Colloid Polym Sci (2004) 282: 985–992
DOI 10.1007/s00396-003-1021-z

ORIGINAL CONTRIBUTION

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Electric conductivity in a fibrous porous medium with thin but polarized double layers

Received: 13 June 2003
Accepted: 30 September 2003
Published online: 6 December 2003

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Abstract The electric conduction in the fibrous medium constructed by a homogeneous array of parallel, identical, charged, circular cylinders having an arbitrary zeta potential filled with the solution of a symmetrically charged electrolyte is analytically examined. The thickness of the electric double layers surrounding the dielectric cylinders is assumed to be small relative to the radius of each cylinder and to the gap width between two neighboring cylinders, but the polarization of the mobile ions in the diffuse layers is allowed. The effect of interactions among individual cylinders is taken into explicit account by employing a unit cell model. The appropriate equations of conservation of electrochemical potential energies of ionic species are solved for each cell, in which a cylinder is envisaged to be surrounded by a coaxial cylindrical shell of the fluid solution. Analytical expressions for the effective electric conductivity are obtained in closed forms as functions of the porosity of the fiber matrix and other characteristics of the porous system. Comparisons of the results of the cell model with different conditions at the outer boundary of the cell are made. Under an otherwise identical condition, the electric conductivity in a porous medium composed of an array of parallel cylinders in the transverse direction is smaller than that of a suspension of spheres. The effect of interactions among the cylinders or spheres on the effective conductivity can be quite significant under appropriate conditions.

Keywords Effective electric conductivity · Porous medium · Thin but polarized double layer · Unit cell model

Introduction

A charged solid surface in contact with an electrolyte solution is surrounded by a diffuse cloud of ions carrying a total charge equal and opposite in sign to that of the solid surface. This distribution of fixed charge and adjacent diffuse ions is known as an electric double layer. When an electric field is imposed on a suspension of charged particles or a charged porous medium, the solid entities or the surrounding mobile ions, or both, are driven to migrate. As a result, the fluid solution is dragged to flow by the motions of the solid entities and/or the ions, and there is an electric current through the suspension or porous medium. In some practical applications, it is necessary to determine the average current density and effective electric conductivity of the suspension or porous system.

A simple formula for the effective electric conductivity of a dilute suspension of charged spherical particles was derived by Dukhin and Derjaguin [1], who considered an infinite plane slab of suspension immersed in an infinite homogeneous electrolyte subjected to an electric field perpendicular to the plane slab. Extending this analysis, Saville [2] and O'Brien [3] assumed that the

particles and their electric double layers occupy only a small fraction of the total volume of the suspension to obtain approximate formulas for the electric conductivity using a perturbation method for particles with low zeta (ζ) potential immersed in a symmetrically charged electrolyte correct to $O(\zeta^2)$. Later, approximate analytical expressions for the electrophoretic mobility and effective conductivity of a dilute suspension of colloidal spheres with an arbitrary zeta potential and thin double layers in symmetric electrolytes correct to order $(\kappa a)^{-1}$ were obtained by Ohshima et al. [4], where κ is the reciprocal Debye screening length (defined right after Eq.10a-10d) and a is the particle radius. When the zeta potential of the particles is small, their reduced result for the electric conductivity is in agreement with O'Brien's [3]. On the other hand, O'Brien [5] derived analytical formulae for the electrophoretic mobility and electric conductivity of a dilute suspension of dielectric spheres with thin but polarized double layers in a general electrolyte solution. The agreement between these formulae and the general numerical solutions [6] is excellent for all reasonable values of the zeta potential when $\kappa a > 20$. Using a similar analysis, O'Brien and Ward [7] also determined the electrophoretic mobility and effective conductivity of a dilute suspension of randomly oriented spheroids with thin polarized diffuse layers at the particle surfaces.

In practical applications of the effective electric conductivity, relatively concentrated suspensions of particles or porous media with a relatively low porosity are usually encountered, and the effect of interactions among the solid entities will be important. To avoid the difficulty of the complex geometry appearing in assemblages of solid entities, the unit cell model was used by many researchers to predict the effect of entity interactions on various transport properties such as the mean sedimentation rate [8, 9, 10, 11, 12, 13] and the average electrophoretic/electro-osmotic velocity and/or electric conductivity [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28] in bounded suspensions or porous systems of identical particles. This model involves the concept that an assemblage can be divided into a number of identical cells, one solid entity occupying each cell at its center. The boundary-value problem for multiple entities is thus reduced to the consideration of the behavior of a single entity and its bounding envelope. Although different shapes of the cell can be employed, the assumption of a spherical [8, 10, 11, 12, 13, 14, 15, 17, 19, 21, 22, 23, 24, 25, 26] or cylindrical [9, 16, 18, 20, 27, 28] shape for the fictitious envelope of fluid solution surrounding each spherical or cylindrical entity is of great convenience.

Recently, the electric conduction in a concentrated suspension of charged spherical particles with thin but polarized double layers was analyzed by the present authors using the unit cell model [29]. A simple closed-form formula for the effective electric conductivity was obtained as a function of κa, ζ, and the volume fraction of the particles. It was found that this formula agrees relatively well with the available experimental data for suspensions of spherical particles with thin but finite double layers [30] in comparison with the classic prediction obtained by Maxwell [14, 31].

In the present work, the previous cell-model analysis for the electric conductivity of a monodisperse suspension of charged spheres with thin but polarized double layers [29] is extended to a homogeneous array of parallel charged circular cylinders. No assumption is made about the value of the zeta potential associated with the cylinder surfaces. The analytical solutions in closed forms obtained with the cylindrical cell model enable the effective electric conductivity to be predicted as functions of the porosity of the fiber matrix and other characteristics of the porous system for various cases. Comparisons of the conductivity results between a system of parallel cylinders and a system of spheres will be given.

Analysis

Consider a liquid solution containing M ionic species filled in the fibrous porous medium constructed by a homogeneous array of parallel, identical, circular cylinders of radius a. Each dielectric cylinder is charged uniformly on its surface and surrounded by an electric double layer whose thickness is small compared with the radius of the cylinder (say, $\kappa a > 20$) and the gap width between two neighboring cylinders. We are interested in the determination of the effective electric conductivity in the fiber matrix, which can be expressed in the tensor form:

$$\Lambda = \Lambda_p \mathbf{ee} + \Lambda_n(\mathbf{I} - \mathbf{ee}), \tag{1}$$

where $\mathbf{e}$ is a unit vector along the axes of the cylinders, $\mathbf{I}$ is the unit dyadic, and Λ_p and Λ_n are the conductivity components parallel and normal, respectively, to the cylinder axes. It is understood that the electric current density in the fibrous medium equals the dot product of Λ and the imposed electric field.

When the ordered array is subjected to a constant applied electric field $\mathbf{E}^\infty$ normal to the cylinder axes, the diffuse ions in the double layers may be polarized, and the average of the local electric field ($\mathbf{E} = -\nabla\psi$) can be expressed as:

$$< \mathbf{E} >= -\frac{1}{V}\int_V \nabla\psi \, dV, \tag{2}$$

where $\psi(\mathbf{x})$ is the electric potential at position $\mathbf{x}$ and V denotes a sufficiently large cylindrical volume to contain many cylinders. There is a resulting volume-average

current density, which is collinear with $<\mathbf{E}>$, defined by:

$$<\mathbf{i}>=\frac{1}{V}\int_V i(x)\,\mathrm{d}V, \tag{3}$$

where $\mathbf{i}(\mathbf{x})$ is the current density distribution. The directional effective electric conductivity Λ_n in the fibrous medium can be assigned by the linear relation:

$$<\mathbf{i}>=\Lambda_n<\mathbf{E}>. \tag{4}$$

Since the measured electric field and current density are equal to $<\mathbf{E}>$ and $<\mathbf{i}>$, respectively, Eq. 4 is the usual experimental definition of electric conductivity, provided that the array of cylinders is everywhere homogeneous.

The integral in Eq. 3 can be calculated by employing the unit cell model in which each cylinder of radius a is surrounded by a coaxial cylindrical shell of the electrolyte solution having an outer radius of b, as shown in Fig. 1, such that the fluid/cell volume (or cross-sectional area) ratio is equal to the porosity $1-\varphi$ of the fiber matrix; viz., $\varphi=(a/b)^2$. For convenience, the polar coordinate system (ρ,ϕ) is used for a cell and its origin is set at the axis of the cylinder. The radial velocity of the fluid relative to the bulk electro-osmotic flow on the outer (virtual) boundary of the cell ($\rho=b$) is taken to be zero. One can first consider a single cylinder in a cell and then multiplying the result by the number of the cylinders in the volume V.

On the basis of the mathematical analysis given in a previous article [29], the average current density is obtained as:

$$<\mathbf{i}> = \Lambda^{\infty}<\mathbf{E}> - \frac{e}{\pi bkT}\sum_{m=1}^{M} z_m n_m^{\infty} D_m \int_0^{2\pi}\left(\rho\frac{\partial\mu_m}{\partial\rho}-\mu_m\right)_{\rho=b}\mathbf{e}_\rho\,\mathrm{d}\phi. \tag{5}$$

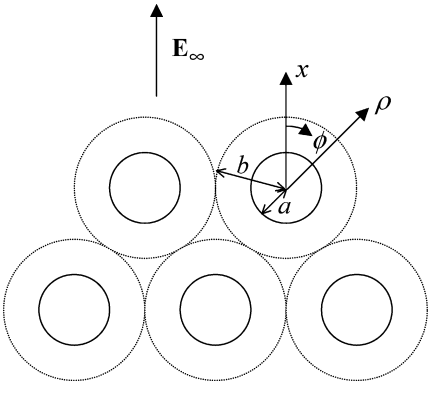

Fig. 1 Geometrical sketch of the unit cell model for a homogeneous array of parallel, identical, and circular cylinders

Here, the electrochemical potential energy field of the mth species, $\mu_m(\mathbf{x})$, is defined as [4, 5]:

$$\mu_m = \mu_m^0 + kT\ln n_m + z_m e\psi, \tag{6}$$

$$\Lambda^{\infty} = \frac{e^2}{kT}\sum_{m=1}^{M} z_m^2 n_m^{\infty} D_m, \tag{7}$$

which is the electric conductivity of the electrolyte solution in the absence of the cylinders, $n_m(\mathbf{x})$, n_m^{∞}, D_m, and z_m are the concentration (number density) distribution, bulk concentration, diffusion coefficient, and valence, respectively, of species m, $\mathbf{e}_\rho$ is a unit vector in the ρ direction, e is the charge of a proton, k is the Boltzmann constant, T is the absolute temperature, and μ_m^0 is a constant. The determination of μ_m in Eq. 5 is concerned with the solution of the basic electrokinetic equations for the electrolyte around the cylinder in a cell. Note that the solution for the fluid velocity is not needed in the calculation of the average current density.

The fluid phase in a cell can be divided into two regions: an "inner" region defined as the thin double layer surrounding the cylinder and an "outer" region defined as the remainder of the fluid (bulk solution), which is neutral. In the outer region, the electrochemical potential energy for each ionic species satisfies the Laplace equation:

$$\nabla^2\mu_m = 0. \tag{8}$$

In the following analysis, we only consider the case of a symmetrically charged binary electrolyte ($M=2$) and let m equal to 1 and 2 refer to the anion and cation, respectively, so $-z_1=z_2=Z>0$.

The governing Eq 8 in the outer region satisfies the following boundary condition at the surface of the cylinder (outer edge of the thin double layer) obtained by solving for the electrochemical potentials in the inner region and using a matching procedure to ensure a continuous solution in the whole fluid phase [5, 28, 32]:

$$\rho = a:\ \frac{\partial\mu_m}{\partial\rho} = -\frac{1}{\rho^2}\sum_{i=1}^{2}\beta_{mi}\frac{\partial^2\mu_i}{\partial\phi^2},\ m=1,\ 2, \tag{9}$$

where the relaxation coefficients:

$$\beta_{11} = \frac{1}{\kappa}\left[4\left(1+\frac{3f_1}{Z^2}\right)\exp(\bar{\zeta})\sinh\bar{\zeta} - \frac{12f_1}{Z^2}\left(\bar{\zeta}+\ln\cosh\bar{\zeta}\right)\right], \tag{10a}$$

$$\beta_{12} = -\frac{1}{\kappa}\left(\frac{12f_1}{Z^2}\right)\ln\cosh\bar{\zeta}, \tag{10b}$$

$$\beta_{21} = -\frac{1}{\kappa}\left(\frac{12f_2}{Z^2}\right)\ln\cosh\bar{\zeta}, \tag{10c}$$

$$\beta_{22}=\frac{1}{\kappa}\left[-4\left(1+\frac{3f_2}{Z^2}\right)\exp\left(-\bar{\zeta}\right)\sinh\bar{\zeta}+\frac{12f_2}{Z^2}\left(\bar{\zeta}-\ln\cosh\bar{\zeta}\right)\right]. \tag{10d}$$

In Eq 10a-10d, $\kappa=(8\pi Z^2e^2n^{\infty}/akT)^{1/2}$, $f_m=ak^2T^2/6\pi\eta e^2D_m$, and $\bar{\zeta}=Ze\zeta/4kT$, where ζ is the zeta potential associated with the cylinder surface and $\epsilon=4\pi\epsilon_0\epsilon_r$,in which ϵ_r is the relative permittivity of the electrolyte solution and ϵ_0 is the permittivity of free space. The physical meaning of Eq 9 is that the net tangential ionic fluxes along the cylinder surface must be balanced by the normal ionic fluxes occurring just beyond the double layer to prevent accumulation of the ionic species. It was shown that, even when κa is as large as 300, the effect of ion transport inside the diffuse layer cannot be ignored if $|\zeta|$ equals several kT/e [32].

According to the definition given by Eq 6, the electrochemical potential energies undisturbed by the presence of the cylinder in a cell can be expressed as:

$$\mu_m^{\infty}=\mu_m^0+kT\ln n^{\infty}-(-1)^mZeE^{\infty}\rho\cos\phi, \tag{11}$$

where $E^{\infty}=|\mathbf{E}^{\infty}|$. At the virtual surface of the cell, the local electrochemical potential gradient of type m ions should be consistent with the gradient $\nabla\mu_m^{\infty}$, according to the Levine–Neale model [15, 18, 20]. Thus,

$$\rho=b:\ \frac{\partial\mu_m}{\partial\rho}=-(-1)^mZeE^{\infty}\cos\phi,\ m=1,\ 2. \tag{12}$$

The solution to Eqs 8, 9, and 12 is:

$$\mu_m=\mu_m^0+kT\ln n^{\infty}+\left(A_{m1}\rho+A_{m2}\frac{a^2}{\rho}\right)ZeE^{\infty}\cos\phi, \tag{13}$$

where the coefficients:

$$A_{m1}=-(-1)^m+\varphi A_{m2}, \tag{14a}$$

$$A_{m2}=-(-1)^m\frac{1}{\Delta}(c_m\Delta_1-\Delta_3\varphi). \tag{14b}$$

In the above equations:

$$c_1=\frac{1}{a^2\Delta_1}\left(a^2-a\beta_{11}+2a\beta_{12}+a\beta_{22}+\beta_{12}\beta_{21}-\beta_{11}\beta_{22}\right), \tag{15a}$$

$$c_2=\frac{1}{a^2\Delta_1}\left(a^2-a\beta_{22}+2a\beta_{21}+a\beta_{11}+\beta_{12}\beta_{21}-\beta_{11}\beta_{22}\right), \tag{15b}$$

$$\Delta=\Delta_1-2\Delta_2\varphi+\Delta_3\varphi^2, \tag{16}$$

$$\Delta_1=\frac{1}{a^2}\left(a^2+a\beta_{11}+a\beta_{22}-\beta_{12}\beta_{21}+\beta_{11}\beta_{22}\right), \tag{17a}$$

$$\Delta_2=\frac{1}{2}(c_1+c_2)\Delta_1-\frac{1}{a}(\beta_{12}+\beta_{21}), \tag{17b}$$

$$\Delta_3=4-(\Delta_1+2\Delta_2), \tag{17c}$$

and $\varphi=(a/b)^2$.

When the continuity of electric current applies to the system, the imposed electric field $\mathbf{E}^{\infty}$ is related to the average electric field $<\mathbf{E}>$ within the array of cylinders by the relationship:

$$\Lambda_n<\mathbf{E}>=\Lambda^{\infty}\mathbf{E}^{\infty}. \tag{18}$$

By substituting Eq 13 into Eq 5, making relevant calculations, and then comparing the result with Eqs 4 and 18, the directional effective electric conductivity in the array of parallel identical charged cylinders is obtained as:

$$\Lambda_n=\Lambda^{\infty}\left[1+\frac{2\varphi}{D_1+D_2}(D_1A_{12}-D_2A_{22})\right]^{-1}. \tag{19}$$

The coefficients A_{12} and A_{22} in the above formula are given by Eq 14b.

The boundary condition of the electrochemical potential energy of type m ions at the virtual surface $\rho=b$ may alternatively be taken as the distribution giving rise to the average of the local electric field in the cell, known as the Zharkikh–Shilov model [16, 17, 22]. In this case, Eq 12 becomes:

$$\rho=b:\ \mu_m=\mu_m^0+kT\ln n^{\infty}-(-1)^mZe\bar{E}\rho\cos\phi,\ m=1,\ 2, \tag{20}$$

where $\bar{E}$ equals the magnitude of $<\mathbf{E}>$ defined by Eq. 2. The solution to the governing Eq. 8, subject to the boundary conditions 9 and 20, is also given by the form of Eq. 13, but with E^{∞} replaced by $\bar{E}$ and coefficients A_{mi} defined as:

$$A_{m1}=-(-1)^m-\varphi A_{m2}, \tag{21a}$$

$$A_{m2}=-(-1)^m\frac{1}{\Delta'}(c_m\Delta_1+\Delta_3\varphi), \tag{21b}$$

where:

$$\Delta'=\Delta_1+2\Delta_2\varphi+\Delta_3\varphi^2. \tag{22}$$

With this solution, Eqs. 4 and 5 lead to:

$$\Lambda_n=,\Lambda^{\infty}\left[1-\frac{2\varphi}{D_1+D_2}(D_1A_{12}-D_2A_{22})\right]. \tag{23}$$

When the homogeneous array of parallel cylinders is subjected to an external electric field parallel to the

cylinder axes, there is no polarization of the thin double layers or disturbance in the electrochemical potential field caused by the curvature of the cylinders, like the above analysis for the transverse electric conduction. Thus, the directional effective electric conductivity Λ_p of the fibrous medium defined by Eq. 1 can be simply written as a linear function of φ:

$$\Lambda_p = \Lambda^\infty(1-\varphi), \tag{24}$$

since the cylinders are assumed to be non-conducting.

For a corresponding porous medium composed of a homogeneous suspension of identical charged spherical particles, the effective electric conductivities obtained by using the Levine–Neale and Zharkikh–Shilov cell models can be expressed as:

$$\Lambda = \Lambda^\infty\left[1+\frac{3\varphi}{D_1+D_2}(D_1A_{12}-D_2A_{22})\right]^{-1} \tag{25}$$

and

$$\Lambda = \Lambda^\infty\left[1-\frac{3\varphi}{D_1+D_2}(D_1A_{12}-D_2A_{22})\right], \tag{26}$$

respectively. The coefficients A_{m2} in Eqs. 25 and 26 were defined by Eqs. 17b and 22, respectively, in ref. [29].

Results and discussion

In this section, we first consider the limiting case of expressions 19, 23, 25, and 26 for the electric conductivities of porous media constructed by parallel cylinders and by spheres with $\kappa a \to \infty$. The correctness of these expressions may be confirmed by comparing them with other available analytical solutions for this limiting case. Numerical results of these expressions for the general cases will then be presented and discussed.

When the double layers surrounding the cylinders in the fiber matrix are infinitesimally thin or $\kappa a \to \infty$, Eqs. 10a-10d, 15a, 15b, and 17a , 17b, 17c give $\beta_{11}/a = \beta_{12}/a = \beta_{21}/a = \beta_{22}/a = 0$, $c_1 = c_2 = 1$, and $\Delta_1 = \Delta_2 = \Delta_3 = 1$, and both Eq. 19 and Eq. 23 reduce to:

$$\Lambda_n/\Lambda^\infty = \frac{1-\varphi}{1+\varphi} = 1-2\varphi+2\varphi^2+O(\varphi^3). \tag{27}$$

The formula for the effective conductivity of a suspension of spheres with $\kappa a \to \infty$ corresponding to Eq. 27 can be obtained from either Eq. 25 or Eq. 26 as:

$$\Lambda/\Lambda^\infty = \frac{2-2\varphi}{2+\varphi} = 1-\frac{3}{2}\varphi+\frac{3}{4}\varphi^2+O(\varphi^3). \tag{28}$$

Note that the expression for Λ in Eq. 28 is the same as that obtained by Maxwell for a homogeneous suspension of uncharged nonconductive spheres, while the expression for Λ_n in Eq. 27 is identical to the result obtained by Rayleigh for a homogeneous array of parallel cylinders [31]. It is known that the effective conductivity predicted by Eq. 28 agrees very well with that obtained by Jeffrey [33] using the concept of statistical mechanics for dilute suspensions of uncharged spheres.

In Fig. 2, the normalized electric conductivity Λ_n/Λ^∞ for a homogeneous array of parallel cylinders, as calculated from Eq. 27 for the case of $\kappa a \to \infty$, is plotted versus the volume fraction φ of the cylinders in solid curves. The calculations are presented up to $\varphi = 0.9$, which corresponds to the minimum attainable porosity for an array of identical parallel circular cylinders (ordered triangularly) [34]. The corresponding result of Λ/Λ^∞ for a suspension of spheres given by Eq. 28 is also drawn by dashed curves in the same figure for comparison. This result is shown up to the maximum attainable volume fraction for a swarm of identical spheres, $\varphi = 0.74$ [15]. Since the dielectric particles with $\kappa a \to \infty$ behave as entirely non-conducting ones, both the analytical results indicate that the effective conductivity decreases with a decrease in the porosity in this limiting case. For a fixed porosity, the effective conductivity in an array of parallel cylinders (transverse component) is smaller than that of a suspension of spheres.

The normalized conductivity Λ_n/Λ^∞ for an array of parallel cylinders with a finite value of κa calculated from Eqs. 19 and 23 is plotted in Fig. 3 as a function of φ with $\zeta e/kT$ as a parameter. The situation associated with $Z = 1$ and $f_1 = f_2 = 0.2$ is chosen here, which is close to the case of aqueous solution of KCl. It can be seen that the two cell models in general lead to quite different predictions of the effective conductivity for a fixed value of φ, especially when the zeta potential of the cylinders is

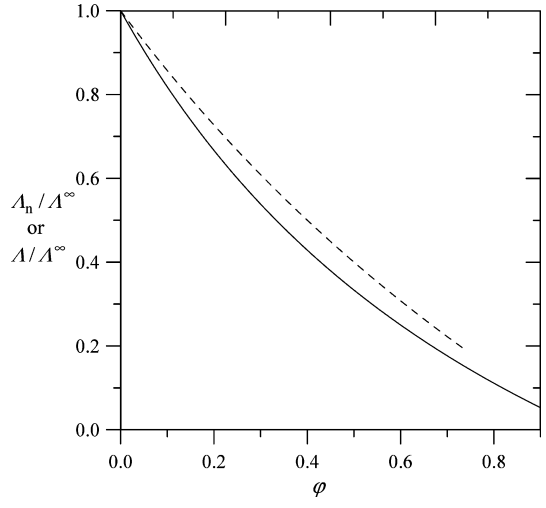

Fig. 2 Plots of the normalized electric conductivities in an array of parallel cylinders (*solid curves*) and a suspension of spheres (*dashed curves*) as calculated from Eqs. 27 and 28 versus the volume fraction of the particles in the limiting situation of $\kappa a \to \infty$

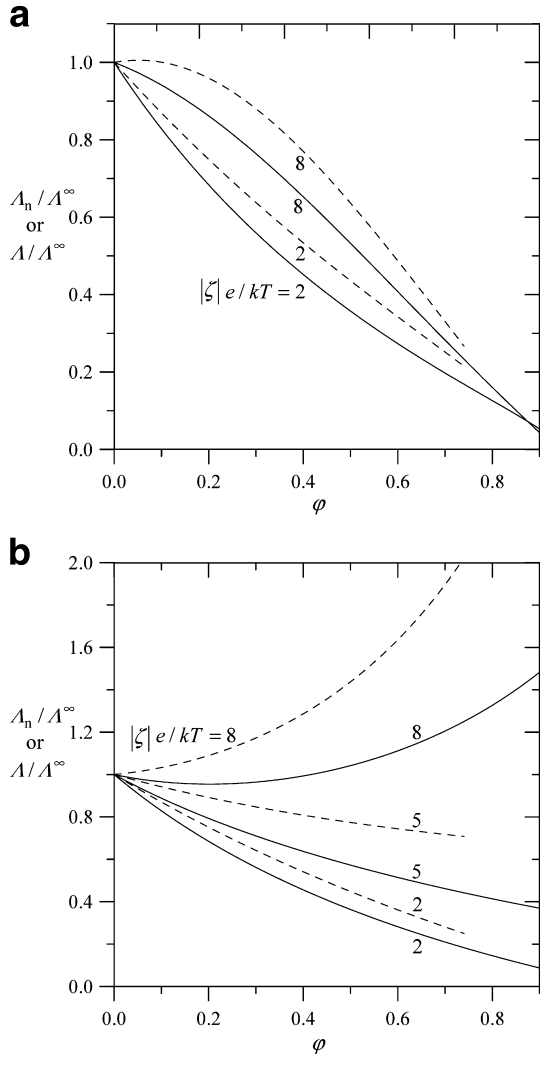

Fig. 3a,b Plots of the normalized electric conductivities in an array of parallel cylinders (*solid curves*) and a suspension of spheres (*dashed curves*) versus the volume fraction of the particles with $Z = 1$, $f_1 = f_2 = 0.2$, and $\kappa a = 50$. **a** Eqs. 19 and 25 for the Levine–Neale model. **b** Eqs. 23 and 26 for the Zharkikh–Shilov model

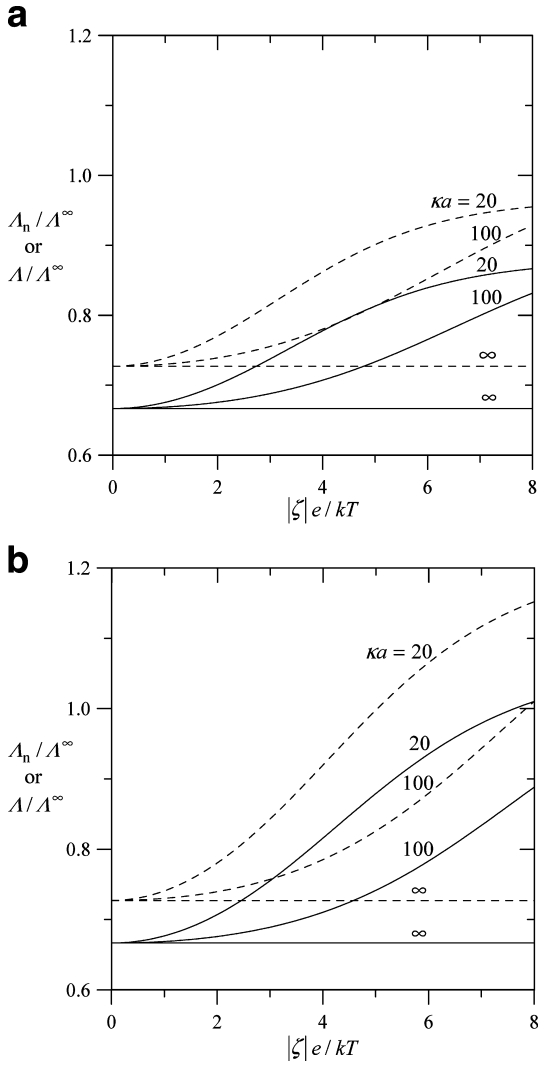

Fig. 4a,b Plots of the normalized electric conductivities in an array of parallel cylinders (*solid curves*) and a suspension of spheres (*dashed curves*) versus the dimensionless zeta potential of the particles with $Z = 1$, $f_1 = f_2 = 0.2$, and $\varphi = 0.2$. **a** Eqs. 19 and 25 for the Levine–Neale model. **b** Eqs. 23 and 26 for the Zharkikh–Shilov model

high. For the case of cylinders with a relatively small magnitude of zeta potential (say, $|\zeta|e/kT < 6$), both cell models predict that the effective conductivity is a monotonic decreasing function of φ. For the case of cylinders with a very large magnitude of ζ, however, the effective conductivity still decreases with an increase in φ as φ is small, but may increase steadily from a minimum with increasing φ as φ is sufficiently large; the value of Λ_n/Λ^∞ can be greater than unity. The effect of interactions among cylinders on the electric conductivity can be quite significant when the value of φ is large. Note that the case of $|\zeta|e/kT = 8$, which is not likely to exist in practice, is considered in Fig. 3 for the sake of numerical comparison.

In Figs. 4 and 5, Λ_n/Λ^∞ for an array of parallel cylinders calculated from Eqs. 19 and 23 is plotted versus their dimensionless zeta potential at different values of κa and Z, respectively, when φ is kept constant. This normalized conductivity is also plotted versus κa in the range from 20 to 10,000 in Fig. 6 with $\zeta e/kT$ as a parameter. As expected, the effective conductivity increases with an increase in the magnitude of $\zeta e/kT$ for fixed values of κa, Z, and φ. The value of Λ_n/Λ^∞ can be greater than unity only when this magnitude is sufficiently large. For a given combination of $\zeta e/kT$, Z, and φ, Λ_n/Λ^∞ in general is a decreasing function of κa in the given range, with the exception of the Levine–Neale

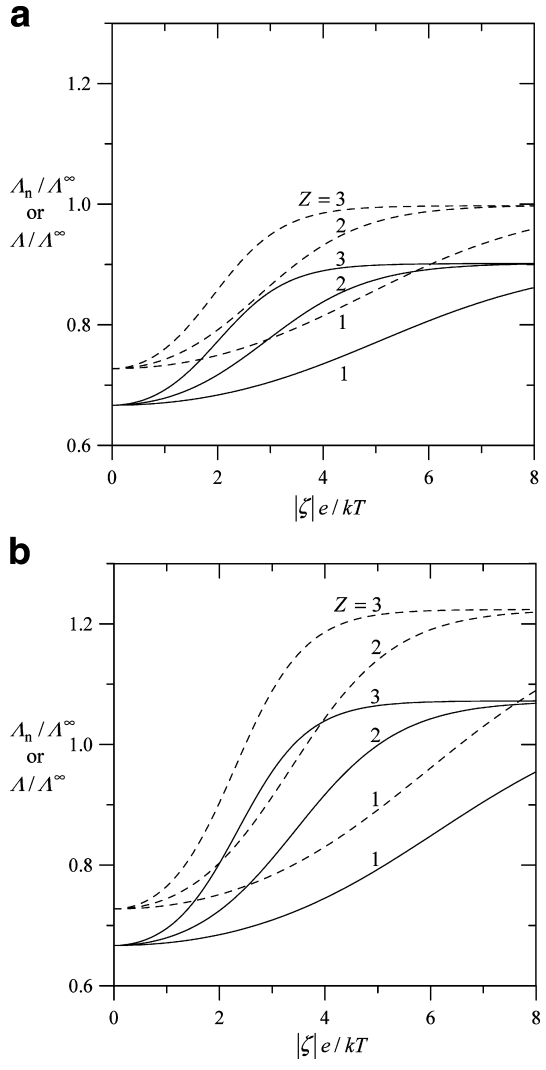

Fig. 5a,b Plots of the normalized electric conductivities in an array of parallel cylinders (*solid curves*) and a suspension of spheres (*dashed curves*) versus the dimensionless zeta potential of the particles with $f_1 = f_2 = 0.2$, $\kappa a = 50$, and $\varphi = 0.2$. **a** Eqs. 19 and 25 for the Levine–Neale model. **b** Eqs. 23 and 26 for the Zharkikh–Shilov model

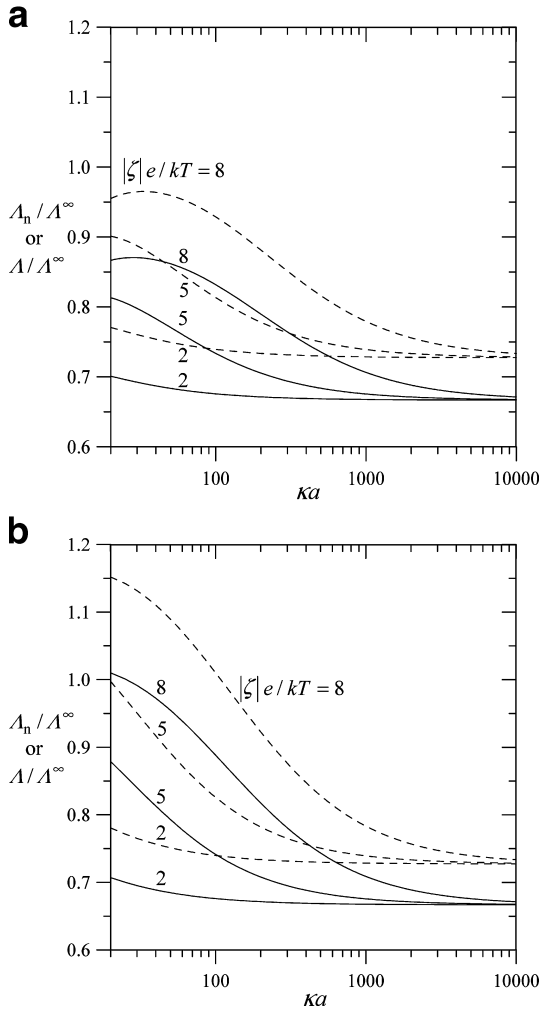

Fig. 6a,b Plots of the normalized electric conductivities in an array of parallel cylinders (*solid curves*) and a suspension of spheres (*dashed curves*) versus κa with $Z = 1$, $f_1 = f_2 = 0.2$, and $\varphi = 0.2$. **a** Eqs. 19 and 25 for the Levine–Neale model. **b** Eqs. 23 and 26 for the Zharkikh–Shilov model

model with a very high zeta potential and $\kappa a < 30$. Under an otherwise identical condition, the value of Λ_n/Λ^∞ increases with an increase in Z. The increase of the effective conductivity with an increase in $\zeta e/kT$ and Z and with a decrease in κa is due to the increase of the surface conductivity of the cylinders. Thus, the feature that the effective conductivity of a suspension or a porous system of non-conducting particles can be greater than the value of Λ^∞ is understandable because the conduction enhancement induced by the surface conductivity of the cylinders may overcome the insulation of their bulk volume.

The corresponding results of Λ/Λ^∞ for a suspension of spheres with various values of κa, $\zeta e/kT$, Z, and φ given by Eqs. 25 and 26 are also exhibited by dashed curves in Figs. 3 to 6, for comparison. For a set of given values of κa, $\zeta e/kT$, Z, and φ, the effective conductivity in an array of parallel cylinders (transverse component) is always smaller than that of a suspension of spheres, no matter whether the Levine–Neale cell model or the Zharkikh–Shilov cell model is employed. On the other hand, for either an array of parallel cylinders or a suspension of spheres with specified values of κa, $\zeta e/kT$, Z, and φ, the effective conductivity predicted by the Levine–Neale model is always smaller than that predicted by the Zharkikh–Shilov model; the difference becomes greater when the magnitude of $\zeta e/kT$ is larger, when κa is smaller, and when Z is larger. Note that some figures for the normalized conductivity Λ/Λ^∞ shown in ref. [29] are in numerical errors.

Concluding remarks

The problem of electric conduction in the fibrous porous medium composed of a homogeneous array of parallel, identical, charged cylinders with thin but polarized electric double layers filled with an electrolyte solution has been analyzed using the unit cell model with two different boundary conditions at the outer (virtual) surface of the cell. The electrochemical potential field in the cell was analytically solved and expressions for the effective electric conductivity as functions of the porosity of the fiber matrix were obtained in closed forms. Comparisons of the results between the two cases of the cell model have been provided. Under an otherwise identical condition, the effective conductivity in the porous system increases with an increase in $|\zeta|e/kT$, with a decrease in κa, and with an increase in Z, due to the increase of the surface conductivity of the cylinders. These effects can be quite significant for both an array of parallel cylinders and a suspension of spheres in general cases.

In a cell-model analysis for the electrophoresis in a suspension of charged spheres with thin but polarized double layers [26], the tendency of the dependence of the mean particle velocity on the particle volume fraction φ predicted by the Levine–Neale model is not correct, in comparison with an ensemble-averaged result, probably due to the fact that the angular component of the electrochemical potential gradient at the virtual surface of the cell is not specified in Eq. 12 . On the other hand, the electrophoretic velocity predicted by the Zharkikh–Shilov model agrees quite well with that calculated from the statistical model for dilute suspensions of particles. Therefore, Eqs. 23 and 26, rather than Eqs. 19 and 25, should be preferably used for the estimation of the effective conductivity in porous systems with a finite value of κa.

Generally speaking, the effect of porosity on the electric conductivity in a porous system is a complicated function of the properties of the electrolyte solution and solid surfaces. Since there is no simple rule for making an adequate prediction for such complicated phenomena, the closed-form analytical results obtained here, which can be conveniently applied in the calculations for various cases with $\kappa a > 20$, should be a useful contribution to the understanding of the effect of porosity on the electric conduction in porous media. Although our analytical results are derived for the solution of a symmetrically charged electrolyte, they can be extended to the solution containing a general electrolyte using O'Brien's [5] reasoning that only the most highly charged counterions play a dominant role in the ionic fluxes along the solid surface.

Acknowledgement This work was supported by the National Science Council of the Republic of China.

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