in relation to the present work.

The low-$n$-increase of $\mu_{ep}$ with $n$ was unequivocally demonstrated by Bellini et al. [22] for a low salt per-fluorinated latex system and later reported for polystyrene spheres [23]. In both studies the investigated range of $n$ was restricted due to sample crystallization. An increase was also seen at elevated salt concentrations in suspensions of small silica particles [24]. Medebach et al. [19] gave the first systematic report of a decrease of mobility with $n$ for spheres with smaller radii. Here insufficient single to noise ratio set a lower bound to the investigated range of particle concentrations. The decrease was later confirmed for spheres of about double that size [20]. A clear plateau-type maximum was first observed by Botin *et al.* [35]. However, also this latter study was performed only for a small limited number of different $n$ and without conductometric control. Fig. 5 shows a compilation of selected previous results for systems with precisely determined electrolyte content together with the data for PS260(mP). We note, that data taken under less quantified conditioning are excluded, but show qualitatively equivalent behavior. Following IUPAC recommendations, we
display mobilities in reduced units to eliminate the influence of solvent viscosity $\eta$, relative permittivity, $\varepsilon_r$, and temperature $T$: 

$$\mu_{\text{red}} = (\frac{3}{2}) \eta \varepsilon R k_B T$$

This data collection covers more than six orders of magnitude in $n$ and some four orders of magnitude in $\Phi$. The data show remarkable qualitative similarities, they either show an increase followed by a plateau, or a short plateau followed by a decrease; each over a restricted range of densities.

![Fig. 5 a and b: Particle concentration dependence of the reduced electro-phoretic mobility for different particle systems. a) log-log plot of $\mu_{\text{red}}$ against number density. The thin solid lines show power laws of exponent 0.25 and 0.31 for comparison. b) semi-log plot of $\mu_{\text{red}}$ against volume fraction $\Phi = n(4\pi/3)a^3$. The plots compare data of previous measurements and of this work. Salmon left triangles poly(n-butyl acrylate)-polystyrene (PnBAPS122, BASF, Ludwigshafen, Germany), $2a_h = (122\pm2)$ nm, $Z_{\text{eff}} = -750$ [20]; black right triangles: poly(n-butyl acrylate)-polystyrene (PnBAPS68, BASF, Ludwigshafen, Germany), $2a_h = (68\pm3)$ nm, $Z_{\text{eff}} = -450$ [19]; red down triangles: sulfate Polystyrene (PS, IDC, Portland Oregon) PS301, $2a_h = (322\pm4)$ nm $Z_{\text{eff}} = -2440$ [23]; yellow up triangles: carboxylate modified Polystyrene (PS260(mP), microParticles GmbH, Berlin, Germany) $2a_h = (269\pm6)$ nm, $Z_{\text{eff}} = -2500$, this study.]

By contrast PS260(mP) clearly shows both. For the first time, this behavior can be demonstrated for a single well-characterized particle species under carefully controlled conditioning. Our observation, in fact, reconciles the conflicting previous results on the type of particle concentration dependence of the electro-phoretic mobility of charged colloidal spheres. Our data strongly suggest that there is a generic density dependence for charged sphere mobilities at realistically salt free conditions: an increase at low $n$, followed by a plateau and a decrease at large $n$.

We next compare to predictions using the SEM for realistically salt free conditions. Present carbon dioxide is allowed to dissolve as carbonic acid, which in turn is subject to a dissociation equilibrium. In addition we consider both water hydrolysis and particle counter-ions to contribute to the overall electrolyte content. We address two limiting cases of $c(\text{CO}_2, \text{g}) = 6.5\times10^{-8}$ mol L$^{-1}$ (corresponding to the minimum conductivity obtained in pure water) and $c(\text{CO}_2, \text{g}) = 1.18\times10^{-5}$ mol L$^{-1}$ (corresponding to the saturation). We calculated the density dependent electro-phoretic mobility for latex particles of $2a_h = (268\pm2)$ nm for these limiting
cases. The colloid renormalized charge \( Z_{\text{eff}} = -2500 \) was taken from the conductivity measurements at elevated \( n \). Fig. 6 compares both predictions to the experimental data on PS260(mP).

The second calculation coincides favorably with the values of the plateau region, while the low salt calculation predicts a much larger mobility. However, the constant charge prediction does not meet the experimentally observed decrease towards small \( n \). Also on the large \( n \) side, the mobility values decrease. However, for the present particles, they decrease considerably faster and starting from lower concentrations than expected from the calculation with constant particle charge. By contrast, the large-\( n \) decrease in mobility of PnBAPS68 is well described by the present theory [15]. From this we conclude that in the present case: \( i \) charge renormalization applies; \( ii \) the effective charge is constant across the plateau; \( iii \) The \( \zeta \)-potential drops quickly both towards smaller and towards larger \( n \) which points at a density dependent bare charge.

Renormalization is theoretically expected for any situation with overlapping, but also for non-overlapping double layers [10, 12, 29, 31] and has been noted before in a number of comparisons of SEM calculations to experimental mobilities [20, 27, 28]. Assuming that the bare charge number is large enough to reach the renormalization limit [29], the amount of renormalization can be estimated from the dimensionless scaling parameter \( A \) via \( Z_{\text{eff}} = Aa(1+\kappa a)/\lambda_B \) [28]. Estimating \( A \) with the Bjerrum length in water of \( \lambda_B = 0.7 \) nm and the Debye-Hückel screening parameter \( \kappa = \frac{e^2}{\varepsilon_0 \varepsilon_m k_B T \sum_i n_i z_i} = 1.5 \times 10^6 \) m\(^{-1} \), we obtain \( A = 7.9 \), in good agreement with previous estimates based on the effective electro-kinetic charges of other highly charged latex spheres [30, 67].

![Fig. 6: Analysis of electro-phoretic mobilities for PS260(mP). Experimental \( \mu_{\text{ep}} \) are compared to two SEM calculations using the effective charge from conductivity \( (Z_{\text{eff}} = -2500) \) and the particle radius \( 2a_h = (268\pm2) \) nm as input. The concentrations of dissolved CO\(_2\) are set to the value derived from minimal conductivity of water in our circuit (dashed) and to the saturation value at 25.2°C (solid). The plateau region of the experi-](image)
mental mobility is met by the second prediction. Experimental mobilities drop below the prediction on both sides of the plateau.

A constant mobility is expected from our SEM calculations under realistically salt free conditions as long, as the effective charge stays constant and the salinity is dominated by the added electrolyte. Only for counter-ion dominance the mobility decreases with increasing $n$, as can be seen on the right side of the theoretical curves in Fig. 6. From charge renormalization, hardly any effect on $Z_{\text{eff}}$ is expected for increasing $n$. Over the complete experimental range, the slight increase in $Z_{\text{eff}}$ with decreasing $\kappa$ is counteracted by an equally mild increase in $A$ [29]. In fact, with SEM based on the renormalized charge, there is hardly any way to reduce $\mu_{\text{ep}}$ in the abrupt way seen in the experiment. Therefore, an experimental drop of mobility has to correspond to a strong decrease of the bare charge such as to leave the saturation limit of charge renormalization.

A decrease of bare charge at large $n$ is readily anticipated considering, that the only counter-ions in our system are $H^+$. Their accumulation in the electric double layer changes the surface pH and thus can influence the dissociation equilibrium for surface groups of sufficiently large pK$_A$. This effect, known as charge regulation, in fact is a straightforward implementation of chemical equilibrium in the calculation of the double layer properties [68]. Experimentally it has been demonstrated from colloidal probe AFM [69], but also from electro-kinetics of non-polar colloids [70]. Charge regulation has recently also attracted considerable theoretical interest due to its influence on double layer forces [71, 72]. We therefore propose that the experimentally observed drop in mobility at large $n$ corresponds to a pronounced decrease of bare charge, i.e. a decrease in the degree of surface group dissociation. This could be implemented into the present SEM approach by the numerically efficient *ab initio* calculations of colloidal bare and effective charges under realistically salt free conditions that were recently introduced for sulfonate and silanol stabilized particles [13]. In turn, charge regulation based SEM calculations could be performed and compared to the experimental data.

Also at low $n$, the qualitative difference in observed electro-kinetic behavior for the two different surfaces investigated in this study supports the idea of a physicochemical equilibrium type mechanism. In fact, the electro-osmotic mobility at the Quartz surface stays constant, and the corresponding $\zeta$-potential is $\zeta_{\text{Quartz}} = -105$ mV independent of $n$ and in good agreement with previous measurements [73]. At the same time the mobility at the PS-surface drops by about a factor of two. However, simple charge regulation as sketched above can presumably be ruled out, since it is unclear, where the required excess in $H^+$ should come from for decreasing $n$. Thus, even while a decreasing bare charge is suggested from the comparison to SEM, the underlying mechanism remains unresolved.

At this point we feel free to speculate and anticipate two lines of thought that might be worth considering. The first line of thought is based on a recent study on the CO$_2$ solubility in low salt water [74]. There we found that the solubility is considerably decreased upon deionization. Considering that this would shift the absorption equilibrium of CO$_2$ to the latex surface, we propose a further shift upon system dilution under deionized conditions. This on the one side would provide a natural explanation of our present observation that the particles act as a significant reservoir of CO$_2$. On the other side, accepting an increased adsorption
of gaseous CO₂ to the surface, this will decrease dielectric constant in the immediate vicinity of the surface. As a consequence, the enhanced electrostatic interaction can lead a shift of the chemical dissociation equilibrium, i.e. charge regulation triggered by dielectric permittivity. Alternatively, one may suspect the build-up of correlations amongst counter-ions and also between surface charges and counter-ions [75]. The first type of correlations has been investigated intensively for systems with smeared surface charge and finite sized counter-ions [76, 77]. It becomes most relevant at large concentrations of electrolyte. The second type of electro-static correlation leads to Bjerrum-pair formation and can, in the case of di- or multivalent counter-ions, even invert the particle charge [78]. For the present case of mono-valent counter-ions, we expect this physical effect to decrease the particle charge with decreasing dielectric constant, i.e. increasing CO₂ adsorption. This could be tested by careful systematic measurements of CO₂ solubility under low salt conditions and further electro-kinetic experiment with particles of differing materials to vary the adsorption equilibrium.

A different line of thought is related to the similarity between deionization and degassing. As our conductivity measurements show, the amount of dissolved CO₂ is greatly reduced upon deionization over extended times. Under de-gassed conditions a change of the surface structure has been observed which increases the surface roughness [37]. From investigations of “hairy surface” particles it is further known, that surface roughness may considerably reduce the electro-kinetic mobility [79]. Force measurements in de-gassed water and surface roughness characterization by AFM comparing as-synthesized to deionized particle may address these suggestions. Also experiments using particles with rigid surfaces should be conducted for comparison.

Conclusion

We have presented a first systematic investigation of charged sphere electro-phoretic mobilities covering a sufficiently large range of concentrations to unequivocally identify a plateau-type mobility maximum. Data were taken on highly dilute samples with non-overlapping double layers as well as on fluid and crystalline ordered samples. Most importantly, we could investigate samples where multiple scattering effects occur and render the systems too turbid for standard instrumentation. We applied a facile multiple scattering correction to our SH-DLS data to obtain high quality Doppler spectra even for very turbid systems of low transmittance.

Our data reconcile conflicting previous results taken over restricted density ranges. They thus solve a long standing experimental challenge. We anticipate that MS-corrected SH-DLS will be very useful also for other systematic investigations on particles over extended ranges in particle concentration.

Our comparison to SEM calculations emphasize the importance of considering realistically salt free conditions. Thus, our predictions for CO₂ saturated conditions meet the experimental data of the plateau region quantitatively and without additional adjustable parameters when taking the independently determined effective charge as input. On one side, this finding is in line with the conductivity measurements which reveal that the particles themselves act as a non-negligible source of CO₂. On the other side, it may also be seen as a stringent test of this SEM model. SEM under realistically salt free conditions works very well even at CO₂ saturated conditions, given the experimental systems have constant charges.
The peculiar behavior of the mobility towards very small and very large densities is not expected from constant charge calculations. The observed decrease points at a reduced bare charge. More experiments on particles of different surface chemistry are needed to clarify the underlying mechanisms. In particular for particles stabilized by weak acids it will be rewarding to extend the present SEM calculations by implementing surface charge regulation.

Solving this puzzle is highly desired for many practical applications of colloidal suspensions requiring systems at different particle concentrations. Additional experiments and implementation of charge regulation should constitute the next steps. We therefore anticipate, that our study will motivate further theoretical and experimental activity in electro-kinetics of charged particle models in both the dilute and concentrated strongly interacting state.

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PS260 (mP)
$n = 3.27 \times 10^{16} \text{ m}^{-3}$
$E = 12.5 \text{ V cm}^{-1}$
$2d = 2 \text{ mm}$
$\omega_{LO} = 2 \text{ kHz}$

$C_{\text{shel}}(q, \omega) (10^{-5} \text{ V Hz}^{-1/2})$

$f = \omega/2\pi \text{ (Hz)}$
$C_{shef}(q, \omega) \times 10^{-5}$ VHz$^{-1/2}$

$\Delta$ MS and Background corrected signal

Red line: fit

$f = \omega / 2\pi$ (Hz)
