

Development of a new pore model II. Electrokinetic transport properties, surface conductance, and convective charge transport

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Development of a New Pore Model

II. Electrokinetic Transport Properties, Surface Conductance, and Convective Charge Transport

A. J. KUIN AND H. N. STEIN

*Laboratory of Colloid Chemistry, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands*

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The semisinusoidal pore model describes the electrokinetic transport correctly when electrical conductance is predominantly bulk conductance. On the basis of irreversible thermodynamics and the semisinusoidal pore model a stability diagram can be constructed showing the conditions under which stationary transport is possible. In describing surface conductance and convective charge transport, differences between model predictions and experimental data exist. It is shown that these differences are related to assumptions concerning the electrical charge distribution rather than to the pore model itself.

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1. INTRODUCTION

The influence of the pore structure on transport phenomena through porous beds is very large. Therefore, an accurate description of this structure is essential for many processes in which porous materials and packed beds are involved, such as heat transfer (1), mass transfer (2), hydrodynamic transport (3), electrical conductance (4), and electrokinetic transport (5).

The present paper will be restricted to electrokinetic and electrical transport. In the past, electrokinetic transport through porous beds was described by semiempirical models (6–8) or use was made of very simple pore forms like straight cylinders (s.c.) or tortuous cylinders (t.c.) (5, 8). A better pore model was used by O'Brien and Perrins (9). They employed a cell theory. Unfortunately, their predictions of the streaming potential were in quantitative disagreement with Van der Put's measurements (10) despite the advanced electrostatic part of their model. In our opinion this may be due to difficulties at the contact points of the particles.

Recently, the more advanced semisinusoidal pore (s.s.p.) model has been introduced (11, 42). This model does not cause any complications in the transport equations at the contact points between the particles as attention is focused on the pore form and not on the particle form.

In the s.s.p. model the pores have cylindrical symmetry and periodic constrictions, and the pore wall also shows sharp angles (11, 42). The validity of the pore model has been tested with hydrodynamic and electrical measurements. Only one free parameter rests when experimental values are introduced for the porosity, average particle size and dimensions of the beds. This free parameter was calibrated with hydrodynamic conductance (which is the reciprocal of the hydrodynamic resistance) measurements. The model was then found to predict correctly the electrical conductance under circumstances where only the bulk conductance was important. The s.c. and t.c. models, however, did not describe the experimental data satisfactorily. In the present paper the model is tested further by comparing it with electrokinetic conductance measure-

ments under conditions where surface conductance has no influence. These conditions are similar to those described by Van der Put (12) and Derjaguin and Dukhin (5). In addition, an attempt is made to describe the influence of surface conductance and the contribution of convective charge transport in terms of the s.s.p. model.

II. CALCULATION OF THE ELECTROKINETIC CONDUCTANCE

The electrokinetic conductance will be defined as the stationary volumetric flow divided by the applied potential difference at zero pressure difference in order to maintain consistency with the concepts of irreversible thermodynamics. It is sometimes colloquially called electroosmosis, but we believe this to be incorrect because in the terminology of irreversible thermodynamics electroosmosis should be restricted to the volume flow per unit current (i.e., L_{12}/L_{22} in Ref. (13)). To calculate the electrokinetic conductance, first the charge density ρ in the diffuse double layer (D.D.L.) has to be known. This charge density is given by the Poisson equation (14)

$$\rho = -\epsilon \nabla^2 \psi, \quad [1]$$

where ϵ is the permittivity and ψ is the potential. It also has to obey Boltzmann's equation (5, 8):

$$n_i = n_i^0 \exp\left(-\frac{z_i e \psi}{kT}\right) \quad [2]$$

combined with

$$\rho = \sum_i z_i e n_i^0, \quad [3]$$

where z_i is the number of unit charges of ion i , n_i^0 is its bulk concentration, e is the electronic charge, k is Boltzmann's constant, and T is the absolute temperature.

Let α , β , and φ be given by the following transformation from the cylindrical coordinate system (11):

$$\alpha = R_s \left(\left(\sin \frac{\pi z}{L} \right)^2 + \sinh^2 C \left(1 - \frac{r}{R_1} \right) \right) \quad [4]$$

$$\beta = -\frac{L^2}{2\pi^2 R_s} \ln \left| \tan \frac{\pi z}{L} \right| + \frac{R_1^2}{2C^2 R_s} \ln \left| \tanh C \left(1 - \frac{r}{R_1} \right) \right| \quad [5]$$

$$\varphi = \varphi \quad [6]$$

and let h_α , h_β , and h_φ be the scaling factors to transform a vector from cartesian coordinates to the semisinusoidal coordinates, α , β , φ .

Then according to Part I (11) of this series

$$h_\alpha = \frac{1}{(f^2 + g^2)^{1/2}} \quad [7]$$

$$h_\beta = \frac{fg}{(f^2 + g^2)^{1/2}} \quad [8]$$

$$h_\varphi = r, \quad [9]$$

where f and g are

$$f = \frac{R_s \pi}{L} \sin \frac{2\pi z}{L} \quad [10]$$

$$g = -\frac{R_s C}{R_1} \sinh 2C \left(1 - \frac{r}{R_1} \right). \quad [11]$$

In these equations R_s is the smallest pore radius and R_1 is the largest, L is the periodicity, C is the pore constant as determined in Part I, and r and z are cylindrical coordinates.

Combining Eqs. [1]–[3], transforming to semisinusoidal coordinates, and assuming that there is only a potential gradient in the β direction gives (15, 16)

$$\frac{1}{h_\alpha h_\beta h_\varphi} \frac{\partial}{\partial \alpha} \frac{h_\alpha h_\beta}{h_\alpha} \frac{\partial \psi}{\partial \alpha} = -\sum_i \frac{z_i e n_i^0}{\epsilon} \exp\left(-\frac{z_i e \psi}{kT}\right). \quad [12]$$

The assumption that there is only a potential gradient in the β direction means that the equipotential surfaces of the D.D.L. contain the parameter curves $\alpha = \text{constant}$ which are orthogonal to the α direction.

This was verified by solving Eq. [12] nu-

merically (see below) for various values of β . It was found that the variation of the potential along a parameter curve $\alpha = \text{constant}$ is smaller than 1%, so the assumption is reasonable. This also shows that the curves $\alpha = \text{constant}$ are a good approximation for the actual streamlines, since the equipotential surfaces are parallel to the streamlines.

Insertion of Eqs. [7]–[9] into Eq. [12] gives

$$\frac{f^2 + g^2}{rgf} \frac{\partial rgf}{\partial \alpha} \frac{\partial \psi}{\partial \alpha} = - \sum_i \frac{z_i e n_i^0}{\epsilon} \exp\left(-\frac{z_i e \psi}{kT}\right) \quad [13]$$

with boundary conditions

$$\alpha = R_s; \quad \psi = \zeta \quad [13a]$$

at the wall and

$$\alpha = \alpha_a; \quad \frac{\partial \psi}{\partial \alpha} = 0 \quad [13b]$$

at the pore axis.

The Navier–Stokes equation, with no pressure gradient and an applied electric potential gradient, is

$$\mu \nabla^2 \mathbf{V} - \rho \mathbf{E} = 0, \quad [14]$$

where μ is the dynamic viscosity, \mathbf{V} is a vector describing the velocity field in the pore, and \mathbf{E} is a vector describing the electrical field in the pore.

For an incompressible liquid the equation of continuity is

$$\nabla \cdot \mathbf{V} = 0. \quad [15]$$

Equations [14] and [15] give

$$\mu \nabla \times \nabla \times \mathbf{V} + \rho \mathbf{E} = 0. \quad [16]$$

In Part I the following equation was derived for the electrical field strength:

$$\mathbf{E} = \frac{1}{h_\beta} \frac{L \Delta V}{l \langle L_\beta \rangle}, \quad [17]$$

where ΔV is the potential difference across the porous bed, l is its length, and $\langle L_\beta \rangle$ is the average length of a parameter curve. α is constant from 0 to L in cylindrical coordinates. $\langle L_\beta \rangle$ equals

$$\langle L_\beta \rangle = \frac{4}{R_1^2} \int_0^{R_1} \int_0^{L/2} \times r \left\{ 1 + \left(\frac{\pi R_1 \sin \frac{2\pi z}{L}}{LC \sinh 2C \left(1 - \frac{r}{R_1}\right)} \right)^2 \right\}^{1/2} dz dr. \quad [18]$$

As \mathbf{V} only has a component in the β direction, denoted as V , Eqs. [16] and [17] give

$$\frac{1}{h_\alpha h_\varphi} \frac{\partial h_\varphi}{h_\alpha h_\beta} \frac{\partial h_\beta V}{\partial \alpha} = \frac{\rho(\alpha) L \Delta V}{\mu l \langle L_\beta \rangle h_\beta} \quad [19]$$

with boundary conditions

$$\alpha = \alpha_a; \quad \frac{\partial V}{\partial \alpha} = 0 \quad [19a]$$

at the axis and

$$\alpha = R_s; \quad V = 0 \quad [19b]$$

at the wall.

For the linear velocity V_a on the pore axis this gives

$$V_a = \frac{\Delta V L}{\mu l \langle L_\beta \rangle h_\beta(\alpha_a)} \int_{\alpha_a}^{R_s} \frac{h_\alpha h_\beta}{h_\varphi} \int_{\alpha_a}^{\alpha} \frac{h_\alpha h_\varphi}{h_\beta} \rho(\alpha) \partial \alpha \partial \alpha. \quad [20]$$

If the D.D.L. thickness is small compared with the local pore radius, the velocity profile is approximately flat in the α , β , φ coordinate system.

Then for the volumetric flow through the pore J_V^{pore} one obtains for a flat velocity profile:

$$J_V^{\text{pore}} = 2\pi V_a \int_{R_s}^{\alpha_a} h(\alpha) \partial \alpha, \quad [21]$$

where $2\pi h(\alpha) \partial \alpha$ is a unit surface element of a surface with its normal in the β direction (Fig. 1). $h(\alpha)$ is derived in Part I. If there are n pores the electrokinetic volume flow $J_V^{\text{e.k.}}$ equals

$$J_V^{\text{e.k.}} = n J_V^{\text{pore}}. \quad [22]$$

If $\langle \pi R^2 \rangle$ is the average pore cross section, then

$$n = pA / \langle \pi R^2 \rangle, \quad [23]$$

where p is the porosity and A is the cross-sectional area of the bed. In the semisinusoidal pore, $\langle \pi R^2 \rangle$ equals (11, 42)

$$\langle \pi R^2 \rangle = \frac{2\pi R_1^2}{C^2 L} \int_0^{L/2} \left[\operatorname{arcsinh} \left(\cos \frac{\pi z}{L} \right) - C \right]^2 dz. \quad [24]$$

Equations [2], [3], [7]–[9] combined with Eqs. [18], [20]–[24] give

$$\begin{aligned} \left(\frac{J_v}{\Delta V} \right)^{\text{e.k.}} &= \left[\frac{ec^2 L^2 p A}{4\mu l} \int_{R_s}^{\alpha_a} h(\alpha) \partial \alpha \right] \\ &\times \left\{ \frac{(f^2 + g^2)^{1/2}}{fg} \right\}_{\alpha=\alpha_a} \int_{\alpha_a}^{R_s} \frac{gf}{r(f^2 + g^2)} \\ &\times \int_{\alpha_a}^{\alpha} \frac{r}{gf} \sum_i n_i^0 z_i \exp \left(-\frac{z_i e \psi}{kT} \right) \partial \alpha \partial \alpha \\ &\times \left[\int_0^{L/2} \left(\operatorname{arcsinh} \left(\cos \frac{\pi z}{L} \right) - C \right)^2 dz \int_0^{R_1} \int_0^{L/2} \right. \\ &\times \left. r \left\{ 1 + \left[\frac{\pi R_1 \sin \frac{2\pi z}{L}}{LC \sinh 2C \left(1 - \frac{r}{R_1} \right)} \right]^2 \right\}^{1/2} dr dz \right]^{-1}. \end{aligned} \quad [25]$$

III. CALCULATION OF THE CONVECTIVE TRANSPORT CONTRIBUTION TO THE ELECTRICAL CONDUCTANCE

To obtain the local velocity in the D.D.L., Eq. [19] has to be solved for general α .

$$V(\alpha) = \frac{\Delta V L}{\mu l \langle L_\beta \rangle h_\beta(\alpha)} \int_{\alpha}^{R_s} \frac{h_\alpha h_\beta}{h_\varphi} \int_{\alpha_a}^{\alpha} \frac{h_\alpha h_\varphi}{h_\beta} \rho(\alpha) \partial \alpha \partial \alpha. \quad [26]$$

The total convective current transported through the D.D.L. equals

$$I^{\text{conv}} = 2\pi \int_{\alpha_a}^{R_s} \sum_i z_i e n_i V(\alpha) h(\alpha) \partial \alpha. \quad [27]$$

Equations [2], [7]–[9], and [26] substituted in Eq. [27] give, for the porous bed,

$$\begin{aligned} \left(\frac{I}{\Delta V} \right)^{\text{conv}} &= \frac{2\pi n L}{\mu l \langle L_\beta \rangle} \int_{\alpha_a}^{R_s} \frac{(f^2 + g^2)^{1/2}}{fg} \\ &\times \sum_i n_i^0 z_i e \exp \left(-\frac{z_i e \psi}{kT} \right) h(\alpha) \int_{\alpha}^{R_s} \frac{gf}{r(f^2 + g^2)} \\ &\times \int_{\alpha_a}^{\alpha} \frac{r}{fg} \sum_i n_i^0 z_i e \exp \left(-\frac{z_i e \psi}{kT} \right) \partial \alpha \partial \alpha \partial \alpha. \end{aligned} \quad [28]$$

The number of pores n is obtained from Eqs. [23] and [24] and inserted in Eq. [28], which gives

$$\begin{aligned} \left(\frac{I}{\Delta V} \right)^{\text{conv}} &= \frac{p A L^2 C^2 \sum_i n_i^0 e z_i \int_{\alpha_a}^{R_s} \frac{(f^2 + g^2)^{1/2}}{fg} h(\alpha) \exp \left(-\frac{z_i e \psi}{kT} \right)}{4\mu l \int_0^{L/2} \left(\operatorname{arcsinh} \left(\cos \frac{\pi z}{2} \right) - C \right)^2 dz} \\ &\times \frac{\int_{\alpha}^{R_s} \frac{fg}{r(f^2 + g^2)} \int_{\alpha_a}^{\alpha} \frac{r}{fg} \sum_i n_i^0 z_i e \exp \left(-\frac{z_i e \psi}{kT} \right) \partial \alpha \partial \alpha \partial \alpha}{\int_0^{R_1} \int_0^{L/2} r \left\{ 1 + \left[\frac{\pi R_1 \sin (2\pi z/L)}{LC \sinh 2C (1 - (r/R_1))} \right]^2 \right\}^{1/2} dr dz}. \end{aligned} \quad [29]$$

IV. CALCULATION OF THE ELECTRICAL CONDUCTANCE INCLUDING THE EFFECT OF SURFACE CONDUCTANCE

The current density i through the D.D.L. equals

$$i = \sum_i |z_i| e n_i \left\langle \frac{\partial a_i}{\partial t} \right\rangle. \quad [30]$$

If a_i is the position vector of ion i and $\langle \partial a_i / \partial t \rangle$ is the average velocity of ions of type i . A derivation analogous to the one in Section VI

of Part I gives for the electrical current through the n pores building up the porous bed

$$I = \frac{2\pi ne\Delta VL}{l\langle L_\beta \rangle} \sum_i |z_i| \mu_i \int_{R_s}^{\alpha_a} n_i h(\alpha) d\alpha, \quad [31]$$

where μ_i is the mobility of ion i as defined in Part I.

Insertion of Eqs. [17], [23], and [24] in [31] gives

$$\left(\frac{I}{\Delta V}\right)^{\text{cond}} = \frac{pAC^2L^2 \sum_i \lambda_i |z_i| c_i^0 \int_{R_s}^{\alpha_0} \exp\left(-\frac{z_i e \psi}{kT}\right) h(\alpha) d\alpha}{4l \int_0^{L/2} \left(\operatorname{arcsinh}\left(\cos \frac{\pi Z}{L}\right) - C\right)^2 dz \int_0^{R_1} \int_0^{L/2} r \left\{1 + \left[\frac{\pi R_1 \sin(2\pi Z/L)}{L \operatorname{arcsinh} C(1 - (r/R_1))}\right]^2\right\}^{1/2} dr dz}, \quad [32]$$

where λ_i is the equivalent conductance of ion i and c_i^0 is the bulk concentration of ion i . Equation [32] can also be obtained by substituting in Eq. [62] of Part I

$$\int_{R_s}^{\alpha} \exp\left(-\frac{z_i e \psi}{kT}\right) h(\alpha) d\alpha \quad \text{for} \quad \int_{R_s}^{\alpha_a} h(\alpha) d\alpha.$$

V. NUMERICAL SOLUTION

Equations [13], [25], [29], and [32] were solved with a Fortran IV program partly written in double precision. The program has been running on a Burroughs 7900 mainframe system. The process time was about 45 min.

The integrals in Eqs. [25], [29], and [32] were computed with the single precision standard subroutine DO1AKF from the NAG library (17). The standard procedure makes use of the Gauss 30 point and Konrad 61 point rules (18). It uses a global acceptance criterion according to Malcolm and Simpson (19). The local error is estimated according to Piessens *et al.* (18).

It was not possible to obtain numerically stable solutions for Eq. [13]. Therefore the exponent $\exp(-z_i e \psi / kT)$ was approximated by $(1 - 1.166z_i e \psi / kT)$. The factor 1.166 was chosen as $1 - 1.166x$ is a better fit to $\exp(-x)$ between $0 < x < 1$ than the first two terms of its Taylor series $1 - x$. In order to maintain consistency the exponentials in Eqs. [25], [29], and [32] were similarly approximated.

It was found more efficient to replace the boundary condition $\alpha = \alpha_a$; $\partial\psi/\partial\alpha = 0$ by $\alpha = \alpha_1$; $\psi = 0$, where α_1 was positioned at an α such that there was hardly any deviation from $\psi = 0$ and its position had no influence on the results. Under these restrictions the boundary value problem [13] was solved with the simple shooting technique (20) combined with a fourth-order Runge Kutta method (20).

Solutions were obtained for various values of β to check the constancy of the equipotential surfaces along the curves $\alpha = \text{const.}$ It was found that the problem was reasonably well conditioned for the condition number

$$\text{COND} = \frac{\Delta\psi}{\Delta^2\psi} \frac{\Delta\alpha}{\alpha}. \quad [33]$$

For an explanation of this terminology see Ref. (20).

A program text and user guide can be obtained from the authors.

VI. EXPERIMENTAL

The electrokinetic and electrical measurements were performed on monodisperse

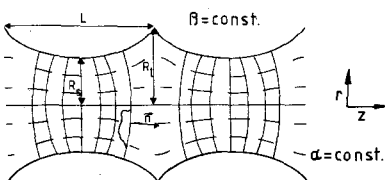


FIG. 1. The surface element $2\pi h(\alpha)d\alpha$ and its normal n together with the parameter curves $\alpha = \text{const.}$ and $\beta = \text{const.}$ in the cylindrical system.

quartz beds. The preparation and particle size and form distributions of the beds have been described in Part I (11). Measurements were performed in electrolyte solutions of $pKCl = 1, 2, 3, 4$ at pH 3 and of $pKCl = 3$ at pH 5.

To interpret the measurements at pH 5, we used the krypton BET specific surface area (21, 42) for sieve fractions below $100 \mu m$. This was done because surface currents were important in these cases and the BET surface area gives a better approximation of the molecular surface area than the T.A.S. and Digitizer measurements described in Part I (11). No hysteresis occurred in the krypton adsorption isotherms; so as far as the krypton molecules are concerned there was no surface porosity.

The electrokinetic conductances of the porous beds were measured with the apparatus developed by Verwey (22) and Stein *et al.* (23, 24) after slight modifications (Fig. 2). The electrokinetic conductance was measured by sending a constant current through the Zn/ZnSO₄ electrodes. A potential difference, measured with the platinum electrodes, arises across the porous bed. The potential difference causes the liquid to flow; this flow can be measured by measuring the velocity of the meniscus in the capillaries.

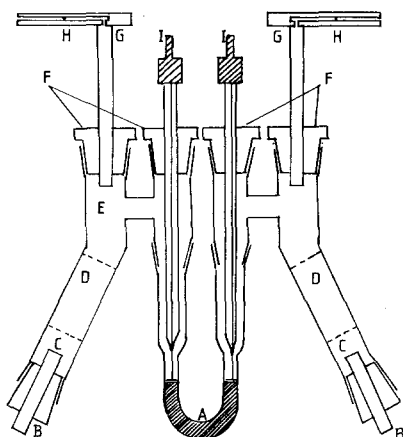


FIG. 2. Schematic design of the used apparatus. A is the porous bed, B are Zn electrodes, C are compartments filled with saturated ZnSO₄, D are compartments filled with 0.5 *m* KNO₃, E is a compartment filled with electrolyte solution, F are stoppers, G are capillaries, H are the menisci and I the Pt electrodes.

The volumetric velocity divided by the potential difference gives the electrokinetic conductance. It was also verified that at pH 3 the electroosmotic conductance $(J_v/I)_{\Delta p=0}$ did not depend on the particle size. Thus surface conductance was negligible.

The dc electrical conductance was directly obtained by simultaneously measuring the potential difference. The ac values were also measured with a Philips PR9500 conductivity bridge at a frequency of 50 and 1000 cps. No differences among the three measurements were observed. It was verified that the electrical and electrokinetic transport processes were linear.

VII. RESULTS AND DISCUSSION

The electrokinetic conductance measurements are given in Fig. 3 together with the predictions of the s.c. and t.c. pore model (4) and Eq. [25]. For the t.c. pore model, the tortuosity was taken equal to 1.55 and for the s.s.p. model the parameter *c* was taken equal to 2.83. These free parameters were obtained from calibration with hydrodynamic measurements (11, 42).

The zeta potential necessary for the computation was obtained from von Smoluchowski's law (5, 8, 25), because in the absence of surface conductance there is no dependence of the pore form, as proven by Overbeek (26). Clearly, again, the s.s.p. model was superior to the other two.

Hydrodynamic, electrokinetic, and electrical conductance under stationary conditions can be described by the following Onsager relations (27):

$$J_v = L_{11}\Delta P + L_{12}\Delta V \quad [34]$$

$$I = L_{12}\Delta P + L_{22}\Delta V, \quad [35]$$

where L_{11} is the hydrodynamic conductance, L_{22} is the electrical conductance, and L_{12} is the electrokinetic conductance. J_v is the volumetric flow through the porous bed, I is the

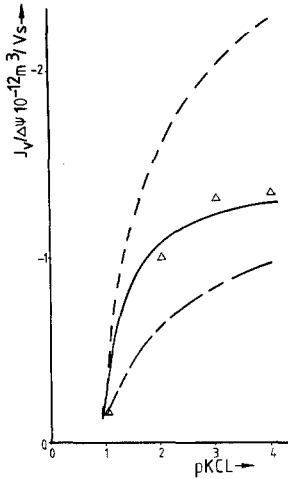


FIG. 3. The electrokinetic conductance at pH 3 as a function of $p\text{KCl}$. (Δ) Experiments; (—) theoretical prediction s.s.p. model; (- - -) theoretical prediction t.c. model; (- · -) theoretical prediction s.c. model.

electrical current, and ΔP and ΔV are the pressure and potential differences across the porous bed, respectively.

The conditions under which relations [34] and [35] are valid have been studied extensively by Rastogi *et al.* (28, 29), Srivastava *et al.* (30, 31), Blokhra *et al.* (32, 33), and Hidalgo-Alvarez *et al.* (34, 35). With respect to the cited references it should be remarked that in our case all the transport phenomena were found to be linear.

From Eqs. [34] and [35] it follows that one can predict any transport phenomenon based on these equations if one knows L_{11} , L_{12} , and L_{22} . For example, the electroosmotic conductance is (12)

$$\left(\frac{J_v}{I}\right)_{\Delta p=0} = \frac{L_{12}}{L_{22}} \quad [36]$$

The electroosmotic conductance as predicted by Eq. [36] and the s.s.p. model is shown in Table I.

The filtration coefficient is given by (12)

$$\left(\frac{J_v}{\Delta p}\right)_{I=0} = L_{11} \left(1 - \frac{L_{12}^2}{L_{11}L_{22}}\right) \quad [37]$$

In our case the dimensionless group $L_{12}^2/(L_{11}L_{22})$ is much smaller than 1 (see below), so the filtration coefficient is nearly equal to the hydrodynamic conductance.

Other transport phenomena have been derived by Van der Put (12) and Staverman (36). It has been shown that for an irreversible process the internal entropy production $d_i S/dt$ is positive (37, 38), so

$$T \frac{d_i S}{dt} = J_v \Delta P + I \Delta V > 0, \quad [38]$$

where T is the temperature.

If Eqs. [34] and [35] are inserted in Eq. [38], the following inequality is obtained for the dimensionless group $L_{12}^2/(L_{11}L_{22})$ (38):

$$\left(\frac{L_{12}^2}{L_{11}L_{22}}\right) < 1. \quad [39]$$

This means that by purely thermodynamic reasoning from Eqs. [34] and [35] an upper boundary for the absolute value of the electrokinetic conductance L_{12} can be predicted:

$$|L_{12}| < (L_{11}L_{22})^{1/2}. \quad [40]$$

Thus, it is thermodynamically impossible to have stationary processes based on Eqs. [34] and [35] if $|L_{12}| > (L_{11}L_{22})^{1/2}$.

An interesting point is that L_{11} , L_{12} , and L_{22} only depend on material and geometrical parameters. Thus there are cases in which the combination of these parameters is such that no linear transport phenomena in the sense of

TABLE I

The Electroosmotic Conductance (m^3/sA) as Calculated with the s.s.p. Model and Eq. [36] as a Function of the KCl Concentration at pH = 3

KCl concentration (mole/liter)	L_{12}/L_{22}
10^{-1}	-2.75×10^{-9}
10^{-2}	-1.13×10^{-7}
10^{-3}	-3.45×10^{-7}
10^{-4}	-5.29×10^{-7}

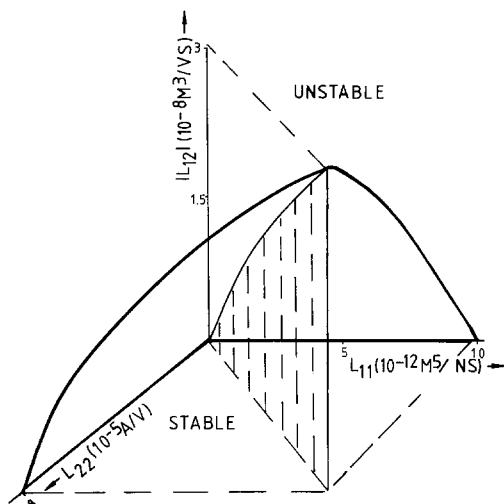


FIG. 4. The stability diagram as obtained from condition [40]. L_{11} , L_{12} , and L_{22} are the conductances (see text) in S.I. units. The stable region is between the bottom plane and the curved surface.

Eqs. [34] and [35] can occur, however small the driving forces and fluxes.

With the s.s.p. model the upper limit of the stability region is calculated. The results are given in Fig. 4. Table II shows that the electrokinetic conductance is well within the stability region. This table contains the upper boundaries (L_{12}) and our electrokinetic ex-

periments at pH 3. Figure 4 can also be used to check if other experimental and theoretical values of transport coefficients of beds consisting of monodisperse granular particles are possible.

The measured electrical conductance as a function of the particle diameter at pH 5 and $pKCl = 3$ is given in Table III, together with the total computed electrical conductance (the sum of Eqs. [29] and [31]) calculated for a zeta potential of 87 mV. The measured and calculated electrokinetic conductances are given in Table IV. From Table III it is clear that the experimental electrical conductance data are about 20% above the theoretical values. Table IV shows that there is even more discrepancy between the experimental and theoretical electrokinetic conductances. The theoretical electrokinetic conductance is not decreasing. The experimental electrokinetic conductance decreases with decreasing particle diameter. There can be many reasons for the discrepancy between theory and experiment. One of the causes of the discrepancy could be that surface conductance behind the plane of shear is not included in the model. According to Zukoski and Saville (39), Van der Put and Bijsterbosch (10), the contribution of this layer could be significant. Another thing is of course

TABLE II

$|L_{12}|$ in $10^{-9} \text{ m}^3/\text{Vs}$ Calculated with the s.s.p. Model and Eq. [40] for Various Particle Diameters and KCl Concentrations (mole/liter) at pH 3

Average diameter (μm)	[KCl]			
	10^{-1}	10^{-2}	10^{-3}	10^{-4}
13.8	2.15	0.71	0.42	0.37
29.1	4.43	1.57	0.85	0.75
32.1	5.1	1.8	1.00	0.9
43.8	5.7	2.03	1.12	1.0
57.1	10.5	3.7	2.05	1.8
100	17.5	6.2	3.43	3.02
214	37.2	13.2	7.3	6.4
Experimental	0.16×10^{-3}	0.99×10^{-3}	1.32×10^{-3}	1.35×10^{-3}

Note. The last values are the values for $|L_{12}|$ actually measured. The particle sizes are obtained as described in Ref. (11).

TABLE III

The Electrical Conductance as a Function of the Average Particle Diameter at pH 5 and $pKCl = 3$

Average particle diameter (μm)	L_{22} (10^{-6} A/V)	
	Experimental	Theory
200	1.1	0.93
93	1.2	0.91
40	1.0	0.88
33	1.1	0.89
13.5	1.2	1.00

TABLE IV

The Electrokinetic Conductance as a Function of the Particle Diameter at pH 5 and $pKCl = 3$

Average particle diameter (μm)	L_{12} (10^{-11} m ³ /Vs)	
	Experimental	Theory
200	0.28	0.28
93	0.26	0.27
40	0.17	0.25
33	0.17	0.27
13.5	0.15	0.27

the linearization of the Poisson-Boltzmann (P.B.) equation. To study the influence of this effect, computations have been performed on the streaming potential measurements of Van der Put and Bijsterbosch (10). This is done, because some models (9, 40, 41) have already been tested with their experiments.

The results together with some data are given in Table V. The theoretical results are obtained by taking the ratio of the electrokinetic and total electrical conductance and multiplying this by the pressure difference of Van der Put and Bijsterbosch (10).

The s.s.p. model describes the experiments at lower concentrations better than the Rice and Whitehead model (40). These authors also applied a linearized P.B. equation; thus the electrostatic part is equivalent to the one employed in the present paper. The results at 0.1 M cannot be considered to be indicative in view of the uncertainty of the measurements (± 2 mV).

TABLE V

The Streaming Potential in Volts as Predicted by the Various Models for the Data of Van der Put and Bijsterbosch as a Function of the Electrolyte Concentration

Electrolyte concn	Experimental	Levine	Rice and Whitehead	s.s.p.
10^{-1}	0.8	0.25	0.3	0.05
10^{-2}	10	5	9	2.3
10^{-3}	41	98	150	47
10^{-4}	66	200	900	650

Levine *et al.* (41) developed a s.c. model in which use was made of much better approximation for the charge density, which greatly reduces the gap between theory and experiment. This suggests that if it had been possible to incorporate numerically a much better approximation to the P.B. equation the difference between our experiments and the theoretical predictions of the s.s.p. model would have been reduced. Both drawbacks of the model used point out that the gap between theory and experiment is mainly due to limitations in the description of the potential profile and not to the pore structure assumed.

VIII. CONCLUSIONS

It can be concluded that the s.s.p. model is superior to the s.c. and t.c. models and that it is possible to use it to predict a validity domain for stationary processes. When there are discrepancies between theory and experiments, these are not due to the assumed pore structure but mainly to assumptions of an electrostatic nature.

APPENDIX: NOMENCLATURE

α	semisinusoidal coordinate
α_a	value of α at the pore axis
β	semisinusoidal coordinate
ϵ	permittivity
φ	semisinusoidal coordinate
ζ	zeta potential
λ_i	equivalent conductance of ion i

μ	dynamic viscosity
ψ	potential due to diffuse double layer
A	cross-sectional area
C	pore constant
c_i	concentration of ion i
E	electrical field strength
e	electronic charge
f	function defined in Eq. [10]
g	function defined in Eq. [11]
h	function defined in Eq. [21]
$h_{\alpha,\beta,\varphi}$	length of unit vector
I	electrical current
i	current density
J_v	volumetric fluid flow
k	Boltzmann's constant
l	length of the bed
L	length of a pore element
L_{ij}	Onsager coefficients
L_β	length of a streamline
n	number of pores
n_i	number of ions per unit volume
P	pressure
p	porosity
R	radius at the pore wall
R_s	smallest radius
R_l	largest radius
r	cylindrical coordinate
S	entropy
T	temperature
V	velocity
v	scalar velocity
V	electrical potential
z	cylindrical coordinate
z_i	valency of ion i

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