

## Complex Investigations of Double Layer of Colloid Particles. Electric Conductivity of Suspensions and Anisotropy of Electrophoresis

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Conditions for obtaining quantitative information on the double layer of colloid particles on the basis of electrosurface measurements have been analyzed. A rigorous theory of electric conductivity of diluted suspensions on the basis of induced dipole moments of particles has been presented.

The isoconductance point of a suspension has been shown to coincide with the isopolarisation state of a particle. A theory of anisotropy of the electrophoresis of long rod-like particles has been put forward. The identity of the formulæ of electrophoresis of a sphere and of cylindrical particles oriented perpendicular towards the field at a small thickness of the double layer has been shown. A good agreement has been found between the values of induced dipole moments and, specific surface conductivity in a wide electrolyte concentration range measured by the methods of electric conductivity of suspensions and anisotropy of electrophoresis. The theories of induced dipole moment, electric conductivity of suspension and anisotropy of electrophoresis have been experimentally examined.

Although electrosurface phenomena (electrokinetic, dielectric, electrooptical, etc.) are, no doubt, of interest, it is more important to get information on the structure of the double electric layer and the presence or absence of the boundary layer (hydrodynamically stagnant part of double layer lying between the surface and the plane of shear). The boundary layer is identified with the polymolecular solvated layer.

Electrosurface phenomena are now successfully used to get information on qualitative and even semiquantitative characteristics. Thus, on the basis of electrokinetic measurements the surface charge sign, the isoelectric point, mechanism of double layer formation<sup>1</sup>, presence of surface ionogenic groups may be determined, surface cleanliness<sup>2</sup>, surface ageing is evaluated<sup>3</sup>, semi-quantitative evaluation of the value of surface density of the charge  $\sigma_s$  is obtained.

### *The Conditions for Obtaining of Quantitative Information on the Double Layer of Colloid Particles*

In reference to rather smooth surfaces it has been shown that the electrokinetic potential  $\zeta$  is quantitative characteristics of the double layer. Thus, in paper<sup>4</sup> the coincidence of the values for  $\zeta$  and  $\psi_d$ -potentials measured by

different methods at oil-water interface in the presence of the adsorbed monolayer of ionogenic surfactants has been demonstrated.

The possibility of obtaining quantitative information on the double layer of colloid particles various systems does, however, entail great difficulties. It is not clear to what extent and in what class of systems they may be overcome. There are at least, three of them<sup>5</sup>. The first is the deformation of the double layer on a non-flat surface by the electric field. At the time when most theories consider the double layer to be in an equilibrium state, very often in a weak field it is so deformed<sup>6</sup> that its polarization field is commensurable with the external one. It has been shown<sup>7</sup> that the polarization of the double layer must not be ignored if the dimensionless relaxation criterion  $Rel$  is not small

$$Rel = \frac{\chi^\sigma}{Ka} \cong \frac{\exp(\psi_d/2)}{\chi a} \quad (1)$$

where  $K$  and  $\chi^\sigma$  are specific volume and specific surface conductivities;  $a$  — the radius of surface curvature or diameter of pores or capillaries  $\tilde{\psi}_d = e\psi_d/kT$  ( $e$  — electron charge;  $k$  — Boltzman constant;  $T$  — absolute temperature);  $a$  — radius of particle,  $\chi^{-1}$  — double layer thickness.

The second problem is that the existence of the boundary layer complicates the structure of the double layer as well as the possibility of its investigation. However the possibility of getting information on the boundary layer on the basis of electrosurface investigations should be considered. It is also necessary to take into account the complicated effect of the boundary layer when obtaining information on the double layer on the basis of electrosurface investigations.

Thirdly, the roughness or porosity of the surface is a factor which is difficult to take into consideration in the theory of double layer equilibrium, and even more so, in the theory of electrosurface phenomena. If roughness scale  $\bar{l}$  is much smaller than  $\chi^{-1}$

$$\chi \bar{l} \ll 1 \quad (2)$$

and the surface density of charge  $\sigma_s$  is not very high a part of the compensating charge of the diffuse layer  $\sigma$  located in hollows on the rough surface may be neglected. In this case, the space structure of the diffuse layer is approximately the same as that of the flat surface. At very large values of  $\sigma_s$  a significant part of compensating charge may be localized in the roughness zone even if condition (2) is satisfied but  $\chi \bar{l}$  is not a very small value (for instance 0.1—0.01).

In the case of a rough surface the concept of the compensating charge density of the diffuse layer  $\sigma_d$  holds good. As the relief of the rough surface and the real value of the latter are not known,  $\sigma_d$  means that it is a compensating charge per unit of smooth surface which include the rough surface and characterizes the macroscopic form of the body. The charge  $\sigma_d$  on the rough surface, in principle, may be measured by ion-exchange methods, for example by the method of conductometric titration which has been recently successfully applied to monodisperse latexes<sup>2</sup>.

Specific surface conductivity on a strongly charged rough surface like that on the flat surface, ignoring the ions effect may be represented in the following manner:

$$\chi^{\sigma} \approx \sigma_d u_i \quad (3)$$

where  $u_i$  is the counterion mobility. The result of calculation according to the formula

$$\sigma_m = \chi^{\sigma} / u_i \quad (4)$$

will be called the mobile charge. Distortion of the current line on roughnesses like that on unflat macrosurface should lead to deformation and polarization of the double layer. The polarization field directed opposite the external one must elicit a decrease in surface current and electroosmotic slipping, so that  $\sigma_z$  and  $\sigma_m$  will be less than  $\sigma_s$ .

While the effect of roughness on  $\sigma_m$  operates only through the double layer polarization for  $\sigma_z$ , the direct effect of roughness on the hydrodynamic flow is also sufficient. Its mathematic application requires solution of the Navier-Stokes equation which includes surface roughness. Therefore, although the roughness effect on  $\sigma_m$  and  $\sigma_z$  is, probably, symbiotic their equality disappears in the presence of the roughness effect. The coincidence of  $\sigma_m$  and  $\sigma_z$  is a criterion for the identification of  $\psi_d$  and  $\zeta$  potentials.

Because of the complications associated with the polarization of the double layer on surface irregularities, it is only possible to indicate three classes of cases in which measurements of  $\sigma_m$  and  $\sigma_z$  may represent a reliable basis for obtaining quantitative information on the double layer on an unporous surface.

1. Very low electrolyte concentrations. 2. Moderate surface charge. 3. Very smooth surface. It remains unclear, however, how low the concentration and the charges should be because there are no quantitative criteria that guarantee smallness of polarization in any of these cases.

### *Electrosurface Phenomena and the Boundary Layer*

The boundary layer investigation method was suggested by Fridrikhsberg<sup>8</sup> in complex studies of pastes of BaSO<sub>4</sub> microcrystals involving ion adsorption measurements, streaming potential and surface conductivity. The data on surface conductivity and adsorption were in good agreement, *i. e.* the mobile charge happened to be near the surface one. As electrokinetic charge was 5 times smaller than the mobile one Fridrikhsberg came to a conclusion on existence of the electroconductive boundary layer in which ion mobilities have approximately the same values as in the volume. Overbeek, in his early works<sup>6</sup> neglected the possible existence of a current between the surface and shear plane; in his most recent work<sup>9</sup>, however, this possibility is taken into account.

The appearance of the hydrodynamically immobile part of the double layer is due to the structurization of polar liquid near the surface but the thermal movement of liquid molecules and dissolved ions can remain so that electroconductivity is also present. This assumption needs greater accuracy because the boundary layer itself is insoluble and, thus, the volume conducting no current may, probably, be distinguished from that adjoining the surface<sup>10</sup>. In this case  $\psi_d$  corresponds to the potential of the boundary of the

insoluble volume and the electroconducting part of the boundary layer. It may be assumed that within the limits of the electroconducting part of the boundary layer the potential distribution can be expressed according to the Gouy-Chapman theory. Then, neglecting the mobility difference between cations and anions and the surface roughness, Bikermans's formula may be generalized in the following manner:

$$\chi^\sigma = \frac{K}{\chi} [2\mu g_1 + 4 \sinh \frac{\zeta}{4} (1 + 3m)] \quad (5)$$

where the dimensionless criterion  $m^6$  reflects electroosmotic contribution and  $g_1 = \cos h \psi_d/2 - \cos h \zeta/2$  is associated with the electric current through the boundary layer;  $\mu$  is equal to the ratio of ion mobilities in the boundary layer and in the volume. According to this formula on the basis of the measured values  $\zeta$  and  $\chi^\sigma$  one may calculate  $\psi_d$ . The potential drop in the thickness of the electroconducting layer  $\delta$  is  $\psi_d - \zeta$  and, besides,  $\zeta$  may be expressed by  $\psi_d$  and  $\delta$  by means of the Gouy-Chapman theory as  $\psi(x)$  at  $x = \delta$ . From this equation  $\delta$  may be easily calculated according to  $\psi_d$  and  $\zeta$ .

In order to carry out this programme we must be assured that inequality  $\sigma_m > \sigma_\zeta$  is caused by the presence of the boundary layer and not by the roughness or gellike layer<sup>11,12</sup>.

According to the discussion presented, with the elevation of temperature rise the structure of the boundary layer, under the effect of thermal movement, becomes destroyed, and above 70°C the boundary layer of water, probably completely collapses<sup>13</sup>.

If the boundary layer is the only reason of difference between  $\psi_d$  and  $\zeta$  with the rise of temperature this difference seems to disappear. If it is caused by roughness there is no ground to expect an approach of  $\sigma_m$  to  $\sigma_\zeta$  with the rise in temperature. The simultaneous effect of both factors is rather probable. Then, at rise in temperature  $\sigma_m$  and  $\sigma_\zeta$  will approach each other but their coincidence will not occur.

Difficulties due to roughness increase because of the double layer polarization on a non-flat macrosurface. Therefore, for example, it is impossible to obtain quantitative information on the double layer on the basis of the widely practiced investigations on powder diaphragms or pastes including the measurement of  $\zeta$  on the basis of the investigation of the electroosmosis and flow potential<sup>14</sup> and often in a number of cases of parallel measurements of conducting surfaces<sup>8</sup>. In paper<sup>7</sup> it is indicated that similar investigations at  $Rel \sim 1$  cannot be interpreted, as in this case it is impossible to take into account the double layer polarization. At  $Rel \ll 1$   $\zeta$ —potential may be calculated according to Smoluchowski but we cannot measure  $\chi^\sigma$  as a small contribution of surface conductivity to the total measured conductivity of the system corresponds to  $Rel \ll 1$ . Therefore, at any value of  $Rel$  in pastes and powders it is not possible to examine the condition of coincidence of  $\sigma_m$  and  $\sigma_\zeta$  nor can one find evidence showing that roughness complicates the double layer structure.

### *Quantitative Electrosurface Investigations on Diluted Suspensions*

Quantitative investigations of the double layer of particles should not be made on powders and pastes but on rather diluted suspensions. The electro-

kinetic potential may be calculated according to the data of electrophoretic measurements on the basis of formulas which take into consideration the double layer polarization effect<sup>15,16</sup>. Specific surface conductivity may be measured by a number of methods.

In paper<sup>16</sup> electrophoretic mobility which may enable distinguishing between  $\sigma_m$  and  $\sigma_\zeta$  is calculated. It is shown that according to  $U_{ef}$  data for three fractions of particles  $\Psi_d$  and  $\zeta$  may be calculated and the theory proposed may be examined. Provided that electro-surface properties  $\sigma_m$ ,  $\zeta$  change simultaneously with particle size these characteristics may be calculated on the basis of measurements of electrophoresis and diffusiophoresis for a fraction only<sup>17</sup>.

In the alternating field surface conductivity leads to the appearance of the oscillating ionic component of the dipole moment of a particles and a giant low-frequency dielectric dispersion (GLDD)<sup>18</sup>. The value of information on surface conductivity obtained on the basis of GLDD lies in the fact that this effect may be measured also at  $\Psi_d \ll 1$  when the roughness effect reduces to a minimum. Low-Frequency measurements, however, are extremely complicated by electrode polarization especially at high electrolyte concentrations.

This difficulty may be overcome if surface conductivity is studied according to suspension conductivity which may be measured at rather high frequencies excluding the electrode polarization effect. Because of this fact and also owing to the simplicity of conductometry the strict theory of electroconductivity of diluted suspensions is being developed.

#### *Criticism of the Generally Accepted Method of Definition of $\chi^\zeta$ according to $\bar{K}$*

If the space between plane-parallel electrodes is filled with a suspension, there is a linear dependence between the potential difference  $\delta V$  given at the electrodes and the electric current  $I$  being measured. The proportionality factor between them  $\bar{K}$  is a macroscopic characteristics of the conductivity properties of a disperse system, similar to the one by which the conductance of an electrolyte is characterized

$$\bar{K} = I/S\delta V \quad (6)$$

where  $S$  is the electrode area,  $l$  — the distance between them. If the electrolyte concentration is sufficiently high, the excess conductance associated with the double layer may be neglected so that  $\bar{K}$  appears to be less than  $K$  due to the decrease in the cross-section for the passage of current

$$\bar{K} = K/F \quad (7)$$

where  $F$  is the so-called structural resistance coefficient,  $F > 1$ . However, with decreasing electrolyte concentration, the experiment indicates a systematic excess of  $\bar{K}$  over  $K/F$

$$\bar{K} = K/F + K_s \quad (8)$$

where  $K_s$  is the contribution of excess ions of the double layer to  $\bar{K}$ , *i. e.* surface conductivity. Equation (8) is irrefutable but the introduction of specific surface conductivity  $\chi^\zeta$  into this equation by Street<sup>19</sup> which leads to the formula

$$(1-p)\overline{K} = (1-p)\frac{K}{F} + \frac{s\gamma\sigma}{F} \quad (9)$$

where  $p$  is the volume fraction of the disperse phase,  $s$  — specific surface was not and cannot be substantiated. Firstly, the introduction of the factor  $F$  into the second term means an assumption of the identity of structural resistance factors for both volume and surface current components which has never been demonstrated by anybody. Secondly, it is not taken into account in this conclusion that the presence of the double layer indicates not only an increase in the number of charge carriers but also a change in the field strength. The double layer of each particle polarizes<sup>6</sup> the incidentally arising polarization field, leaving the limits of the double layer opposite to the applied one and compensate it. Thus, the effective field bringing the current appears to be much smaller than the external one, and this is not taken into consideration in formula (9).

### *Dipole Theory of the Electroconductivity of Dispersions*

The loose development of formula (9) is compared favourably with Fricke's formula<sup>20,21</sup> based on Maxwell's strict method<sup>22</sup> and widely used in dielectric investigations<sup>23</sup> and equally suitable also for the description of electroconductivity of suspensions provided  $\overline{p}$  has a small value. Maxwell's formula<sup>22</sup> and its new deductions in<sup>24,25</sup> bind  $\overline{K}$  with the value of dipole moments  $d$  which under the influence of the current, both of charged and uncharged particles requires

$$\overline{K} = K - 4\pi nd/E \quad (10)$$

where  $n$  is the number of particles per unit volume.

Substituting in (10) the expressions of dipole moments of charged spherical and uncharged ellipsoidal particles Fricke obtained formulas of the suspension electroconductivity of such particles. Formula (10) is equally applicable to charge ellipsoidal particles, which is evident from its evaluation. In this formula the expressions for  $d$  of charged ellipsoidal particles will be included. The dipole moments of anisometric particles depend on the orientation with regard to the field vector. Restricting our considerations by the discussion of ellipsoids of revolution let us introduce symbols  $d_c$  and  $d_a$  for dipole moments at the coincidence of the field direction with the direction of the axis of symmetry  $c$  and, with the direction of the axis in the equatorial plane  $a$  respectively. Taking into account that all the orientations of suspension particles are equally probable and that the dipole moment of a particle at the arbitrary orientation is expressed by  $d_c$  and  $d_a$  at the average of all the orientations Fricke<sup>21</sup> obtained

$$\overline{K} = K + \frac{4\pi n}{E} \left( \frac{1}{3} d_c + \frac{2}{3} d_a \right) \quad (11)$$

Dipole moments of uncharged particles  $d_{ao}$ ,  $d_{co}$  may be expressed by the so-called depolarization factors  $A_a$ ,  $A_c$

$$\overline{K} = K + \frac{4\pi n}{E} \left( \frac{2}{3} d_{ao} + \frac{1}{3} d_{co} \right) = K(1 + kp) \quad (12)$$

$$k = \frac{2}{3} \frac{1}{1-A_a} + \frac{1}{3} \frac{1}{1-A_c} \quad (13)$$

In case of  $c \gg a$  when substituting  $A_a = \frac{1}{2}$ ,  $A_c = 0$  so that  $k = 5/3$  and from the formula (12) the formula for  $F$  follows

$$F = 1 + \frac{5}{3} p \quad (14)$$

These Fricke's results may be easily generalized in case of charged ellipsoids the dipole moments of which may be expressed by the sums of  $d_{a0} + d_{a1}$  and  $d_{c0} + d_{c1}$ , where  $d_{a1}$  and  $d_{c1}$  characterize the contribution of the double layer polarization to the dipole moments. Substituting these binomials in (11) rearranging the terms and using formulas (12—14) we shall obtain

$$\frac{\bar{K}}{F} = \frac{K}{F} + \frac{4\pi n}{3E} (d_{c1} + 2d_{a1}) \quad (15)$$

for electroconductivity of suspensions of charged needlelike particles.

The polarization of a cylinder in the transverse field is very similar to the polarization of a sphere<sup>5</sup> recently formula<sup>26</sup> has been developed

$$d_{a1} = a^2 c \text{Rel} (1 + 2 \text{Rel})^{-1} E \quad (16)$$

which is suitable under the condition of

$$\text{Rel} = \chi^\sigma / Ka \gg 1$$

The development of the formula for  $d_{c1}$  is given in <sup>27</sup>

$$d_{c1} = a^2 c \text{Rel} E \quad (17)$$

By substituting these expressions into (15) and taking into consideration, that  $p = 2\pi nca^2$  we obtain the expression for the relative conductance

$$\frac{\bar{K}}{K} = 1 + p \left[ -\frac{5}{3} + \frac{2}{3} \text{Rel} \left( 1 + \frac{2}{1 + 2 \text{Rel}} \right) \right] \quad (18)$$

At complete linear orientation

$$\frac{\bar{K}}{K} = 1 + p (2 \text{Rel} - 1) \quad (19)$$

In order to compare formulas (18) and (9) after substitution of  $s = 2p/a$  the latter will be

$$\frac{\bar{K}}{K} = 1 + p (2 \text{Rel} - \frac{5}{3}) \quad (20)$$

### Isopolarization State

Let's discuss the dependence of  $\bar{K}$  on  $p$  at different values of  $K$  assuming that  $\chi^\sigma$  weakly depends on  $K$ . At sufficiently large values of  $K$ , as it was

mentioned above, the first term in formula (18) is of importance; with the increasing of  $p$   $\bar{K}$  diminishes. At sufficiently small  $K$  the second term appears to play the main role: with increase of  $p$   $\bar{K}$  increases as the increase in the number of charge carriers seems to be essential.

At the definite intermediate value of  $K$  these two factors operate in opposite directions compensating each other. Then  $\bar{K}$  appears to be independent and deserves much attention. Conditions where the compensation of the deficit of conductivity associated with  $F$  and conductivity excess associated with  $\chi^\sigma$  exists, are called by isoconductance conditions. The electrolyte concentration at which the electroconductivity of the disperse system  $\bar{K}$  is equal to electrolyte electroconductivity is called the isoconductance point. In the isoconductance point  $\bar{K}$  does not depend on  $p$ .

These qualitative considerations have been repeatedly applied in order to interpret experimental data<sup>28</sup>, however, in the light of the dipole theory of electroconductivity, the interpretation of similar experiments gains a new content. The qualitative distinctions of  $\bar{K}(p)$  dependence below and above the isoconductance point indicate that when the induced dipole moments of particles are oriented in different ways to the field vector parallelly and anti-parallelly. The isoconductance point coincides with the isopolarization state of the particles. Here the induced dipole moment is absent. If the right part of formula (18) is equal to zero the isoconductance point  $Rel$  is 1,72.

#### *Experimental Investigations of the Electroconductivity of Suspension of Stick-Like Particles*

Experimental investigations of the above-mentioned theory of electroconductance have been conducted by Ovcharenko and Malyarenko<sup>29,30</sup>. The electroconductance of suspensions of palygorskite (of monocationic forms), chrysotile-asbestos and fibreglass depending on volume fraction, electrolyte concentration, and pH has been investigated. In palygorskite<sup>29</sup>, chrysotile-asbestos and glass<sup>30</sup> suspensions the linear dependence of  $\bar{K}$  on  $p$  has been observed up to  $p = 0.08 - 0.10$ . In the low electrolyte concentration areas  $\bar{K}$  increases with  $p$  and decreases in the high electrolyte concentration areas. The angle of the slope of the lines decreases with the increase in electrolyte concentration.

Curves 1, 2, 3, 4 shown in Figure 1, which define  $\bar{K}(p)$  at the frequency of 1000 Hz for suspensions of chrysotileasbestos at the various electrolyte concentrations corresponds to the chaotic orientation of particles as the measurements were made after preliminary mixing of the suspension at the moment the fields had been created. It is convenient to bring about anisotropy of electroconductivity by the treatment of the diluted suspension with sufficiently strong alternating current. Figure 2 shows a typical dependence of the anisotropy of electroconductivity expressed by the ratio  $\bar{K}_0/\bar{K}$  ( $\bar{K}_0$  — electroconductivity at the current effect during  $t$  period of time). Microscopic observations confirm that the increasing of  $\bar{K}_0$  with time up to a certain limit corresponds to the orientation of all particles with the long axis parallel to the field.



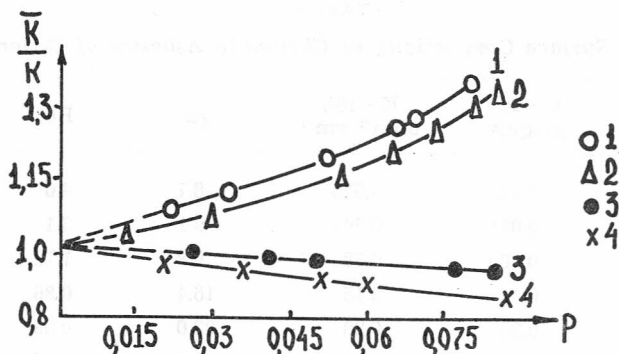


Figure 1. The effect of the volume fraction of the disperse phase on the relative electric conductivity of chrysotile-asbestos suspension. Electric conductivity of solution  $\text{ohm}^{-1}\text{cm}^{-1}$ :  
 1 —  $3.5 \cdot 10^{-6}$ ; 2 —  $4.1 \cdot 10^{-6}$ ;  
 3 —  $1.5 \cdot 10^{-5}$ ; 4 —  $2.0 \cdot 10^{-5}$ .

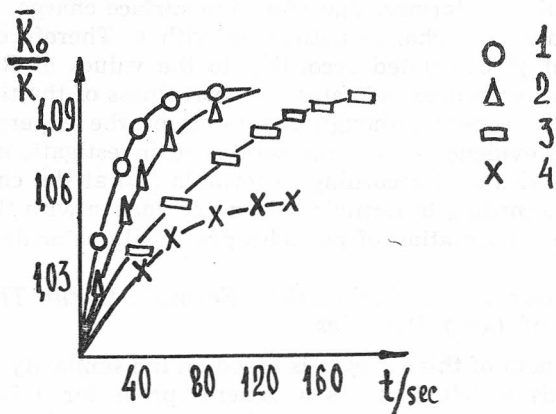


Figure 2. Kinetics of the anisotropy of electric conductivity of chrysotile-asbestos suspensions. Potential gradient, cm: 1 — 25, 2.4 — 20; 3 — 15; volume fraction p: 1, 2, 3 — 0.076; 4 — 0.041.

In order to examine the correspondence of the form factor of the objects investigated to the theoretical values electroconductivity was determined at such high concentrations where it is assumed that  $Rel = 0$ . The experimental values of the slope tangent are very close to the theoretical ones for strongly elongated cylinders: —  $5/3$  in the case of arbitrary orientation, —  $1$  — in that of longitudinal orientation.

In order to define  $Rel$  within the electrolyte concentrations studied the slope tangent corresponding to the line is equated with the expression in the square brackets of formula (18) and the equation obtained in such a way is solved in regard to  $Rel$ . On equating the formula for  $Rel$  (1) with the numerical values which are given in the fifth column of the Table I. and substituting the values of  $K$  and  $a$  into this equation the values of  $\chi^\sigma$  are defined. They are shown in the last column of the table. According to the electronic microscopy data for chrysotile-asbestos  $2a = (1 \pm 0.5) 10^{-4}$  cm and for fiberglass  $2a = (2 \pm 0.5) \cdot 10^{-4}$  cm.

TABLE I  
*Specific Surface Conductivity of Chrysotile Asbestos of Different K*

number of curve on Figure 1	$C \cdot 10^3 / \text{g/equiv.}$	$K \cdot 10^4 / \text{ohm}^{-1} \text{cm}^{-1}$	$\chi^a$	Rel	$\chi^\sigma \cdot 10^9 / \text{ohm}^{-1}$
1	0.028	0.035	8.7	4.0	0.70
2	0.031	0.041	9.1	3.1	0.70
	0.060	0.78	9.8	1.72	0.67
3	0.10	0.15	16.4	0.86	0.64
4	0.20	0.28	23.0	0.39	0.55
	0.32	0.43	29.4	0.24	0.52
	1.3	1.5	59.0	0.066	0.50

At low electrolyte concentrations it is scarcely probable that the Stern layer is filled with counterions. Therefore the surface charge, the diffuse layer charge and  $\chi^\sigma$  must not change noticeable with  $c$ . Therefore, the practically constant value of  $\chi^\sigma$  calculated according to the values of Rel which change approximately in two orders indicates the correctness of the theory and a good quality of the experiment although the range of the experimental points is wide. The second evidence of the correctness of investigations is the fact that the values of  $\chi^\sigma$  calculated according to formula (18) at the chaotic orientation of particles and according to formula (19) in accordance with the measurements at the preliminary orientation of particles practically coincide.

#### *On the Application of Smoluchowski's Formula to the Theory of Electrophoresis of Long Particles*

The development of this formula is based on the similarity of hydrodynamic and electric fields which provides a general proof for a body of arbitrary forms<sup>31</sup>. However, the electrophoresis of a long particle in the transverse field is an unusual case which needs special consideration like the problem of the hydrodynamic flow around a cylinder which needs special discussion in the hydrodynamics of low Reynolds numbers.

#### **At low Reynolds numbers**

$$\text{Re} = \frac{Ua}{\nu} \quad (21)$$

where  $\nu$  is kinematic viscosity, in the Navier-Stokes equations the inertial term is being neglected as a small value. It is, however, known<sup>32</sup> that when the transverse flow is around the cylinder at small Re and at a sufficient distance from the surface, then the inertial term is not small in the hydrodynamic equation so for the solution of this problem the non-linearized equation should be used

$$\rho(\vec{u} \nabla) \vec{u} = \text{grad } p + \eta \nabla^2 \vec{u}, \text{div } \vec{u} = 0 \quad (22)$$

Excluding pressure distribution from equation (22) and applying the curl operation to its left and right side<sup>32</sup> we obtain

$$\frac{\partial}{\partial t} \text{curl } \vec{u} = \text{curl} [\vec{u} \text{ curl } \vec{u}] \quad (23)$$

The similarity of the hydrodynamic and electric fields during electrophoresis<sup>31</sup> is expressed mathematically by the following ratio of the velocity distributions to the electric potential

$$\vec{u}(\vec{r}) = \frac{\varepsilon \zeta}{4\pi\eta} \text{grad } \varphi(\vec{r}) \quad (24)$$

which under the conditions of

$$\gamma a \gg 1 \quad (25)$$

$$\text{Rel} \ll 1 \quad (26)$$

satisfies the boundary conditions<sup>31</sup> of problem concerning electrophoresis. As the gradient curl is also equal to zero, a solution like in (24) satisfies equation (23) both in the linearized and nonlinearized form.

The theory of the longitudinal polarization of DL and of the long cylinder particles<sup>27,33</sup> allows to find conditions when it is possible to express longitudinal electrophoretic mobility by Smoluchowski's formula. Equation (27) shows the polarization charges formed at the back of a cylinder

$$Q^{\pm} = \pm \varepsilon a \frac{\Gamma}{2c} E \quad (27)$$

where  $\Gamma$  is the adsorption of the counterion in the diffuse layer calculated per unit particle square. Because of the electrostatic repulsive forces between the counterions the shorter the particle and the greater the Rel criterion the wider this charge spreads on the surface. The calculation given in<sup>33</sup> that the localization of the polarized charges and the application of formula (27) holds good under the condition  $a < 5 \cdot 10^{-3}$  which may be expressed in the following way

$$\frac{Q}{\varepsilon l^2 E} \ll 5 \cdot 10^{-3} \quad (28)$$

In order to apply Smoluchowski's formula the field created by the polarized charges  $Q^{\pm}$  on the basic part of the surface should be much smaller than the external field  $E$ . At a distance of  $x$  from the back, the field  $E(x) = Q/\varepsilon x^2$  is being created. It is evident that condition (28) is equivalent to the requirement  $E(x) \leq E$  at  $x > \sqrt{5 \cdot 10^{-3} l}$ . Therefore, formula (28) may be considered as a condition for the application of Smoluchowski's formula. This condition may be written as

$$\text{Rel} \left( \frac{a}{l} \right)^2 < 5 \cdot 10^{-3} \quad (29)$$

### *The Anisotropy of Electrophoresis*

In case of weakly charged particles which satisfy condition (25) the velocity of electrophoresis according to Smoluchowski's theory does not depend on the form of particles, or on the orientation of a particle to the external field. The anisotropy of electrophoresis appears if either condition (25) or (26) is not

fulfilled. The anisotropy of electrophoresis on the rupture of condition (25) and fulfillment of condition (26) follows from the theory of Henry and Gorin<sup>34</sup>. According to the formulas they obtained coefficient  $f$  in the formula of electrophoresis

$$U_{ef} = \frac{\zeta \varepsilon}{4\pi\eta} fE \tag{30}$$

is equal to 1/4 at the parallel orientation while at the perpendicular one  $f$  is the function of  $\gamma a = 1000$  up to 1/8 at  $\gamma a = 0.01$ . The graphical representation of this function (Figure 3, curve 1-) indicates that anisotropy takes place at  $\gamma a < 10$ , since under condition (25)  $f$  is close to 0.25.

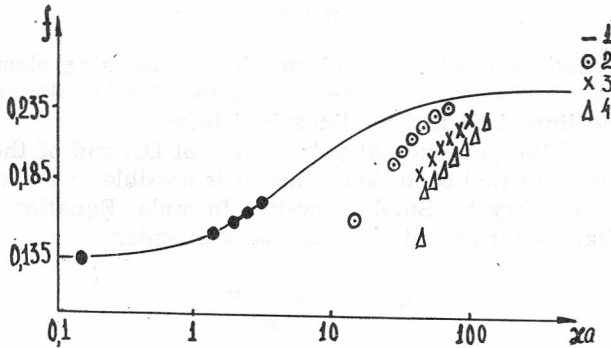


Figure 3. Dependence of coefficient  $f$  in formula (30) on the value of  $\gamma a$ : 1 — theoretical, according to Henry and Gorin; 2 — chrysotile-asbestos, 3 and 4 — glass at pH 6.8 and 10.0.

The results obtained above allow to predict a new kind of anisotropy which is realized when condition (25) is met in the case of strongly charged particles. In fact, if condition (26) is broken condition (29) is fulfilled as  $l \gg a$ . Then  $U''_{ef} = U^{S_{mol}}_{ef}$ , and  $U^{\perp}_{ef} < U^{S_{mol}}_{ef}$  because of the transverse polarization of the double layer. Taking into consideration the formula for  $U^{\perp}_{ef}$  we may also get information both on  $\gamma^{\sigma}$  and  $\zeta$  on the basis of measurement of  $U^{\perp}_{ef}$  and  $U''_{ef}$ .

*On the Identity of a Formula for Electrophoresis of a Sphere and a Cylinder in the Transverse Field at Thin DL Polarization*

We shall try to solve the question of the thin double layer polarization effect on the velocity of the electrophoresis of a long cylindrical particle with an axis oriented across the field. Now it is possible to derive the formula for  $U^{\perp}_{ef}$ , without an apparent solution of the rather complex non-linear hydrodynamic problem.

In the realization of a similar programme one of the leading factor is the possibility<sup>32</sup> of the change of the non-linear inertial term  $(\vec{u} \nabla) \vec{u}$  (22) by the approximate expression  $(\vec{u}^{\perp}_{ef} \nabla) \vec{u}$  where  $\vec{u}^{\perp}_{ef}$  is the constant rate of the liquid flow at a large distance which is not perturbed by the presence of a cylinder (the equation is written in the system of coordinates connected with

a cylinder). In this so-called Ossen approximation the equation of hydrodynamics is linear in regard to the unknown distribution of rates

$$\rho \left( u_{ef}^{\perp} \nabla \right) \vec{u} = \text{grad } P + \eta \nabla^2 \vec{u} \quad (31)$$

In the theory of the transverse polarization of the thin DL of a long cylinder, which was mentioned above, it appears that like in the case of a sphere<sup>15</sup>, the distribution of potential beyond the limits of the polarized DL is similar to the distribution of  $\varphi_0$  in the case of uncharged particle. Therefore, like in the case of a sphere, the velocity distributions of the electroosmotic slipping on the cylinder surface  $u_{\theta}$  ( $\theta$ ) are geometrically similar when polarization is present or is absent, *i. e.*

$$u_{\theta}(\theta) = u_{\theta} \sin \theta \quad (32)$$

Without the solution of the hydrodynamic equation it may be so, but in view of its linearity the distribution of velocities which satisfies the boundary condition (32) and the condition of equality to zero of the normal component of rate, it linearly depends on  $U_{\theta}$ . Therefore, a tensor component of viscous tension also depends on  $U_{\theta}$  linearly, thus the integral of a tensor  $p$  of viscous tension on the surface of a sphere is

$$\iint p ds = K_{eo} u_{\theta} \quad (33)$$

However,  $K_{eo}$  does not really depends on  $U_{\theta}$ ; it is the non-linear function of  $U_{ef}^{\perp}$  in equation (31). The considerations which have led to formulas (32) and (33) indicate that function  $K_{eo}(U_{ef}^{\perp})$  is the same both when polarization of the thin DL occurs and when it is absent. The resulting effect of electroosmotic slipping causes particle motion in regard to the medium  $U_{ef}^{\perp}$  and crossing of viscous resistance  $K_{Os}^{-1} U_{ef}^{\perp}$ , so that

$$U_{ef}^{\perp} = K_{eo} K_{Os} U_{\theta} \quad (34)$$

where the symbol  $K_{Os}$  is introduced for the coefficient of the hydrodynamic resistance of a cylinder in order to emphasize that it should be calculated from Ossen approximation. Coefficient  $K_{Os}$  cannot be associated with polarization at all. Therefore, the product of  $K_{eo} K_{Os}$  is expressed by function  $U_{\perp}^{ef}$  under the conditions of polarization and when polarization is absent. However, under conditions which are not complicated by polarization equation (34) is transformed into Smoluchowski's formula. Hence, it follows that the the product of  $K_{eo} K_{Os}$  does not depend on  $U_{\perp}^{ef}$  and that it is the number coefficient

$$U_{ef}^{\perp} = K_{eo} K_{Os} U_{\theta} = \text{const } U_{\theta} \quad (35)$$

We shall consider this equation for both conditions and exclude const by using the ratio of the left and right sides. Then we shall obtain

$$U_{ef}^{pol} = U_{ef}^{Smol} \frac{U_{\theta}^{pol}}{U_{\theta}^{Smol}} = \frac{\epsilon \zeta E}{4\pi\eta} \frac{U_{\theta}^{pol}}{U_{\theta}^{Smol}} \quad (36)$$

Here the upper indices indicate that the given value is being considered either under the conditions of polarization or when it is absent under Smoluchowski's conditions.

The conclusion made and formula (36) are equally applicable in the case of a sphere<sup>16</sup>. Since both hydrodynamic parts of the problem of electrophoresis and that on polarization of DL are formulated almost identically for a sphere and a cylinder it is convenient to consider them parallelly. Thus, in the case of a sphere<sup>16</sup>

$$\Psi^*(r, \theta) = \varphi(r, \theta) + c_p(r, \theta) Y_c(f_0) \quad (37)$$

where  $\varphi$  and  $c_p$  are potential distributions and concentrations beyond DL. The distributions  $\varphi$  and  $c_p$  which satisfy the Laplace equations have been developed like

$$\tilde{\varphi} = - \left[ \tilde{x} + \left( \frac{1}{2} + \frac{A_{\text{sph}}}{\tilde{x}^2} \right) \right] \delta \varphi_0 \cos \theta; \quad c_p = \frac{B_{\text{sph}}}{\tilde{x}^2} \cos \theta \quad (38)$$

in the case of a sphere, while in the case of a cylinder they should be developed as

$$\tilde{\varphi} = - \left[ \tilde{x} + \left( 1 + \frac{A_{\text{cy}}}{\tilde{x}} \right) \right] \delta \varphi_0 \cos \theta; \quad \tilde{c}_p = \frac{B_{\text{cy}}}{\tilde{x}} \cos \theta \quad (39)$$

If (37) and (38) are substituted into two boundary conditions<sup>16</sup> connecting normal flows and the surface divergence of the tangential flows in the diffuse layer for cations and anions, systems consisting of two heterogeneous linear equations for the determination of  $\mathbf{B}$  and  $\mathbf{A}$  are obtained.

It appears that these systems differ only because the inhomogeneous term of equations is 4/3 times greater in the case of a cylinder than in the case of a sphere. Hence,

$$A_{\text{cy}} = \frac{4}{3} A_{\text{sph}}, \quad B_{\text{cy}} = \frac{4}{3} B_{\text{sph}} \quad (40)$$

When the expression of  $\Psi^*$  is derived in accordance with (37) and integration in formula (16) is carried out

$$U_{\Theta} = \int_0^{\infty} \left[ 2 \int_x \Psi^* \frac{d^2 f_0}{dx^2} dx - \Psi^* \frac{df_0}{dx} \right] dx \quad (41)$$

we obtain:

$$U_{\Theta \text{cy}}^{\text{pol}} = \frac{\varepsilon}{4\pi\eta} \left[ (2 + A_{\text{cy}}) \tilde{\zeta} - B_{\text{cy}} 4 \ln \cos h \frac{\tilde{\zeta}}{4} \right] \quad (42)$$

$$U_{\Theta \text{sph}}^{\text{pol}} = \frac{\varepsilon}{4\pi\eta} \left[ \left( \frac{3}{2} + A_{\text{sph}} \right) \tilde{\zeta} - B_{\text{sph}} 4 \ln \cos h \frac{\tilde{\zeta}}{4} \right] \quad (43)$$

Expressing  $A_{\text{cy}}$  by  $A_{\text{sph}}$  and  $B_{\text{cy}}$  by  $B_{\text{sph}}$  in formula (42) by means of (40) it is concluded that

$$U_{\Theta \text{cy}}^{\text{pol}} = \frac{4}{3} U_{\Theta \text{sph}}^{\text{pol}} \quad (44)$$

and that when polarization is absent, *i. e.* at  $A = 0, B = 0$

$$U_{\text{ocy}}^{\text{Smol}} = \frac{4}{3} U_{\text{osph}}^{\text{Smol}} \quad (45)$$

Comparing this result with formula (36) it can be concluded that the velocity of the electrophoresis of a sphere and of a cylinder as the functions of  $\zeta$ ,  $\tilde{\Psi}_d$ ,  $\chi a$  is described by formula (16) and for a sphere — by formula (46).

$$\tilde{U}_{\text{ef}}^{\perp} = \frac{3}{2} \tilde{\zeta} - \frac{3}{2} \frac{\tilde{\zeta} [4(1+3m) \sinh(\tilde{\zeta}/4) + 2g_1] + [2(1+3m) \sinh(\tilde{\zeta}/2) - 3m\tilde{\zeta} + 2g_2] 4 \ln \cosh(\tilde{\zeta}/4)}{\chi a + 8(1+3m) \sinh(\tilde{\zeta}/4) - 24m \ln \cosh(\tilde{\zeta}/4) + 4g_1} \quad (46)$$

$$g_2 = \mu (\sinh \tilde{\psi}_d/2 - \sinh \tilde{\zeta}/2), \quad \tilde{\zeta} = e\zeta/kT$$

### Experimental Investigations of the Anisotropy of Electrophoresis

Experimental examination of these assumptions was made by V. V. Malyarenko who used the method of microscopic electrophoresis for the measurement of  $U_{\text{ef}}''$  and  $U_{\perp}^{\text{ef}}$  particles of chrysotile-asbestos and fibreglass with the length  $l$  of  $2 \cdot 10^{-3}$  cm and the radius  $5 \cdot 10^{-5}$  cm and  $10^{-4}$  cm respectively. At large particle length the drop of the electroosmotic velocity in the cross-section of the microelectrophoretic close type cell prevents the measurement of  $U_{\perp}^{\text{ef}}$ . In order to overcome this difficulty the measurements have been made near the horizontal plane of symmetry of the flat cell of great height. The calculations show that with  $10^{-3}$  cm deviation from the plane of symmetry the velocity of electrophoresis changes 0.5%. The measurements of  $U_{\text{ef}}''$  were made in the centre of the cell and at the wall. According to Jackson's method<sup>35</sup> they allowed exclusion of the electroosmotic component from the value of the velocity observed.

When the electrolyte concentrations were below the centinormal ones the measurements were made in the open type cell<sup>36</sup>. With the increase of conductance the electrode gassing near the bubble<sup>36</sup> prevented the measurement.

First, the dependence of  $U_{\text{ef}}''$  on the length of a particle was studied. The increase of  $U_{\text{ef}}''$  with  $l$  (Figure 4) reflecting the decrease in the average value of the polarization field with the extension of the distance between the polarization charges at the ends and in the middle of the particle, equals to  $1/2$ . At the rather long length of a particle  $U_{\text{ef}}''$  does not depend on  $l$ , it indicated that the field of polarization charges of the ends averaged through the surface of a particle is small in comparison with the external one.

Thus on the basis of the measurements of electrophoretic mobility of such long particles which are not complicated by the polarization  $\zeta$  may be calculated according to Smoluchowski's formula.

The transverse velocity of electrophoresis  $U_{\text{ef}}^{\perp}$  does not appear not to be dependent on the particle length since the latter exceeds its diameter, *i. e.*  $l > 2a$ . Hence, a number of important conclusions follow. The analysis of the mechanism of concentration polarization shows that the linear sizes of a particle have a more significant effect than its form. Therefore the velocity

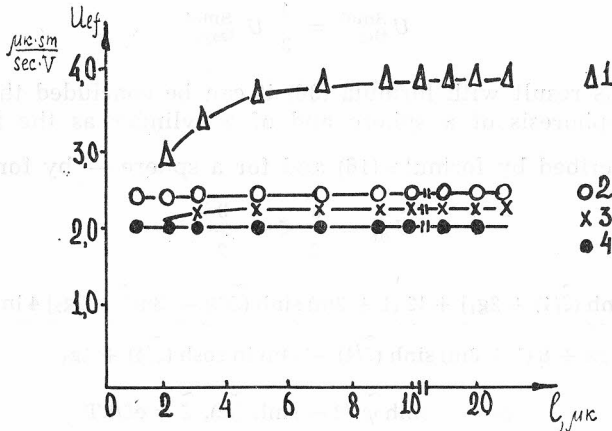


Figure 4. Dependence of the longitudinal  $U$  (curves 1,3) and transverse  $U$  (curves 2,4) velocities of electrophoresis of chrysotile-asbestos particles on their length at electrolyte concentrations  $10^{-4}$  M/liter (curves 1,2),  $10^{-3}$  M/liter (curves 3,4).

of a spherical particle and of a cylindrical one of the same diameter may be equalized if, the length and the diameter of a cylinder are equal  $U_{ef}^{sph} = U_{ef}^{\perp} |_{l=2a}$ . Thus the invariability of  $U_{ef}^{\perp}$  at  $l > 2a$  confirms the identity of the formulas for  $U_{ef}^{sph}$  and  $U_{ef}^{\perp} |_{l > 2a}$ :  $U_{ef}^{\perp} |_{l > 2a} = U_{ef}^{\perp} |_{l \sim 2a} = U_{ef}^{sph}$ . In addition, the coincidence of  $U_{ef}^{sph} \approx U_{ef}^{\perp} |_{l \sim 2a}$  and  $U_{ef}^{\perp} |_{l > 2a} = U_{ef}^{sph}$  allow to expecte that  $U_{ef}^{sph} = U_{ef}^{\perp}$  not only at the limiting values  $l (l = 2a, l \gg 2a)$  but in all intermediate cases ( $2a < l$ ). This can also be proved experimentally as  $U_{ef}^{\perp}$  is not dependent on  $l$  at  $l > 2a$ .

The experimentally established independence of  $U_{ef}^{\perp}$  on  $l$  and a theoretical conclusion on the identity of  $U_{sph}$  and  $U_{ef}^{\perp} |_{l > 2a}$  lead to the assumption that at the orientation of the long axis across the field, the polarization of the double layer and electrophoresis are sensitive only to the transverse (minimum) sizes of a particle.

As Figure 4 shows at a small ionic force  $U_{ef}^{\perp}$  is approximately by 1.5 times smaller than  $U_{ef}''$ . With an increase in ionic force and in  $\chi$  a the polarization diminishes and in accordance with these assumptions the values of  $U_{ef}''$  and  $U_{ef}^{\perp}$  approach each other. A comparison between the curve lines in Figure 3 reveals that in the  $\chi$  a interval studied the anisotropy mainly depends on the polarization of the double layer.

Taking into consideration the fact that under condition (25) polarization is perceptible only at the values of  $\tilde{\Psi}_d$ , which markedly exceed the unit, formula (46) can be simplified at  $\tilde{\Psi}_d > 1.5$  without restricting of its generalization

$$\tilde{U}_{ef}^{\perp} = \frac{3}{2} \left[ \tilde{\zeta} \left[ 1 - \frac{\text{Rel} (1 + 4\tilde{\zeta}^{-1} \ln \cosh (\tilde{\zeta}/4))}{1 + 2 \text{Rel}} \right] \right] \quad (47)$$



where Rel is expressed by the formula

$$\text{Rel} = \frac{\exp(\psi_a/2) + 3m \exp(\tilde{\zeta}/2)}{\chi a} \quad (48)$$

By substituting  $U_{\text{ef}}'' = 3/2 \tilde{\zeta}$  into expression (47) and solving the latter in regard to Rel we shall obtain

$$\text{Rel} = (n - 1) [2 - n (1 - 4\tilde{\zeta}^{-1} \ln \cosh(\tilde{\zeta}/4))^{-1}] \quad (49)$$

where  $n = U_{\text{ef}}''/U_{\text{ef}}^{\perp}$ .

On substitution of the value of Rel calculated according to this formula into formula (48) we shall obtain a simple equation for the calculation of  $\tilde{\zeta}$ . With the help of these formula and with the results of the measurements of the anisotropy of electrophoresis Rel and then  $\chi^{\sigma}$  can be calculated. A comparison of the data on  $\chi^{\sigma}$  in the wide concentration range which were obtained by two independent methods with the anisotropy of electrophoresis and electric conductivity of suspensions is of interest. The data given in Table II. for the suspensions of chrysotile-asbestos and glass indicate that both of these methods give the close values. The data on  $\chi^{\sigma}$  obtained by the method of electric conductivity weakly dependent on the electrolyte concentration seem to be more reliable. Further improvement of the theory of the anisotropy of electrophoresis and of the experimental technique are necessary.

If certain variations in  $\chi^{\sigma}$  due to electrolyte concentration are neglected, the values of Rel and  $\chi^{\sigma}$  measured by various methods should be close to

TABLE II  
Specific Surface Conductivity of Chrysotile Asbestos and Glass Determined by Various Methods

$C \cdot 10^3 /$ g/equiv.	Experimental method		$C \cdot 10^3 /$ g/equiv.	Experimental method	
	electro- phoresis	Electric conductivity of suspension		electro- phoresis	Electric conductivity of suspension
chrysotile-asbestos					
0.028	—	0.70	0.32	—	0.52
0.031	—	0.70	0.40	0.34	—
0.060	—	0.67	1.0	0.22	—
0.10	0.30	0.64	1.3	—	0.50
0.20	0.30	0.55	2.0	0.22	—
fiberglass					
0.047	—	1.15	0.40	0.84	—
0.073	—	1.2	0.46	—	1.35
0.099	—	1.25	0.60	1.1	—
0.10	0.52	—	0.80	1.3	—
0.20	0.67	1.3	1.0	1.4	1.35

each other. This indicates that the induced dipole moments are the basis of both effects: of the anisotropy of electrophoresis and of the anisotropy of electric conductivity. Analogous information on the induced dipole moments and on  $\text{Re}l$  and  $\chi^\sigma$ , respectively, may be obtained by electrooptical investigations<sup>37</sup>.

Electric conductivity measurements provide precise quantitative information only in case of a thin DL. Therefore  $\chi^\sigma$  cannot be calculated by using the interesting data in papers<sup>38,39</sup> where condition (25) was not satisfied.

The difference between  $\zeta$  and  $\Psi_d$  potential in glass particles is not surprising since drop in potential in the gel-like layer<sup>40</sup> takes place. The contribution of the Stern layer ions to the surface electric conductivity is, perhaps, small since the surface is usually hydrated<sup>41,42</sup>, and the distance between the counterion and the surface is of such a value to decrease the filling of the Stern layer by the counterions.

However, a considerable contribution of the Stern layer to  $\chi^\sigma$  is possible<sup>43</sup> at a wide electrolyte concentration range particularly for univalent counterions. The difference between the mobile and electrokinetic charges may be caused by the filling of the Stern layer by counterions, by surface roughness and by boundary layer.

Unfortunately, the experimental results presented above do not include data on temperature dependences, which would be necessary for a better understanding of the role of the boundary layer<sup>13</sup>. However, the theories of induced dipole moment, electric conductivity of suspensions and anisotropy of electrophoresis were experimentally examined.

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### SAŽETAK

**Složeno istraživanje dvostrukog sloja koloidne čestice. Električna vodljivost suspenzija i elektroforetska anizotropija**

*S. S. Duhin*

Analizirane su kvantitativne informacije za dvostruki sloj koloidnih čestica dobivene na osnovi električnih mjerenja površina. Na osnovi inducirano dipolnog momenta čestica izvedena je stroga teorija električne vodljivosti razrijeđenih suspenzija.

Pokazana je podudarnost točke jednake vodljivosti sa izopolarizacijskim stanjem čestice. Razvijena je teorija elektroforetske anizotropije za čestice dugoljastog štapičastog oblika. Pokazana je jednakost formula za elektroforezu okruglih i cilindričnih čestica okomito orijentiranih prema polju za male debljine dvostrukog sloja. U širokom rasponu koncentracija elektrolita dobivena je dobra podudarnost između vrijednosti inducirano dipolnog momenta i specifične površinske vodljivosti, i to na osnovi mjerenja električne vodljivosti suspenzija i mjerenja elektroforetske anizotropije. Teorije inducirano dipolnog momenta, električne vodljivosti suspenzija i elektroforetske anizotropije provjerene su na osnovi eksperimenata.

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