Evidence for charge regulation in the sedimentation of charged colloids

LETTER TO THE EDITOR

Evidence for charge regulation in the sedimentation of charged colloids

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Abstract
Recent experimental data for the centrifugal sedimentation–diffusion profile of charged colloidal silica ($\varnothing \sim 44$ nm) in ethanol is analysed based on local charge neutrality and by either assuming a fixed particle charge or incorporating charge regulation. Especially at a high Debye length (>30 nm) the two models deviate at higher particle volume fractions ϕ (>0.1 vol%) with the data much better reproduced when charge regulation is included.

1. Introduction

The sedimentation–diffusion profile of charged colloids is strongly inflated compared to non-charged colloids due to a macroscopic electric field [1–9]. Recently, Raşa and Philipse [6] measured centrifugal sedimentation profiles for colloidal silica in ethanol, for the case where the Debye length was of the order of the particle size. They compared the data with a local electroneutrality, Donnan, model based on a fixed particle charge, Z. To describe the data at intermediate and high radial coordinates (their regions II and III) significantly different values for Z had to be used, leading the authors [6] to conclude that 'clearly, an extension of the theory is needed to further clarify the sedimentation–diffusion profiles at low altitude'.

Of the several model improvements discussed in [9], we will focus on the influence of particle concentration on surface charge. Indeed, the charge on a colloidal particle not only depends on the concentration of adsorbing species (pH for protons) and ionic strength [10] but also on the proximity to other colloids [11]. The latter influence is called charge regulation and for a one-component system leads to a reduction in charge when the particle concentration increases. For silica the surface charge is due to the release of protons, $SiOH \leftrightarrow SiO^- + H^+$ [10], and regulation of the surface charge is due to a more negative electrostatic surface potential when the diffuse ion clouds around the particles are compressed. The decrease in potential results in an increase of the proton concentration at the surface and an increased recombination of protons with ionized groups [11].

Here we extend the theory for the equilibrium sedimentation profile of charged colloids by incorporating charge regulation in the local electroneutrality balance, add the corresponding chemical contribution to the chemical potential, and derive an analytical expression for the particle density as a function of altitude in the case of surface charge regulation.

2. Theory

In a gravity field, the sedimentation profile is described by [1, 4, 5]

$$L\frac{\mathrm{d}\Pi}{\mathrm{d}x} = -\frac{\phi}{v} \tag{1}$$

where Π is the osmotic pressure (in kT per volume), x the altitude, ϕ the volume fraction of colloids, v the particle volume and L the gravitational length given by

$$L = \frac{kT}{g(\rho_c - \rho_s)v} = \frac{kT}{mg} \tag{2}$$

where m is the buoyant mass of the colloidal particle, ρ the density of colloid (c) and solvent (s) and $g = 9.81 \text{ m}^2 \text{ s}^{-1}$. Equation (1) is equivalent to [2, 8]

$$\frac{\mathrm{d}\mu}{\mathrm{d}x} = -\frac{1}{L} \tag{3}$$

when the chemical potential μ contains all contributions except those due to the gravitational field. In a centrifugal field, equation (3) must be replaced by

$$\frac{\mathrm{d}\mu}{\mathrm{d}r} = \frac{r}{L_\omega^2} \tag{4}$$

in which r is the radial coordinate and L_ω the centrifugal length [8]

$$L_\omega = \sqrt{\frac{kT}{m\omega^2}} \tag{5}$$

where ω is the rotational velocity in rad s^{-1}. Integrating equation (4) once results in

$$\frac{r^2}{2L_\omega^2} = \mu + C \tag{6}$$

with C an integration constant determined by overall conservation of particle mass.

Local electroneutrality is given by

$$Z\phi - 2n_\infty v \sinh y = 0 \tag{7}$$

when we neglect gradients in the dimensionless electrostatic potential y on the scale of the Debye length ($y = e\psi/kT$ with ψ the electrostatic potential). In equation (7) Z is the surface charge (number of charges per colloidal particle) and n_∞ the ionic strength. Equation (7) neglects the volume excluded by the particles (not available to solvent) and can be rewritten as [6, 8]

$$y = \text{arcsinh} \frac{Z\phi}{2n_\infty v}. \tag{8}$$

The electric component of the chemical potential is $\mu^{\text{el}} = Zy$ which results in

$$\mu^{\text{el}} = Z \, \text{arcsinh} \frac{Z\phi}{2n_\infty v}. \tag{9}$$

Implementing equation (9) together with an ideal gas entropy term, $\ln \phi$, in equation (6) results in

$$\ln \phi + Z \operatorname{arcsinh} \frac{Z\phi}{2n_\infty v} = \frac{r^2}{2L_\omega^2} + C \tag{10}$$

which is equal to equation (6) in Raşa and Philipse [6] (who use γ for ϕ, z for Z, and y for $Z\phi/(2n_\infty v)$).

When the surface charge is due to the adsorption or desorption of a single type of ion (e.g., proton), the surface charge Z can be described by a Langmuir isotherm which results in [11–13]

$$Z = \frac{Z_{\text{max}}}{1 + e^{y-y_N}} \tag{11}$$

when Z, Z_{max} and y are taken as positive numbers; Z_{max} is the number of ionizable groups on the surface. Silica in ethanol has a negative surface charge due to the dissociation of Si–OH into Si–O$^-$ and a free proton [4, 6, 10]; Z and y must then be interpreted as the magnitude of surface charge and potential. The Nernst potential, y_N, is the required surface potential for Z to be half of Z_{max} and is a function of the adsorption energy, $\Delta\mu_{\text{ads}}$ (related to the intrinsic pK-value of adsorption), and the concentration (activity) of adsorbing species in bulk solution (pH for protons). In the limit that $Z \ll Z_{\text{max}}$, equation (11) simplifies to

$$Z = Z_{\text{max}} e^{y_N} e^{-y} = Z_\infty e^{-y} \tag{12}$$

with Z_∞ the surface charge at infinite dilution. The second equality holds for the Donnan model, equation (7). Interestingly, the charge regulation model based on equation (12) does not require more fitting parameters than the fixed charge model. Whereas Z is used as a free parameter in the fixed charge model, the charge regulation model uses Z_∞.

The surface charge and potential are obtained by combining equations (7) and (12) which results in

$$y = \frac{1}{2} \ln \left(1 + \frac{Z_\infty \phi}{n_\infty v} \right), \qquad Z = Z_\infty \left(1 + \frac{Z_\infty \phi}{n_\infty v} \right)^{-\frac{1}{2}}. \tag{13}$$

With charge regulation we must add a chemical term to the chemical potential μ, given by [12, 13]

$$\mu^{\text{chem}} = -\int_0^Z y \, dZ \tag{14}$$

with the relation between y and Z given by an adsorption isotherm such as equation (12). Developing equation (14) results in

$$\mu^{\text{chem}} = \int_0^Z \ln \frac{Z}{Z_\infty} \, dZ = Z \left(\ln \frac{Z}{Z_\infty} - 1 \right) = -Z \, (y + 1) \tag{15}$$

after which equation (9) becomes

$$\mu^{\text{el+chem}} = -Z = -Z_\infty \left(1 + \frac{Z_\infty \phi}{n_\infty v} \right)^{-\frac{1}{2}} \tag{16}$$

which can be used directly in equation (6) together with an ideal gas entropy term, $\ln \phi$.

The osmotic pressure, which in the Donnan model for a fixed charge is given by [4, 5, 8]

$$\Pi_{\text{CC}} = \frac{\phi}{v} + 2n_\infty \left[\sqrt{1 + \left(\frac{Z\phi}{2n_\infty v} \right)^2} - 1 \right] \tag{17}$$

Table 1. Fitted values for the surface charge at infinite dilution, Z_∞.

λ_D (nm)	ϕ_0 (vol%)	Z_∞
54	0.06	31
47	0.20	52
44	0.30	63
39	0.48	78
20	0.30	110
16	0.30	110
12	0.30	90

is replaced by

$$\Pi_{CR} = \frac{\phi}{v} + 2n_\infty \left[\frac{1}{2} \left(X + X^{-1} \right) - 1 \right], \qquad X = \sqrt{1 + \frac{Z_\infty \phi}{n_\infty v}} \qquad (18)$$

in the case of charge regulation according to equation (12). (In equations (17) and (18) ideal gas entropy is assumed.)

Expansion of the expressions for Π around $\phi = 0$ results in $\Pi = \phi/v(1 + B_2\phi + B_3\phi^2 + \mathcal{O}(\phi^4))$. For a fixed surface charge the second virial coefficient is $B_2 = Z^2/(4n_\infty v)$ and the third virial coefficient is zero, $B_3 = 0$. With charge regulation, the second virial coefficient is the same as for fixed charge (with Z_∞ replacing Z, $B_2 = Z_\infty^2/4n_\infty v$), but the third virial coefficient is $B_{3,CR} = -Z_\infty^3/4(n_\infty v)^2$. (Note that Z_∞ is the magnitude of the surface charge at infinite dilution, thus $Z_\infty \geqslant 0$.) Because $B_{3,CR} < 0$, the osmotic pressure of charge regulating colloids will be lower than for particles with a fixed surface charge.

3. Results and Discussion

Data [6] together with calculation results are presented in figure 1. The original data are converted from attenuance into volume fractions ϕ using the appropriate conversion factors kindly provided by the authors [6]. Calculations are made for a particle radius of 21.9 nm as measured by transmission electron microscopy [6], resulting in volume $v = 44 \times 10^3$ nm^3. The rotational velocity ω is $1100/60 \times 2\pi = 115$ rad s^{-1} and the buoyant mass density is $\rho_c - \rho_s = 1.600 - 0.785 = 0.815$ g ml^{-1}, resulting in a centrifugal length of $L_\omega = 0.294$ cm. For each experiment a Debye length $\lambda_D = \kappa^{-1}$ was derived from conductivity measurements [9]; see table 1. The ionic strength, n_∞, is back-calculated from these values for λ_D using $\kappa^2 = 2n_\infty e^2/(\varepsilon kT)$ (for ethanol $\varepsilon_r = 24.3$, Bjerrum length $\lambda_B = 2.3$ nm [4]). The initial particle volume, ϕ_0, is not a direct input in the calculation because C is used as a free fitting parameter.

When we try to fit the fixed charge model, equation (10), to the data, using Z as free parameter, we find that for the lowest Debye length ($\lambda_D = 12$ nm) the data are rather well described, while the charge regulation model remains very close; see figure 1(b). In this case the electrostatic potential y remains close to zero for all values of ϕ. Consequently, proton concentration gradients are low, and the charge remains fairly constant across the column. However, for higher Debye lengths the calculated profile bends too much concave downward with increasing r^2, see figure 1(c) for the $\lambda_D = 39$ nm case. Now, using the charge regulation model, based on equations (6) and (16) and Z_∞ as free parameter, a much better fit is obtained, especially for $\lambda_D > 30$ nm, see figure 1(a), with the approximately linear region at higher ϕ (in a $r^2 - \log\phi$ plot) much better reproduced.

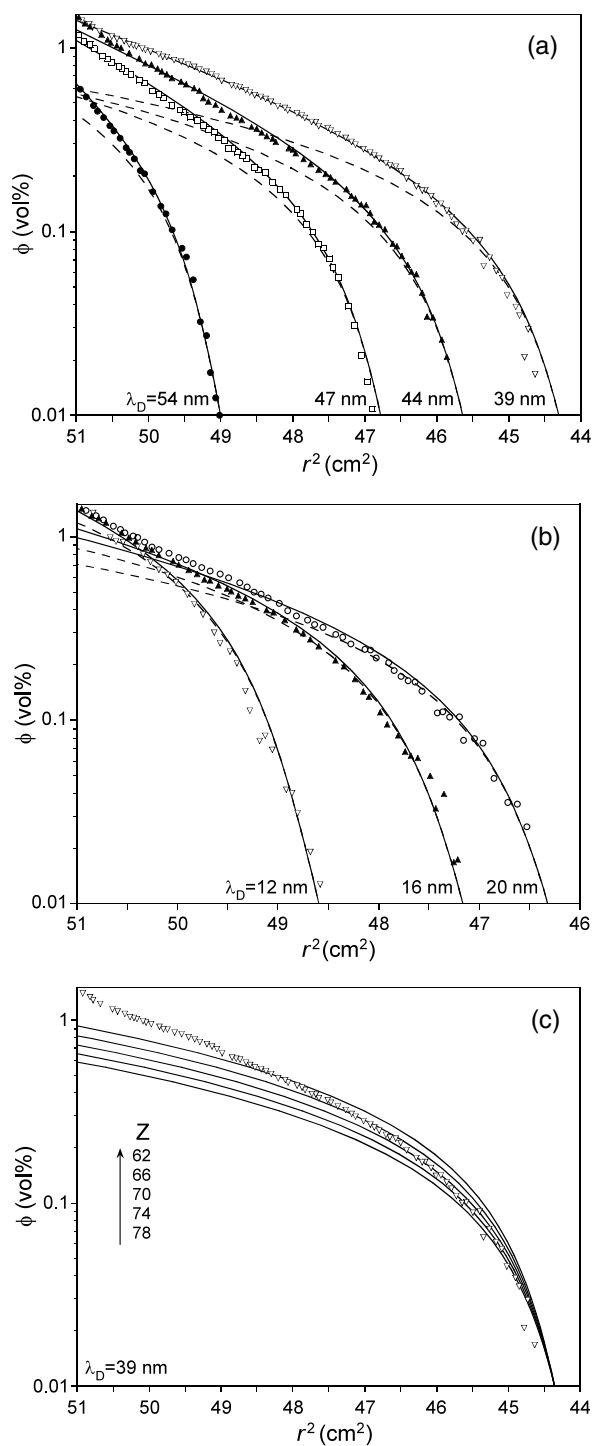**Figure 1.** Centrifugal sedimentation–diffusion profiles for ∅ 44 nm colloidal silica in ethanol [6] at different values of the ionic strength. In figures (a) and (b) dashed curves represent model calculations based on a fixed surface charge, while solid curves include surface charge regulation. (c) compares data with the fixed charge model for different values of Z.

In figures 1(a) and (b) the solid curves are based on the charge regulation model using the values for Z_∞ as given in table 1. The dashed curves are based on the fixed charge model using for Z the fitted values of Z_∞. If Z is used as a free fitting parameter in the fixed charge model, the quality of the fit does not improve much; see figure 1(c) for the $\lambda_D = 39$ nm case.

The values we find for Z and Z_∞ are of the same order as calculated by Raşa and Philipse [6] ($Z = 40$–80 in their region II). These values for Z (not more than one charge per 50 nm^2 of particle surface) are very low, which is due to the large Debye length when pure ethanol is used as solvent, resulting in a large electrostatic energy penalty for the charging process.

How much does the surface charge change with r, for instance for $\lambda_D = 39$ nm? At infinite dilution the surface charge is $Z = Z_\infty = 78$ when we fit the model to the data, which decreases to $Z = 44$ at $r^2 = 51$ cm^2 (where $\phi \sim 1.4$ vol%) which implies a $\sim 44\%$ decrease in Z. The charge decreases by about the same amount for the $\lambda_D = 44$ and 47 nm experiments but by less in the other experiments. In any case, the predicted decrease is less dramatic than suggested in [6] but still leads to a significant adjustment of the predicted sedimentation–diffusion profile.

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