Electrical conductivity of dilute colloid electrolytes

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Abstract. We discuss the mechanism of the influence of the multiply-charged colloidal clusters on linear electric transport in diluted polyelectrolytes. The structure of these colloids has well known form. They are effectively neutral and cannot participate in the transfer of charges in the solution. Nevertheless, there is a linear increase in the conductivity of colloidal polyelectrolyte with an increase in the density of colloids. This phenomenon is observed experimentally. It is shown that this happens due to the change of electric field in the polyelectrolyte under the effect of colloidal particle polarization.

1. Introduction

By $Z : 1$ colloids are commonly called massive, spherical formations of radius $R$ with a minimum size dispersion $\delta R \ll R$ and bare charge $Ze \gg e$. A special property of $Z : 1$ colloidal solutions is their resistance to the coagulation process (due to Van der Waals forces), which is usually present in colloidal solutions. Stability is achieved by selecting a special stabilizing electrolyte. As shown by Deryagin and Landau [1] (and also by the authors of the book [2], which served as the basis for the abbreviation DLVO—Deryagin–Landau–Verwey–Overbeek), the presence of Debye screening shells around each of the charged colloids generates repulsion between them at Debye distances, which prevents the coagulation.

The statistics of DLVO colloid solutions is an integral part of the theory of polyelectrolytes, which allows the existence of different charges in a solution. It is based on the assumption that it is possible to represent all interactions in a solution (including the interaction between different charges) by pair potentials. If so, all microscopic formal approaches become available [3]. In particular, the phenomenon of “condensation”, when the nuclei charged to the $Ze \gg e$ ($Z : 1$ electrolyte) is practically completely screened at large distances from the center of the colloid according to the calculated distribution of ions [3]. Microscopic theory explains the conductivity of the diluted electrolyte. The calculations in the Mean Spherical Approximation (MSA approximation) were performed using the Kubo formulas, which requires the existence
of effective charge $\delta Z$ of colloids. This parameter $\delta Z$ is self-consistently calculated in the MSA formalism for the conductivity of a colloidal solution. The final results are presented in the review [3, figure 2]. These data show that the effective colloid charge is a function of its transport velocity. Such a transport cannot be ohmic.

From our point of view, to describe the transport properties of a polyelectrolyte, it is more appropriate to dwell on the DLVO theory [1], where a colloid has the form of a charged core of radius $R$ and charge $Ze$ surrounded by a completely screened counter-ion shell. This property (effective neutrality) must be preserved in linear transport of any nature, especially under condition (1). If in addition to DLVO theory we consider a colloidal solution as a two-phase conducting mixture in presence of conductivity $\sigma_0$ of the stabilizing electrolyte and a small fraction of well conducting droplets with conductivity $\sigma_* \gg \sigma_0$, the main observed facts: the existence of ohmic conductivity $\tilde{\sigma}(n^*)$ and its linear dependence on the density $n^*$ of colloids can be easily explained with reference to the known transport properties of two-phase conductive mixtures (see [4]). Details of this scenario are discussed in this paper.

2. DLVO linear transport

2.1. General relations

From a formal point of view, we solve the continuity equation for the current density $\mathbf{j}(r)$ with suitable boundary conditions. Under the conditions (1), this problem can be formulated in the vicinity of an individual colloid in spherical coordinate system with the origin in its center

$$\text{div } \mathbf{j}(r) = 0, \quad \mathbf{j} = \sigma \mathbf{E}, \quad \sigma_0 \mathbf{E}_n^0 = \sigma_* \mathbf{E}_n^*, \quad \sigma_* \gg \sigma_0. \quad (2)$$

Here, $\sigma_0$ is the conductivity of the stabilizing electrolyte, $\sigma_*$ is the effective conductivity of the Debye layer around the charged nucleus of the DLVO-colloid. The boundary condition from (2) relates the normal components of the current from the volume to the thickness of the Debye layer (subscripts in the definition of the fields $\mathbf{E}_n^0$, $\mathbf{E}_n^*$ mean that we are talking about normal to the surface of the colloidal sphere components of these fields). Inequality $\sigma_* \gg \sigma_0$ implies that the density of counter-ions in the Debye shell of the DLVO-colloid is much higher than that in the surrounding stabilizing electrolyte (if the Debye shell is not crystallized “according to Wigner” scenario).

To extract the information about conductivity $\tilde{\sigma}(\sigma_0, \sigma_*)$ from the solution of the problem (2), it is necessary to realise the volume averaging of local currente distribution $\mathbf{j}(r)$ according to scheme [4] for average dielectric constant $\tilde{\varepsilon}(\varepsilon_0, \varepsilon_*)$. The average dielectric constant $\tilde{\varepsilon}(\varepsilon_0, \varepsilon_*)$ of a suspension containing a small fraction $C_* \ll 1$ of particles with a dielectric constant $\varepsilon_*$ other than $\varepsilon_0$ of the main medium is calculated in [4]. Formally, this problem and problem (2) are identical in the following sense: $\mathbf{j}(r) \rightarrow \mathbf{D}(r)$, $\mathbf{E}(r) \rightarrow \tilde{\mathbf{E}}(r)$, $\sigma_0 \rightarrow \varepsilon_0$, $\sigma_* \rightarrow \varepsilon_*$. As a result, by defining $\tilde{\varepsilon}(\varepsilon_0, \varepsilon_*)$, we can use this formula to determine $\tilde{\sigma}(\sigma_0, \sigma_*)$.

Averaging from [4] looks as

$$\frac{1}{V} \int (\mathbf{D} - \varepsilon_0 \mathbf{E}) dV = (\tilde{\mathbf{D}} - \varepsilon_0 \tilde{\mathbf{E}}). \quad (3)$$

The integrand is nonzero only inside each of the small spheres with $\varepsilon_* > \varepsilon_0$. Therefore, the integral itself is proportional to $C_*$. Calculating this integral, we can assume that the suspension particles are in an external field equal to the average field $\tilde{\mathbf{E}}$. Assuming the particles are spherical and using the general formula connecting the fields inside and outside the ellipsoid

$$\mathbf{E}^{(i)} = \frac{3\varepsilon^{(e)}}{2\varepsilon^{(e)} + \varepsilon^{(i)}} \mathbf{E}^{(e)}, \quad (4)$$

we obtain

$$\tilde{\varepsilon}(\varepsilon_0, \varepsilon_*) = \varepsilon_0 + 3C_* \frac{(\varepsilon_* - \varepsilon_0)}{2\varepsilon_0 + \varepsilon_*}. \quad (5)$$
Taking into account the relationship between $\tilde{\varepsilon}(\varepsilon_0, \varepsilon_\ast)$ and $\tilde{\sigma}(\sigma_0, \sigma_\ast)$, we have

$$\tilde{\sigma}(\sigma_0, \sigma_\ast) = \sigma_0 \left[ 1 + 3C_\ast \frac{(\gamma - 1)}{(2\gamma + 1)} \right], \quad C_\ast \simeq \frac{4\pi}{3} R^3 n^\ast, \quad \gamma = \sigma_\ast/\sigma_0 > 1. \quad (6)$$

Here $R$ is from (1).

It is possible to make more visual the structure of the model, considering the colloid as not "all metal", as it is supposed in (6), but having shell form. We can take into account the structure of a spherically symmetric sandwich: there is no conductivity in its central core of radius $R_0$, and the shell of the thickness $(R - R_0)$ is conductive. The calculations performed by analogy with (2) give the following result

$$\tilde{\sigma}(\sigma_0, \sigma_\ast) = \sigma_0 \left[ 1 + 4\pi \frac{(2\gamma + 1)(\gamma - 1)}{(2\gamma + 1)(\gamma + 2) - 2(\gamma - 1)^2 R_0^3/R^3(R^3 - R_0^3)} \right]. \quad (7)$$

In the limit $R_0 \to 0$ formula (7) transforms into (6).

Formula (7) contains two geometric parameters: $R$ and $R_0$. Radius $R$ is available to ohmic measurements. The value of $R_0$ should be estimated from independent sources. The difference $(R - R_0)$ can be associated with the length $\lambda_0$ from (1) or supposed to be an observable parameter. In any case, this definition as compared to (6) is useful for discussion of the details of linear transport in colloidal electrolytes.

2.2. Comparison with experimental data

The effective conductivity $\tilde{\sigma}(\sigma_0, \sigma_\ast)$ (6) under assumptions (1) and $\gamma \gg 1$ is transformed to

$$\tilde{\sigma} \simeq \sigma_0 (1 + 4\pi R^3 n^\ast). \quad (8)$$

It follows from (8), that

$$\frac{\tilde{\sigma} - \sigma_0}{\sigma_0} = \frac{\sigma(n^\ast) - \sigma_0}{\sigma_0} = 4\pi R^3 n^\ast. \quad (9)$$

Consideration between (2) and (9) leaves no doubt about the existence of ohmic conductivity regime of diluted polyelectrolyte with DLVO colloids, when $(\tilde{\sigma} - \sigma_0) \propto n^\ast$. It remains to verify how the predictions (8), (9) are related to the data in the review [3, figure 2] for the fulfillment of inequality (1).

The left side of (9) can be estimated with experimental data [3]. Using the linear part of the dependence $\sigma(n^\ast)$ between the points $\phi = 0.0$ vol % and $\phi = 0.6$ vol % we have at the “right” point

$$n^\ast \simeq 5.45 \times 10^{15} \text{ cm}^{-3}. \quad (10)$$

The left side of (9) takes the form

$$\frac{\tilde{\sigma}(n^\ast) - \sigma_0}{\sigma_0} \simeq \frac{0.06 - 0.035}{0.035} \simeq 0.7. \quad (11)$$

Comparing (9), (11), we have

$$4\pi R^3 n^\ast \simeq 0.7, \quad R^3 n^\ast_0 = 0.7/4\pi < 1, \quad R = 2.17 \times 10^{-6} \text{ cm}. \quad (12)$$

Here $n^\ast$ corresponds to the density of colloids (10). The definition of $n^\ast R^3 \ll 1$ (12) correlates with requirement (1).

The effective colloid size $R$ looks reasonable. It should not be less than the core radius $R_0$ of the central part of the colloid. The same data [3] give for $R_0$ the value of $R_0 \simeq 6 \times 10^{-7}$ cm. The difference

$$\Delta R = (R - R_0) \propto \lambda_0 \quad (13)$$

correlates with estimation of the Debye thickness $\lambda_0$ in the diagnosis [3] of the DLVO colloid structure.
3. Conclusions

A self-consistent picture of electrical conductivity in dilute colloid electrolytes is proposed. The details of such a linear transport are observed experimentally.

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