ON SMOLUCHOWSKI'S EQUATION FOR THE ELECTROPHORESIS OF COLLOIDAL PARTICLES

by J. TH. G. OVERBEEK.   541.18:537.363

Summary

This article deals with the theory of the time-of-relaxation effect in the case of colloidal particles with a very thin double layer. Its influence on the electrophoretic velocity proves to be negligible, so that the electrophoresis is adequately described by Smoluchowski's equation

$$U = \frac{D \zeta E}{4 \pi \eta},$$

no correction for the time-of-relaxation effect being necessary.

1. *Introduction*

Helmholtz [1]) was the first to indicate how the electrokinetic potential ζ could be calculated from the electrokinetic phenomena. His deductions were improved by Smoluchowski [2]), who introduced the dielectric constant, D, of the medium and came to the well-known equation (1) for the electrophoretic velocity, U.

$$U = \frac{D \zeta E}{4 \pi \eta} \tag{1}$$

(η = viscosity of the medium, E = strength of the applied field).

Hückel [3]) called in question the factor 4 in the denominator of equation (1) and maintained, that this factor depends on the form of the particles. The factor should be 6 for spherical particles, according to Hückel.

The question remained unsolved until Henry [4]) showed that both factors were correct in themselves and that the difference was due to the different premises used. In particular Henry was able to demonstrate that Smoluchowski's equation (1) holds good for insulating particles [5]) *having a double layer which is thin compared with the dimensions of the particle, irrespective of the form of the particle.*

In all these deductions, however, the supposition is made that the electrical double layer is not deformed during the movement of the particle. Now this supposition is quite unfounded and almost certainly wrong. The process of electrophoresis cannot be conceived without a certain deformation of the double layer. In the case of the strong electrolytes the influence of this deformation on the ionic mobility (the so-called time-of-relaxation effect) has been calculated by Onsager [6]), and an extrapolation of Onsager's equations to particles with a very thin double layer would even lead to a very large influence of the time-of-relaxation effect on electrophoresis. The direct calculation of this effect for colloidal particles has been undertaken by various authors [7])[8]), but this proves to be very complicated; it has certainly led to some results [8]) but, owing to the intricate mathematical aspects of the problem, these are neither simple nor very accurate.

In the following it will be shown by a simple argument [9]) that the time-of-relaxation effect is small and that it may be disregarded precisely under the premises used by Smoluchowski, viz. that the thickness of the double layer is small compared with the dimensions of the particle.

2. *The time-of-relaxation effect*

During the movement of a colloidal particle in an electric field, the ions of the double layer tend to lag behind. This brings about space charges in front of and behind the particle, giving rise to an electric field which is opposed to the primary field and retards the electrophoretic movement.

The magnitude of these space charges is governed by two influences. On the one hand these charges are built up by the movement of the counter-ions under the influence of the applied field and by the flow of the liquid. On the other hand the space charge is continuously being dispersed as a result of the conductivity of the liquid and of the diffusion process. In the stationary state of electrophoresis these building-up and breaking-down processes must counterbalance each other.

It would be somewhat more exact to state that not only is a continuous accumulation of charge impossible but also an accumulation of neutral electrolyte. In the process sketched above the increase of the space charge is the result of a displacement of ions charged oppositely to the particle. The decrease of the space charge, however, is caused by the displacement of ions of both signs, the result being an accumulation of neutral salt behind the particle and a corresponding deficit on the other side. This displacement of neutral salt will be counteracted by diffusion (not by conduction), but as there are no space charges involved it is not of much interest for calculations of the time-of-relaxation effect.

We shall now proceed to give a more quantitative treatment of the argument outlined above. We will consider an insulating particle of arbitrary form with a positive surface charge of density σ, immersed in a solution of a simple electrolyte containing n_+ positive ions of charge e_+ and n_- negative ions of charge e_- per cm³. According to the theory of the diffuse double layer, the negative charge balancing the surface charge may for many purposes be thought of as being situated at a distance $1/\varkappa$ from the surface, $\varkappa^2$ being equal to

$$\varkappa^2 = \frac{4\pi\,(n_+\,e_+{}^2 + n_-\,e_-{}^2)}{D\,k\,T} \qquad (2)$$

Even when the surface potential is large, so that it is not allowed to introduce the usual approximation for small potentials ($\exp\,[ne\Psi/kT] = 1 + ne\Psi/kT$) leading to the value $D\varkappa/4\pi$ for the capacity of the double layer, the capacity of the double layer remains proportional to $\varkappa$, that is to the square root of the concentration of electrolyte. The proportionality factor, however, is no longer equal to $D/4\pi$. (Cf. Verwey and Overbeek "Theory of the stability of lyophobic colloids" in the press.)

We suppose $1/\varkappa$ to be much smaller than the dimensions of the particle. As a consequence of the applied electric field there is a current of negative charge along the surface of the particle. This current is equal to

$$i_I = \frac{Ee_-}{\varrho_-}\,\sigma\,d\,f \qquad (3)$$

($1/\varrho_-$ gives the mobility, the velocity of the negative ions under unit force;

d is one of the main dimensions of the particle, and f is a form factor of the order of unity).

If the particle is a cylinder, moving with its axis in the direction of the field, and d its diameter, f is equal to π.

Apart from this movement of ions with respect to the liquid immediately surrounding them there is a movement of this liquid as a whole, which gives rise to a current i_{II}, equalling

$$i_{II} = U\,\sigma\,d\,f. \qquad (4)$$

Here the double layer is best thought of as a Helmholtz layer moving with a velocity U with respect to the particle. The form factor is the same as in equation (3), as in every point of the surface the local velocity of the liquid is proportional and parallel to the local field *). Here use is made implicitly of the premise that the particle is non conducting, so that E has no component perpendicular to the surface.

To find a value for the return current i_{III} we assume that the space charges of relaxation generate a counterfield having the strength F in the immediate neighbourhood of the double layer and dying out at greater distances from the particle according to the laws of electrostatics. Bearing in mind that the counter-current caused by this field runs almost entirely through the liquid outside the double layer and that the excess conduction in the double layer is the less important the larger the proportion between d and $1/\varkappa$, the return current may be put equal to

$$i_{III} = F\,\lambda\,d^2\,g, \qquad (5)$$

where λ is the conductivity of the solution and g another form factor of the order of unity, the factor d^2 arising from the fact that with increasing dimensions of the particle the area through which this current passes increases as the square of the dimensions.

In the case of a spherical particle of diameter d and a charge distribution such as to cause a field F in the double layer and outside of it a pure dipole field, the current passing through the median plane can be easily calculated, the factor g proving to be $\pi/2$.

In order to evaluate the magnitude of the diffusion current i_{IV}, we must form an idea of the concentration gradient of the space charge involved. We remark that to generate a field F in a plane condenser of surface d^2 with a plate distance d, the surface charge necessary is equal to $d^2DF/4\pi$. If a charge of this magnitude is spread out over the volume d^3 the concentration gradient will be of the order of $d^2DF/4\pi \cdot 1/d^3 \cdot 1/d$. Assuming that this charge is entirely built up of counter-ions having a diffusion constant kT/ϱ_-, the diffusion current i_{IV} passing through an area of the order of d^2 is found to be

$$i_{IV} = \frac{d^2\,DF}{4\pi}\cdot\frac{d^3}{1}\cdot\frac{1}{d}\cdot d^2\cdot\frac{kT}{\varrho_-}\cdot h = \frac{FD\,kT}{4\pi\varrho_-}\cdot h\,, \qquad (6)$$

where h is again a form factor.

Substituting for λ the value

$$\lambda = \frac{n_+\,e_+{}^2}{\varrho_+} + \frac{n_-\,e_-{}^2}{\varrho_-} \qquad (7)$$

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*) cf. Smoluchowski's original article in Krak. Anz. 1903, p. 182.

we find for the ratio i_{IV}/i_{III}

$$\frac{i_{IV}}{i_{III}} = \frac{h}{g} \cdot \frac{D k T}{4\pi \left(n_+ e_+^2 \frac{\varrho_-}{\varrho_+} + n_- e_-^2\right) d^2} \sim \frac{1}{\varkappa^2 d^2} \qquad (8)$$

Disregarding the differences between h and g and between ϱ_- and ϱ_+ and using expression (2) we find i_{IV}/i_{III} to be of the order of $1/\varkappa^2 d^2$. In the case considered here, where $1/\varkappa$ is much smaller than d, the diffusion current i_{IV} may be regarded as negligible compared with the conduction current i_{III}.

One may remark here that the currents (i_I and i_{II}) responsible for the building up of the relaxation charges are proportional to σd, that is to $d\sqrt{n}$, and that the return current i_{III} is proportional to λd^2, that is to $d^2 n$. So it can be seen here already that the relaxation effect will disappear with increasing d and n as $1/d\sqrt{n}$ or as $1/\varkappa d$.

In the stationary state of electrophoresis the return current i_{III} must be equal to the sum of the currents i_I and i_{II}, or

$$\left(\frac{E e_-}{\varrho_-} + U\right) \sigma \, df = F \lambda d^2 g. \qquad (9)$$

From this equation we can isolate the ratio F/E, which forms a measure for the influence of the time-of-relaxation effect on electrophoresis. Substituting for σ in a first approximation

$$\sigma = \frac{D \zeta \varkappa}{4\pi}, \qquad (10)$$

and for U and λ the expressions (1) and (7) respectively [10]), we find

$$\frac{F}{E} = \frac{\left[\frac{e_-}{\varrho_-} + \frac{D\zeta}{4\pi\eta}\right] \frac{D\zeta\varkappa}{4\pi} \cdot d \cdot f}{d^2 \left(\frac{n_+ e_+^2}{\varrho_+} + \frac{n_- e_-^2}{\varrho_-}\right) g} = \left[1 + \frac{\varrho_-}{e_-} \cdot \frac{D\zeta}{4\pi\eta}\right] \times$$

$$\times \frac{D k T}{4\pi \left(n_+ e_+^2 \frac{\varrho_-}{\varrho_+} + n_- e_-^2\right)} \cdot \frac{\zeta e_-}{kT} \cdot \frac{\varkappa}{d} \cdot \frac{f}{g}. \qquad (11)$$

If we put the ratios f/g and ϱ_-/ϱ_+ equal to one, which does not alter the order of magnitude of the calculated effect and use equation (2), we finally obtain

$$\frac{F}{E} = \frac{1}{\varkappa d} \cdot \frac{\zeta e_-}{kT} \left(1 + \frac{\varrho_-}{e_-} \cdot \frac{D\zeta}{4\pi\eta}\right) \qquad (12)$$

and instead of equation (1) the electrophoretic velocity is found to be given by

$$U = \frac{D\zeta}{4\pi\eta}(E - F) = \frac{D\zeta E}{4\pi\eta} \left\{1 - \frac{1}{\varkappa d} \cdot \frac{\zeta e_-}{kT}\left(\left(1 + \frac{\varrho_-}{e_-} \cdot \frac{D\zeta}{4\pi\eta}\right)\right)\right\} \qquad (13)$$

This equation tallies very well with the expression derived earlier [8]) in a more exact (but much more complicated) way for the electrophoretic velocity of a spherical particle of diameter d, viz.

$$U = \frac{D\zeta E}{4\pi\eta}\left\{1 - \frac{6}{\varkappa d} - \frac{1}{\varkappa d} \cdot \frac{(e_- - e_+)\zeta}{kT}\left(\frac{3}{2} + \frac{e_+ \varrho_+ + e_- \varrho_-}{(e_+ + e_-)(e_- - e_+)} \cdot \frac{D\zeta}{4\pi\eta}\right)\right\} \qquad (14)$$

the term $6/\varkappa d$ being a correction on the electrophoresis equation calculated by Henry [4]) and having nothing to do with relaxation.

Now for the usual ζ potentials $\zeta e/kT$ has the order of magnitude one and $\varrho/e \cdot D\zeta/4\pi\eta$, representing the ratio of velocities of a colloidal particle and a common ion, is also about unity. Therefore the correction needed for the time-of-relaxation effect in the case of large $\varkappa d$ is of the order of $1/\varkappa d$ and approaches zero, when the double layer is thin enough.

3. Conclusion

Summarizing our argument very briefly, it may be stated that the time-of-relaxation effect is small for a thin double layer, because the building up of the relaxation charge is proportional to reciprocal thickness of the double layer, $\varkappa$, and to the *linear* dimensions of the particle, whereas this charge is dissipated by a conduction proportional to the concentration of the electrolyte, that is to $\varkappa^2$, and to the *square* of the dimensions of the particle. Hence, under the premises used by Smoluchowski, the deformation of the double layer, while existing, is small enough to be negligible in calculating ζ from the electrophoretic velocity when using equation (1). If $\varkappa d = 100$ the error is of the order of a few per cent, and if $\varkappa d = 1000$ the error will most probably be less than one per cent.

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9) The fundamental principle of this paper has been mentioned very briefly in the author's contribution for the Symposium on Strong Electrolytes held at Utrecht (Holland) on July 4th, 1944.
10) It is not necessary to use for U the more exact expression $U = D\zeta(E-F)/4\pi\eta$, as F proves to be much smaller than E.