Experiments on the Conductivity of Suspensions of Ionically-Conductive Spheres

This is a report on the ionic conductivity of monodisperse, neutrally-buoyant suspensions of ion-exchange beads, both AC total-ion conductivity and DC specific-ion conductivity of an electrochemically-active species. They represent the zero Péclet-number and the large Péclet-number limits of mass transfer, respectively.

A rotating disc electrode was employed for the DC studies and a well mixed conductivity cell for the AC—for particle volume fractions ϕ ranging from zero to about 45%. Novel techniques were developed for rapidly determining the particle AC conductivity and for modifying the relative conductivity α of ion-exchange beads by poisoning with immobilely-bound ions. For α values, $0.044 \leq \alpha \leq 1.48$, of this study Maxwell's classical relation is shown to be adequate for $\phi \leq 0.5$, which is, in agreement with Turner (1973, 1976).

Our results for the DC conductivity differ somewhat from those of Andersen (1987) land show the weak dependence on particle Péclet number predicted by the dilute-suspension theory of Nir and Acrivos (1976) for $Pe \gg 1$.

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Introduction

As many engineering problems involve the transport of matter and energy through particulate and granular media, it is useful to understand the role of the particle phase in enhancing or inhibiting this transport. Since the transport through such materials depends not only on the particle concentration and shape but also on the particle arrangement and motion, the knowledge of transport properties can also shed light on the structure and dynamics of the medium and thus on its mechanical properties. Thus, the present study was originally motivated by a desire to develop and characterize an idealized conductive granular material, in which both mechanical and scalar transport properties might be studied simultaneously.

We recall that many investigators have theoretically and experimentally studied the transport of heat or mass through suspensions of particles, with Maxwell being one of the first to theoretically relate the effective conductivity of a dilute stationary suspension of solid spheres to the properties of the individual phases and the concentration of the spheres. His well-known relation is given by (Meredith and Tobias, 1962; Jeffrey, 1973):

$$\frac{\kappa}{\kappa_m} = \frac{1 + 2\beta\phi}{1 - \beta\phi} \tag{1}$$

where

$\beta = (\alpha - 1)/(\alpha + 2)$
α = ratio of conductivity of the particle to that of the matrix
κ = effective conductivity of the suspension
κ_m = conductivity of the matrix
ϕ = solid volume fraction

To the order of terms in ϕ to which it is exact, Eq. 1 takes the form:

$$\frac{\kappa}{\kappa_m} = 1 + 3\beta\phi + O(\phi^2) \tag{2}$$

Jeffrey (1973) has in recent times extended the work of Maxwell to the second-order terms in the volume fraction ϕ for "well-stirred" random suspensions of equal spheres to give the effective conductivity as:

$$\kappa = \kappa_m[1 + 3\beta\phi + \hat{\beta}\,\phi^2 + O(\phi^3)] \tag{3}$$

where $\hat{\beta} = \hat{\beta}(\beta)$ is given in Jeffrey (1973) as a slowly-convergent infinite series in β.

On the other hand, Batchelor and O'Brien (1977) theoretically treat the conduction of heat or electricity through static particulate media in the limit of maximum volume fraction ϕ where the particles make point contact with one another. They find that when $\alpha \gg 1$ the effective conductivity of random arrays is given by:

$$\frac{\kappa}{\kappa_m} = \ln\alpha + E \tag{4}$$

where E is an $O(1)$ constant, not explicitly given by the theory, which with $E \doteq 11$ fits various experimental results reasonably well.

An exhaustive historical review of the work up to 1960 on conductivity of stationary suspensions can be found in Meredith and Tobias (1962). Their conjecture, reflected in the above theory of Batchelor and O'Brien, that $\kappa \longrightarrow \infty$ for $\alpha \longrightarrow \infty$ only if the solid volume fraction approaches its maximum value may be rendered invalid, however, by the so-called *percolation* phenomenon, in which one achieves sample-spanning clusters well below the maximum, at a critical value ϕ corresponding to the *percolation threshold*.

Several investigators have also studied shear-enhanced diffusive transport through suspensions, where the effective diffusivity of the suspension also depends on the motion of the medium. The importance of such microscopic convection effects is governed by the magnitude of an additional parameter, the *Péclet number*:

$$Pe = \frac{\dot{\gamma} d^2}{\mathcal{D}_m} \tag{5}$$

where

$\dot{\gamma}$ = characteristic rate of deformation or shear
d = characteristic particle diameter
$\mathcal{D}_m$ = characteristic diffusivity in the matrix phase

With the κ's replaced by $\mathcal{D}$'s, the relations 1–4 correspond, of course, to the limit $Pe = 0$. For small, but nonzero, Péclet numbers, Leal (1973) has theoretically calculated the effective conductivity of dilute suspensions, from which the cross-stream diffusivity ratio is given by:

$$\frac{\mathcal{D}}{\mathcal{D}_m} = 1 + [3\beta + (3.0 - 0.14\,\beta + 1.176\beta^2)Pe^{3/2} + O(Pe^2)]\phi + O(\phi^2) \tag{6}$$

which, we note, for the case of equal solid and matrix conductivities, $\beta = 0$, reduces to:

$$\frac{\mathcal{D} - \mathcal{D}_m}{\mathcal{D}_m} = [3.0\,Pe^{3/2} + O(Pe^2)]\phi + O(\phi^2) \tag{7}$$

With heat transfer measurements, Chung and Leal (1982) experimentally tested the validity of Eq. 7 and found that the exponent of the Péclet number ranged from 1.2 to 1.9 for $Pe \sim O(1)$ and $\phi \leq 0.25$, and they conclude that Eq. 6 is good mainly for order-of-magnitude estimates.

The thermal conductivity of sheared suspensions at high Péclet number is treated by Nir and Acrivos (1976), and according to their analysis the effective cross-stream diffusivity of dilute suspension as $Pe \longrightarrow \infty$ is given by (after correction of a typographical error):

$$\frac{\mathcal{D}}{\mathcal{D}_m} = 1 + [BPe^{1/11} + C]\phi + O(\phi^2) \tag{8}$$

where B, independent of β, and C are $O(1)$ numerical coefficients which they do not evaluate explicitly. The notably weak dependence on Pe and lack of dependence of B on the conductivity of the suspended solid can be attributed to the presence of regions with closed streamlines surrounding each particle, which for very large Pe appear as regions with infinite conductivity.

All the above theories refer to uniform shear fields in the absence of boundaries. However, thanks to the work of Tobias and coworkers (Muller et al., 1982 and Andersen, 1987), there is much interest in enhanced diffusion to bounding electrode surfaces in electrochemical systems. Here, based on the size of particles relative to the thickness of preexisting transport boundary-layers, Andersen (1987) identifies two distinct mechanisms of transport enhancement. For particles smaller than the boundary-layer, microconvective enhancement of the type described by the above theories for dilute systems, is assumed. On the other hand, for particles larger than the boundary-layer, the enhancement is attributed to the increase of the shear rate in a particle-depleted slip layer adjacent to the electrode surface, like that proposed by Watkins et al. (1976). In his empirical correlations, Andersen (1987), therefore, adopts a modified definition of the Pélect number in order to incorporate two length scales: the particle size d and a mass transfer boundary-layer thickness δ_m. As an empiricism, he proposes an expression for the effective ionic diffusivity $\mathcal{D}$ through suspensions of nonconductive particles in electrolytes, of the form:

$$\mathcal{D} \sim \overline{Pe}^{m(\phi)} \tag{9}$$

where $\overline{Pe} = Pe(\delta_m/d)$ and the exponent $m(\phi)$ is a function of the solid volume fraction ϕ. Using a rotating disc electrode for the reduction of ferricyanide ion, which we also employ in the present study, he finds that the exponent m ranges from 0.067 to 0.636 for Péclet number in the range $50 \leq Pe \leq 2 \times 10^3$. He also finds that the slip-layer mechanism underestimates the limiting current and fails to account for its dependence on the area of the working electrode.

In view of the limited experimental data against which the various theoretical analyses can be compared, we have carried out an experimental study of the electrical conductivity of suspensions of monosized, neutrally-buoyant, spherical ion-exchange beads suspended in an electrolyte, in order to shed light on the effect of the solid volume fraction and the change of the conductivities of the individual phases on the conductivity of the suspension, for both zero and large Péclet number.

Basic Theory

Transport equations

Since the detailed discussions of transport in liquid electrolytic systems is available elsewhere (Riddiford, 1966; Newman, 1967, 1973; Adams, 1969; Pleskov, 1976), only a very brief account is given here in order to illustrate certain problems associated with theoretical interpretations of our data. In the presence of excess supporting electrolyte, the diffusivity $\mathcal{D}_i$ of species i can be assumed uniform throughout the medium, and the species migration due to potential gradients can be neglected. With these approximations and in terms of the appropriate nondimensional entities $\hat{x}$, $\hat{\nabla}$, $\hat{t}$, $\hat{\mathcal{D}}_i$, $\hat{v}(\hat{x}, \hat{t})$, and $\hat{c}_i(\hat{x}, \hat{t})$, the species material balance can be put into the standard form:

$$\frac{\partial \hat{c}_i}{\partial \hat{t}} + \hat{v} \cdot \hat{\nabla}\hat{c}_i = \frac{1}{Pe}\hat{\nabla} \cdot (\hat{\mathcal{D}}_i \hat{\nabla}\hat{c}_i) \qquad (10)$$

where with v_0, l_0 and $\mathcal{D}_m$ being characteristic velocity, length and diffusivity, respectively, $Pe = v_0 l_0/\mathcal{D}_m$ is a Péclet number. In two-phase systems, $\hat{v}$ and $\hat{\mathcal{D}}_i$ assume values appropriate to each of the phases. As indicated by Eq. 10, diffusion is dominant or negligible, respectively, as $Pe \rightarrow 0$ or $Pe \rightarrow \infty$.

In the present context, as in the theories of Leal (1973) and of Nir and Acrivos (1976), Eq. 10 can be assumed to govern the diffusion of DC-current-limiting species at the microscopic or particle-scale level, with $l_0 = d$ and $v_0 = \dot{\gamma} d$. Of course, the above theories deal with isolated particles in otherwise steady homogeneous shear fields and concentration gradients, none of which applies strictly to the rotating disc experiments discussed below. We nevertheless shall attempt to interpret our data in terms of an effective diffusivity ratio $(\mathcal{D}/\mathcal{D}_m)$ for the current-limiting species which is assumed to depend only on the representative values of the parameters introduced previously. More will be said below regarding the limitations associated with the rotating disc.

For the AC ohmic-conductivity experiments, matters are somewhat simpler and one obtains an equation of the form (Newman, 1967, 1973):

$$\frac{\partial \rho_e}{\partial t} = \nabla \cdot (\kappa \nabla \Phi) + \mathcal{F} \sum_i z_i \nabla (D_i \nabla c_i) - \rho_e v \qquad (11)$$

where Φ is the electrical potential, $\rho_e = \Sigma_i \mathcal{F} z_i c_i$ is ionic charge density and $\kappa = \mathcal{F}^2 \Sigma_i (z_i^2 u_i c_i)$ is the conductivity of the medium, with u_i denoting the ionic mobility. For uniform $\mathcal{D}_i$ and assuming (based on small Debye number) that the electroneutrality assumption $\rho_e = 0$ applies, Eq. 11 becomes:

$$\nabla \cdot (\kappa \nabla \Phi) = 0 \qquad (12)$$

This equation, in which once again κ takes on values appropriate to the two phases, corresponds mathematically to Eq. 10 for $Pe \rightarrow 0$.

Thus, it is seen by Eqs. 10 and 12 that one can obtain the conductivity of the system at both large and negligibly small Péclet numbers by simultaneous measurement of both DC and AC conductivities.

Rotating disc polarography and hydrodynamics

An often-used configuration for electrochemical measurements, which can in principle be adapted for simultaneous measurement of both electrolytic-DC and ionic-AC conductivities, is the rotating disc electrode (RDE). The primary utility of the RDE is the presumed uniformity and the well-known variation of the diffusion-limited DC current with the rotation rate, which for a Newtonian fluid is given by the classical Levich formula (Levich, 1962; Riddiford, 1966; Adams, 1969; Newman, 1967, 1973; Pleskov, 1976) as:

$$i_L = 0.62 nFA\nu^{-1/6}\mathcal{D}^{2/3}c_b\omega^{1/2} \qquad (13)$$

where

A = area of working electrode
c_b = concentration in the bulk solution
$\mathcal{D}$ = effective diffusivity of current-limiting species
i_L = limiting current
n = number of electrons transferred in the red-ox reaction
ν = kinematic viscosity
ω = rotation speed

We recall that Eq. 13 results from the large-Pe solution to an equation of the general form (Eq. 10) for steady-state conditions and von Karman disc flow, where Pe is now based on macroscopic length scales (e.g., disc radius) and an *effective* diffusivity $\mathcal{D}$. Several assumptions underlie the application to the RDE experiments of Muller et al. (1982), Andersen (1987) and the present work; while the RDE provides an easy method for many purposes, we readily acknowledge that it is not best suited for measurement of the effective diffusivity $\mathcal{D}$ of sheared suspensions. First of all, the shear rate and hence the particle Péclect number vary over the disc, since the local shear rate $\dot{\gamma}$ is given approximately by (Schlichting, 1965):

$$\dot{\gamma} \doteq r\left(\frac{\omega^3}{\nu}\right)^{1/2} \qquad (14)$$

whence the local Péclet number is directly proportional to the distance r from the axis of rotation, varying from zero at the center of the disc to $O(10^6)$ at the rim for typical values of the rotation speed and physical properties of our systems. Thus, since the effective diffusivity $\mathcal{D}$ is shear-rate-dependent, its variation across the surface of the RDE causes the surface to be no longer uniformly accessible as assumed in (Eq. 13). Fortunately, it turns out that the weak dependence of $\mathcal{D}$ on Pe, for large Pe, makes this a minor problem. More important for the interpretation of data in terms of steady-state theories such as those of Nir and Acrivos (1976) are length scale or wall effects, arising from the size of the particle relative to the hydrodynamic boundary layer (Watkins et al., 1976), and time-scale effects arising from the short particle residence time over the disc, effects which will be discussed further below. Finally, there is possible non-Newtonian effect in concentrated suspensions which could also invalidate Eq. 13.

Despite these obvious disadvantages, we chose to work with the RDE, both because it is simple to operate and allows us to compare with previous experimental work on this standard electrochemical device (Muller et al., 1982; Andersen, 1987).

Experimental Studies

DC cell

Our rotating disc electrode was fabricated from a 0.125-cm-thick cylindrical nickel disc, 2.51 cm in diameter, flush-mounted on the cylindrical head of a steel shaft, using silver-filled epoxy glue. A PVC insulating sleeve is used to cover the shaft except the lower surface of the nickel disc which occupies the center of the 3.4-cm-dia. PVC disc. The RDE serves as the cathode for the reduction of ferricyanide ions. Another nickel disc of 7.62 cm in diameter is used as stationary electrode. Since the cathodic surface area is much less than the anodic, the mass transfer through the circuit is cathode-limited. The RDE is centered in a cylindrical vessel, 10.5 cm high and 10.5 cm in diameter. The cathode-anode distance throughout the experiment was kept constant at 5.0 cm. A Lambda LQ-410 potentiostat is used down to 1 μAmp is used to measure current. A schematic diagram of the setup is shown in Figure 1.

For the DC conductivity measurements, the limiting current plateaus at different rotation speeds for both the solution and the suspensions at various solid volume fractions were determined by incrementing the voltage by about -0.05 V between 0 and -0.9 V (relative to a Ag/AgCl reference electode) and simultaneously recording the current. The plateaus were well-defined in all cases, but narrower for some suspensions especially at very high rotation speeds (-0.64 to -0.83 V compared to -0.35 to -0.85 V for the solution). Therefore, a constant potential in the range -0.7 to -0.8 V was imposed during measurement of the limiting current at various rotation speeds and solid volume fractions. Figure 1 shows a schematic diagram of the setup.

In the DC experiments, neutral buoyancy of the beads was achieved by employing a concentrated 2.55N KCl solution as electrolyte. While not contributing to the DC conductivity, the KCl would dominate the AC conductivity. Therefore, since convection *per se* is not important for the AC conductivity (in accordance with Eq. 12), high concentrations of KCl or other salts are no longer needed to achieve neutral buoyancy for good dispersion which can be accomplished simply by vigorous stirring with a magnetic stirrer. With this in mind, we chose to employ a separate, more convenient device for our AC measurements.

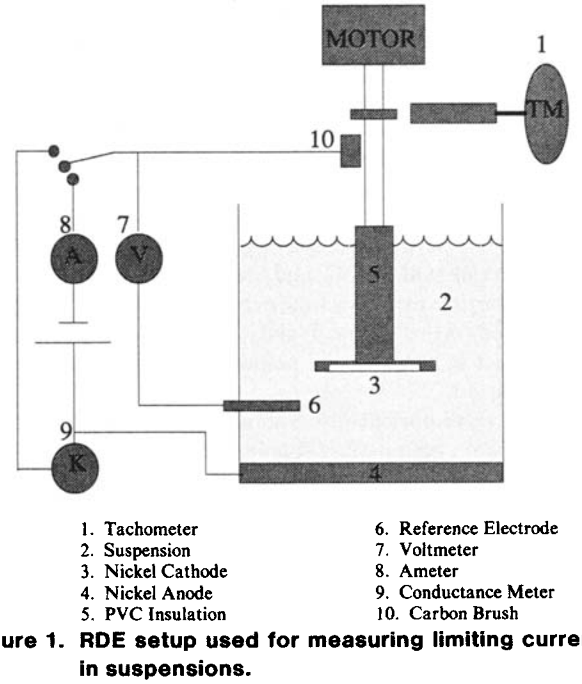


Figure 1. RDE setup used for measuring limiting current in suspensions.

AC cell

The AC cell is a cylindrical vessel, 12.5 cm high and 10.0 cm in diameter, with plexiglas baffles and cover. Two 2.8-cm-long parts of an otherwise insulated 0.8-cm-dia. stainless steel rods serve as electrodes 3.8 cm apart. The conductance is measured using a YSI-35 (YDI Scientific) conductance meter. A schematic diagram is shown in Figure 2. By measuring the conductances of two standard (0.1N and 0.05N) KCl solutions with known conductivities, the cell constant S is estimated as 0.24 ± 0.015 cm^{-1}, which is within 7% error of a theoretical value of 0.255 cm^{-1} for infinitely-long parallel rods (Andrews, 1955). We shall report our AC conductivity data below simply as conductance $K = \kappa/S$ since we are ultimately interested only in conductivity ratios. With the accuracy reflected in our measured S values, K can be converted to conductivity κ if desired.

Solid particles

Three types of particles are used:

1. DOWEX TG 550 OH-form anion-exchange resin (DOW USA): a monosized spherical ion-exchange resin with diameter of 0.550 mm. The DC electroylte is composed of equal amounts of potassium ferricyanide and potassium ferrocyanide dissolved in aqueous solution of potassium chloride and potassium hydroxide. The hydroxide is used to maintain the alkalinity of the solution against possible generation of toxic HCN. The chloride is used both as a supporting electrolyte and to increase the density of the solution to render the suspended solid neutrally-buoyant. The resin is first soaked overnight in a solution made up of potassium ferricyanide (1.00N), potassium ferrocyanide (1.00N), potassium hydroxide (1.00N) and potassium chloride (2.55N). The concentration of ionic sites in the resin, for which all ions compete, is approximately 1.1 eq/l. Due to the large charge on the ferri- and ferrocyanide ions and also to their high polarizability, they occupy the active sites almost exclusively (Helfferich, 1962; Kennedy, 1980). An electrolyte solution with lower ferro/ferricyanide concentration is used as a suspending medium, and RDE polarographic measurements are taken for different solid volume fractions ranging from 0 to 0.45.

2. DOWEX TG 550 H-form cation-exchanged resin (DOW USA): also monosized spherical ion-exchange resin with diameter of 0.550 mm. After replacing the hydrogen ions with mono- and/or bivalant cations, a portion of the cations is replaced with less mobile trivalant ions, and then the effect of the concentration of the less mobile cations on the AC conductivity of the resin is studied. It is reasonable to expect the conductivity to decrease with higher concentrations of the less mobile ions absorbed on the resin. For this purpose, this form of resin was soaked in an electolyte composed of cupric and cuprous bromide to replace the hydrogen ions with cupric and cuprous ions. Then the cupric and cuprous ions on the beads are partially replaced by ferric ions by soaking the cupric/cuprous-saturated beads overnight in a solution of ferric chloride. The conductivity of the resin with only cupric/cuprous ions is expected to be higher than that of the same resin with a portion of the cupric/cuprous ions replaced fully or partially by the less mobile ferric ions. This change in conductivity can be utilized to study the effects of the relative conductivity of the solid to that of the solution on the suspension effective conductivity holding all other parameters constant.

3. Monodisperse Polymatte latex spheres (Anderson Dev. Co.): these 5.6-μm-dia. particles are used in the DC cell with the

potassium ferro/ferricyanide system to test the effect of particle size and thus the Péclet number on the results obtained. Use of surfactant proved to be necessary since, owing to the size of the particles, they tend to agglomerate. Their density is slightly higher than that of the solution, and thus a 1.9N solution of KCl is needed to achieve neutral buoyancy.

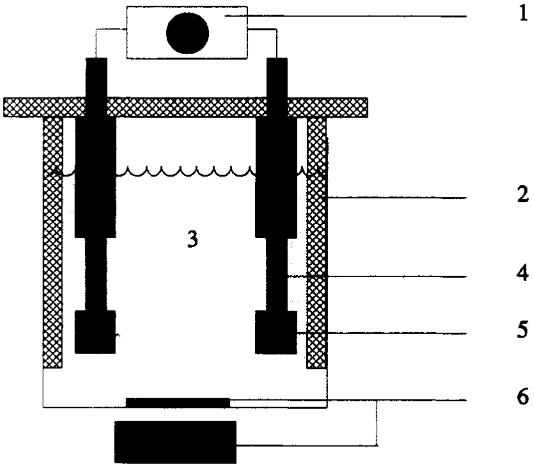
While no attempt was made to rigorously control solution or suspension temperatures for either the AC or DC measurements, the conductivity cells were exposed to an ambient laboratory temperature of approximately 22°C. Suspension temperatures may have varied over time by as much as 2°C, with the consequent effect on solution diffusivities and conductivities of 5% (as estimated from the Stokes-Einstein relation) (cf. Newman, 1973), which with other sources of error is reflected in the error bars of Figures 2 and 3. Since the experiments on the suspending solution and the bead suspensions were generally all done with a two-hour period, we estimate the effect on conductivity *ratios* to be much less.

Results and Discussion

Electrolytic DC conductivity

To check the apparatus, the classical relationship (Eq. 13) between the limiting current and the speed of rotation was tested by placing a 500 mL of 0.01125M ferri/ferrocyanide solution in the cell and measuring the limiting current at different rotation speeds. Figure 2 shows limiting current vs. the square-root of rotation speed, together with a least-squares fit and the theoretical prediction. As can be seen from the figure, the data fall on a straight line, which within experimental error, is close to the theoretical. The deviations from theory might be attributed to confinement effects of the walls in our relatively small vessel. In view of the good agreement without corrections for such effects, our further measurements on the suspensions were carried out in the same manner. Following is a summary of technique.

After measuring the limiting current at various rotation speeds for the solution, small volumes of the previously-soaked resin are added, making sure to remove the same volume of liquid in order to keep the total volume of the suspension constant. The limiting current at various rotation rates is again measured. The process of addition of small volumes of resin and removal of equal volumes of liquid is repeated for solid volume fraction ranging from 0 to 0.45, for the ion-exchange resin, and up to 0.35 for the smaller latex beads. The results are summarized in Figures 4 and 5 for the ion-exchange resin and latex particles, respectively, which show that limiting current appears proportional to square root of the rotation speed for both types of suspensions, so that non-Newtonian effects are either absent or else masked by other effects. Also, the smaller latex particles are observed to enhance the mass transfer by about 10–20% more than the ion-exchange resin.



1. Conductance Meter
2. Plexiglas Baffles
3. Suspension
4. Stainless Steel Electrode
5. Rubber Insulators
6. Magnetic Stirrer

Figure 2. Setup used for measuring the AC conductivity of the suspensions.

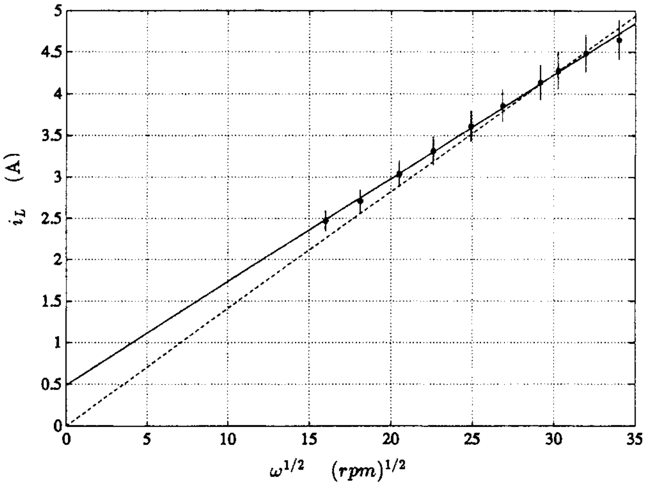


Figure 3. RDE setup: theory vs. experiment.

Solid line is the least-square fit of the experimental points, shown here with error bars, while the broken line is the classical RDE theory.

By means of Eq. 13, the ratio of limiting current in the suspension i_L to that in the suspending solution without beads i_{Lm} is given in terms of effective diffusivity and kinematic viscosity ratios by:

$$\frac{i_L}{i_{Lm}} = \left(\frac{\mathcal{D}}{\mathcal{D}_m}\right)^{2/3}\left(\frac{\nu_m}{\nu}\right)^{1/6} \tag{15}$$

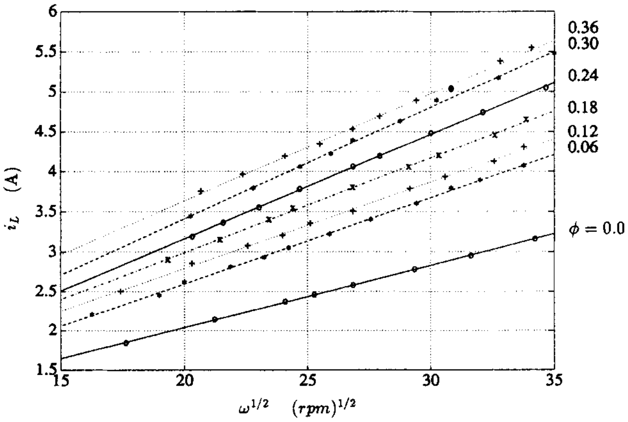


Figure 4. Limiting current vs. square root of the rotation speed for the suspension at different solid volume fractions ϕ of the anion-exchange resin.

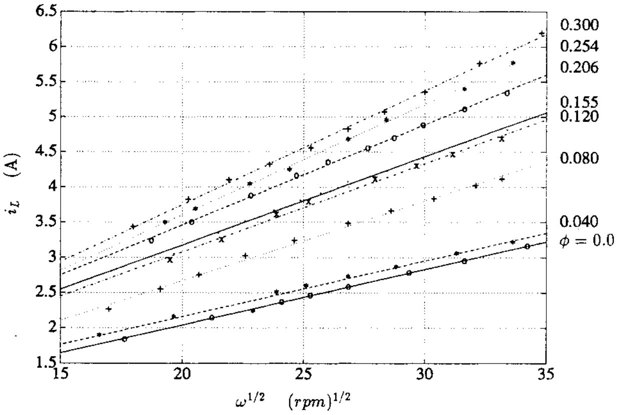


Figure 5. Limiting current vs. square root of the rotation speed for the suspension at different solid volume fractions ϕ of the latex particles.

where ν is the kinematic viscosity of the presumably Newtonian suspension. Following Andersen (1987), ν can be estimated using Thomas' correlation (Thomas, 1965). Figure 6 gives a straight-line fit of $\mathcal{D}/\mathcal{D}_m - 1$ vs. ϕ for the extremes of rotation speed and corresponding Péclet numbers, $Pe = 1.13 \times 10^6$ and 6.08×10^6 for the anion-exchange resin and $Pe = 2.17 \times 10^2$ and 1.16×10^3 for the latex particles. The Péclet number is calculated as an average value from Eqs. 5 and 14 with ν calculated at $\phi = 0.2$ and r = half the disc radius. The least-squares slopes are 6.32 and 6.34 for the ion-exchange resin and 7.72 and 8.39 for the latex particles. Both show an extremely weak dependence on Péclet number, in qualitative agreement with the theory of Nir and Acrivos (1976). If we assume their 1/11 value for m we obtain $B = 2.32$ and $C = 3.93$ from the slopes for the latex particles. Note that $B + C = 6.25$ which is very close to the slope obtained for the ion-exchange beads. Given the weak dependence on Pe it appears that at any reasonable values of the Schmidt number Sc (for $Re < 1$) one can take the coefficient of ϕ in Eq. 8 to be ≈ 6.

A word of caution is in order in equating the constants in the Nir and Acrivos (1976) theory to the estimates obtained above. First of all, their theory is for dilute regimes where $O(\phi^2)$ terms are negligible, which may not be the case for the above estimates. Secondly, the theory is valid for systems with small Reynolds number, $Re = \dot{\gamma} d^2/\nu$, where inertia is negligible. With average values of r = half the RDE radius, ω = 800 rpm and ν at $\phi = 2.0$, Re is 5×10^2 for the ion-exchange beads and 5×10^{-2} for the smaller latex. While the latter is satisfactory, the former is not. Thirdly, length-scale or wall effects might arise from the size of the particles d relative to that of the hydrodynamic boundary layer δ. The latter is given approximately by (Schlichting, 1965):

$$\delta \approx \sqrt{\frac{\nu}{\omega}} \tag{16}$$

and with ν at $\phi = 0.2$ and $\omega \approx 800$ rpm, δ is found to be approximately 0.15 *mm*. Therefore, the diameter of the ion-exchange resin is more than three times *larger* than δ while that of the Polymatte latex spheres is about thirty times *smaller*.

Another serious difficulty in comparing with the Nir and Acrivos theory may arise from the unsteadiness or time-scale effects due to small particle residence time under the disc, of order ω^{-1}. A pessimistic estimate based on an unsteady concentration field around each particle requires a time-scale $\sim d^2/\mathcal{D}_m$ to achieve the steady state, consistent with Eq. 10. In this case, the diffusion-to-residence time ratio is $\sim O(10^4)$ for the ion-exchange resin and $\sim O(1)$ for the latex particles. Therefore, meaningful comparison with the above theory may not be possible, especially for the ion-exchange resin. In a more optimistic view, each particle may be assumed to transport with it from the free stream a surrounding fluid layer with concentration close to that of the steady state, requiring then only a time scale order $\sim d^2/\nu$ to achieve the steady-state velocity field postulated in the theory. In this case, the time ratio becomes of order of particle Reynolds number, which is satisfactory for the latex particles.

The same comments apply to the results of Muller et al. (1982) and Andersen (1987), which, however, may suffer from additional hydrodynamic effects caused by their heavier (2,460–2,490 kg/m^3) glass spheres, baffles and extensive stir-

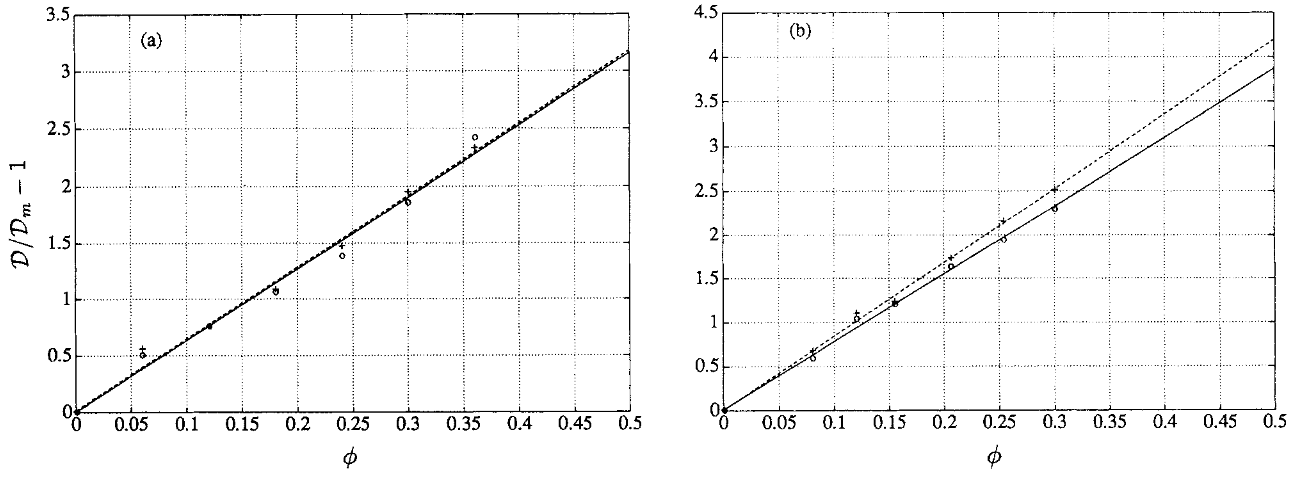


Figure 6. ($\mathcal{D}/\mathcal{D}_m - 1$) vs. solid volume fraction ϕ at different Péclet numbers.

a. Ion-exchange: $Pe = 1.13 \times 10^6$ (o), 6.08×10^6 (+)
b. Latex particles: $Pe = 2.17 \times 10^2$ (o), 1.16×10^3 (+)

ring required to achieve a homogeneous suspension. Since $\delta_m \approx d(Re^{-1/2}Sc^{-1/3})$ and $Pe \sim \omega^{3/2}$, it follows from the definition of $\overline{Pe}$ in Eq. 9 that $\overline{Pe} \sim \omega$. With the assumption that effective diffusivity is proportional to the mth power of $\overline{Pe}$ and since from Eq. 13 the limiting current $i_L \sim D^{2/3}\omega^{1/2}$, i_L should be porportional to the $[(2/3)m + (1/2)]$th power of rotation speed ω. For Péclet numbers in the range $50 \le Pe \le 2 \times 10^3$, Andersen (1987) obtains values for the exponent m ranging from 0.067 to 0.636. In our experiments, the effect of Péclet number on the diffusivity is found to be almost completely negligible, corresponding to extremely small values of the exponent m for all solid volume fractions ϕ employed.

Since the internal diffusivity of the particles, which appears relatively unimportant in the dilute high-Pe theory in Eq. 8, may become important at higher concentrations, we were interested in enhancing particle diffusivity, possibly by employing ions with higher mobility than ferro/ferricynide, the latter of which (due to their high valancy) tend to be immobilely bound to the resin. Copper deposition in suspensions of cation-exchange resin saturated with Cu^+/Cu^{++} ions could in principle provide a system where particle diffusivity can be controlled. This can be achieved by partially replacing Cu^+/Cu^{++} with highly charged less mobile cations (e.g., Fe^{+++}). Unfortunately, the mixture of copper(II) and copper(I) sulfate electrolyte in the RDE setup gave no limiting current plateau for copper deposition, also the case in other investigations of metal deposition (Hsueh and Newman, 1967; Ibl and Schadegg, 1967; Selman and Tobias, 1978). Thus, the cation-exchange resin saturated with Cu^{++} and Cu^+ ions could not be used in the DC conductivity measurement.

Total ionic AC conductance

Using the specially-designed cell illustrated schematically in Figure 7, the AC conductance of suspensions of the two forms of ion-exchange resin in KCl solutions was measured for various solid volume fraction at different solution concentration and, therefore, different solution conductance K_m.

To interpret the data, we note that the quantity β in Eq. 1 is given by:

$$\beta = \frac{K_b/K_m - 1}{K_b/K_m + 2} \tag{17}$$

with K_b and K_m denoting the bead and matrix conductances, respectively. As can be seen from Eq. 17, β must satisfy the condition:

$$-0.5 \le \beta \le 1, \quad \text{for} \quad 0 \le K_b \le \infty.$$

By plotting effective conductance vs. ϕ and fitting the results with a second-degree polynomial, one obtains estimates for K_m and β from Eq. 3. Once K_m and β are known, we can thus find the conductivity of the solid phase. Figure 3 shows such a plot for the anion exchange-resin in dilute solution of KCl, together with Maxwell's relation (Eq. 1) and Jeffrey's relation (Eq. 3). The best second-degree polynomial fit gives the conductance as:

$$K = 13.96\,(1.0 - 1.4025\phi + 0.506\phi^2) \quad \text{(mMho)} \tag{18}$$

implying that $K_m = 13.96$ mMho and $\beta = -0.4675$, from which one obtains: $K_b = 0.6184$ mMho and $\alpha = 0.044$, and thus from Jeffrey (1973) $\hat{\beta} = 0.48$, which compares favorably with 0.506 in Eq. 18. As seen from Figure 3, Maxwell's relation is adequate for volume fractions $\phi \le 0.5$. A similar observation has been reported by Turner (1973, 1976).

Figure 8 is a plot of the effective conductance against particle volume fraction for solution with conductances higher than, comparable to and lower than that of the solid particles, from which the values for the solution conductances, the parameter β, and then the conductance of the beads themselves can be obtained, as mentioned above by least-squares fit of the experimental points.

To this end, we cast Eq. 17 into the form:

$$G \equiv \frac{1 - \beta}{1 + 2\beta} = \frac{K_m}{K_b} \tag{19}$$

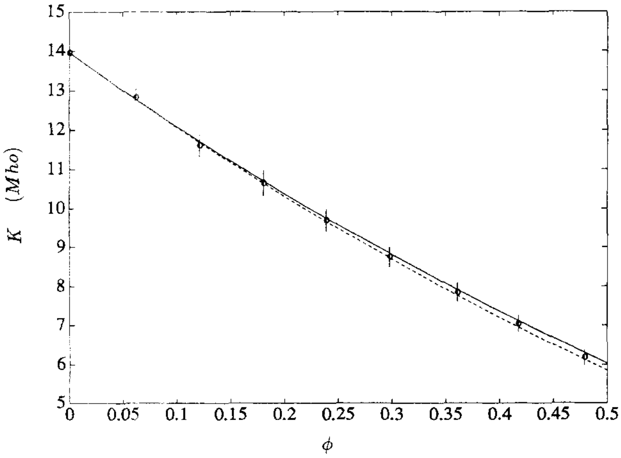


Figure 7. Effective conductance vs. solid volume fraction of ion-exchange beads in dilute KCl solution, shown with error bars.

The solid line is Maxwell's relation, while the broken line is Jeffrey's.

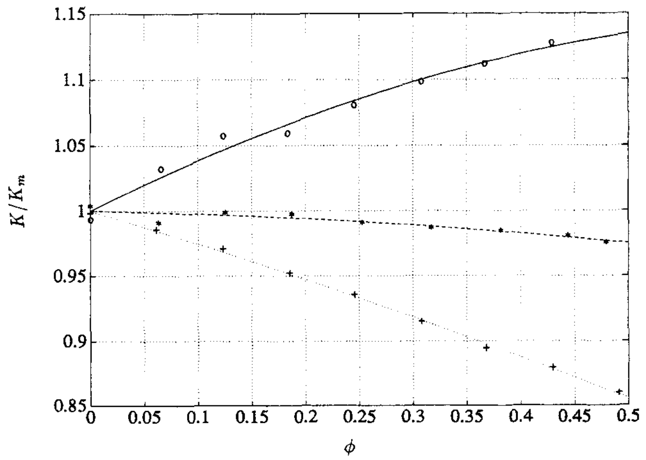


Figure 8. Effective conductance ratio K/K_m of the suspension vs. solid volume fraction in solution of KCl of different concentration: 0.100N (o), 0.163N (*) and 0.250N (+).

Thus, if one obtains the β's for suspensions with different solution conductances and employs Eq. 19 to plot G vs. K_m, then the resulting plot should be a straight line passing through the origin with slope K_b^{-1}. Figure 9 shows such a plot for the data in Figure 8 and Table 1.

As can be seen, the plot of Figure 9 gives the expected straight line, for the cases when the solution has conductivity higher than, comparable to, or lower than that of the beads. This method of measuring the particle conductivity is more systematic and much easier than that employed by Turner (1973, 1976), where 16 different runs, required merely to *estimate* the solid conductivity, preceded a more accurate measurement at an isoconductance point. By contrast, the present method requires only a single run in principle, with only a few more serving to enhance accuracy and reproducibility.

Changing the bead conductivity

Since ion-exchange beads preferentially absorb ions with higher polarizability (Sterlow, 1960; Helfferich, 1962; Kennedy, 1980), i.e., with highest valancy and largest volume, it is expected that the anion-exchange resin used would absorb ferrocyanide in preference to ferricyanide. It happens this way simply because, while being of similar size, the former has a higher charge. This, therefore, renders the ferrocyanide less mobile than any other ion present. Similar arguments carry over to the cation-exchange resin. To study this experimentally, the anion-exchange resin is initially soaked in a concentrated solution of only potassium ferrocyanide, thus saturating the active sites on the beads with highly charged, less mobile ions. The conductance of the resulting beads is then measured in a very dilute solution of KCl. The results are displayed in Figure 3, which clearly shows the conductance of the beads very close to zero. This result is attributed to the very low mobility of the highly charged ferrocyanide ions that occupy the positively charged sites on the beads, thus inhibiting exchange of ions between the resin and the solution and lowering ionic conductivity. Equation 18 gives the polynomial fit for the conductance of the resin saturated with the less mobile ferrocyanide ions, from which we find $K_b = 0.6184$ mMho.

Table 1. Coefficients c_n of ϕ^n in the Second-Degree Polynomial Fit for Anion-Exchange Resin Suspensions in KCl Solutions of Different Concentrations

KCl (*eq/l*)	c_0	c_1	c_2	β	K_b (mMho)	α	G
0.100	51.45	21.28	−4.87	0.138	76.14	1.48	0.676
0.163	77.20	−1.29	−5.17	−0.01	75.92	0.98	1.017
0.25	101.99	−25.11	−8.71	−0.08	78.78	0.77	1.295

To examine, this same selective absorption phenomenon for the cation-exchange resin, the following procedure is carried out. Since cuprous bromide is very slightly soluble in water, a saturated solution of this salt is prepared to which enough cupric bromide salt is added to make the solution 1.0N with the cupric ions. The cation-exchange resin is then soaked overnight in this solution, separated and washed with deionized water, and then its AC conductance in a dilute solution of cupric and cuprous bromide is measured as described above. A mass of ferric chloride [Fe(III)Cl$_3$ · 5H$_2$O] is added to the suspensions. The beads are allowed to establish equilibrium with the solution, separated from the solution and then washed with deionized water. The bead conductance is then measured. As expected, it is less than the conductance of the beads without ferric ions. The process is repeated with more ferric ions and the same result is obtained: the higher the concentration of ferric ions on the beads, the lower their conductivity. These results are shown in Figure 10 and Table 2. Similar results are obtained for resin saturated with potassium ions and then partially replaced with less mobile ferric ions.

Therefore, it appears possible to decrease the conductivity of the resin by absorbing less mobile ions. This "poisoning" phenomenon may be useful in studies where one wishes to investigate the effects of changing conductivity of the solid while holding other parameters constant.

Conclusions and Recommendations

Based on dilute-suspension theory, a rapid and easy measurement of the solid AC conductivity is possible via Eq. 19. In

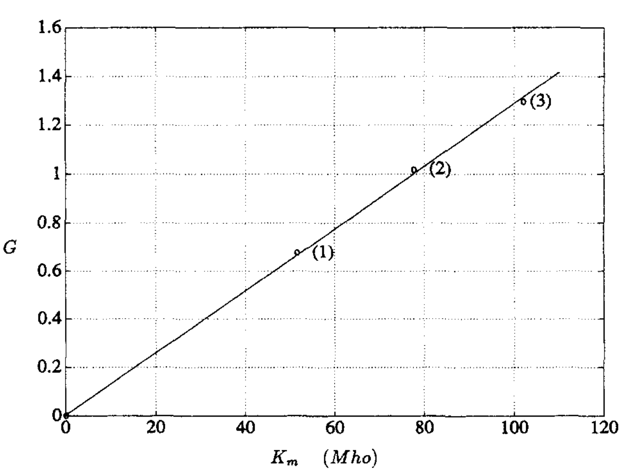


Figure 9. $G = (1 - \beta)/(1 + 2\beta)$ vs. solution conductance for KCl solution concentrations: 0.100N (1), 0.163N (2), 0.250N (3).

The solid line is the least-squares fit of the points.

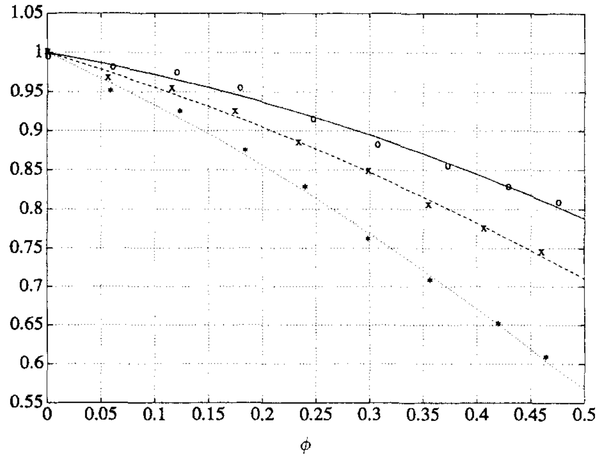


Figure 10. Conductance ratio of the cation resin vs. solid volume fraction at different concentrations of ferric ions absorbed on the resin: 0.0N (o), 0.166N (x) and 0.470 (*).

The lines are the least-squares fit of the experimental data.

Table 2. Coefficients c_n *of* ϕ^n in the Second-Degree Polynomial Fit for Suspensions of the Cation-Exchange Resin, with and without Fe(III) Ions

Fe(III) (*eq/l*)	c_0	c_1	c_2	β	K_b (mMho)	α
0.0	300.48	−72.05	−110.80	−0.08	233.79	0.78
0.166	301.68	−122.37	−104.28	−0.135	193.89	0.64
0.470	300.50	−184.64	−154.76	−0.20	147.26	0.49

agreement with Turner's (1973, 1976) conjecture for $\alpha \leq 1.0$ and $\phi \leq 0.5$, we find that Maxwell's relation (Eq. 1) is accurate for our range of α: $0.044 \leq \alpha \leq 1.48$. In this case, Jeffrey's relation (Eq. 3) does not offer a substantial correction, since $\hat{\beta} \leq 0.5$ for $\alpha \leq 1.0$.

As for the DC conductivity we observe, contrary to the findings of Muller et al. (1982) and Andersen (1987), the classical proportionality of limiting current and square root of rotation speed for $1.13 \times 10^6 \leq Pe \leq 6.08 \times 10^6$ with the ion-exchange resin and $2.17 \times 10^2 \leq Pe \leq 1.16 \times 10^3$ with the two orders of magnitude smaller latex particles, and volume fractions $0 \leq \phi \leq 0.45$. Furthermore, the latex particles are observed to enhance the limiting current by 10–20% more than the vastly larger ion-exchange resin particles, which we attribute to enhanced boundary-layer penetration by the latter. Also, our results are not inconsistent with the theory of Nir and Acrivos (1976) for dilute suspension and large Péclet number which predicts a weak dependence of the effective diffusivity on Pe. While the effective diffusivity for both types of particles used exhibits negligible dependence on the Péclet number, using $m = 1/11$ from the theory of Nir and Acrivos (1976), the constants B and C in Eq. 8 are crudely estimated to be equal to 2.3 and 4, respectively.

As mentioned above, the RDE does not offer the ideal method for the study of shear-dependent diffusivity, since the shear rate varies across the surface of the disc. An apparatus with uniform shear rate and uniformly accessible electrode surface, such as a rotating-cylinder and concentric-cylinder apparatus, would be much better. Also, careful selection or synthesis of an ion-exchange resin with the proper density and minimum degree of swelling (e.g., a highly cross-linked resin) might eliminate the need for high concentrations of salts to achieve neutral buoyancy, thus allowing easier simultaneous measurement of DC and AC conductivities in the same apparatus.

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Notation

A = area, *cm*^{2}
B = numerical coefficient
C = numerical coefficient
c_b = concentration in the bulk solution, mol/m^3
c_i = concentration of species i, mol/m^3
$\hat{c}_i$ = dimensionless concentration of species i
d = partice diameter, m
$\mathcal{D}$ = effective diffusivity, m^2/s
$\mathcal{D}_m$ = diffusivity in the matrix phase, m^2/s
$\mathcal{D}_i$ = diffusivity of species i, m^2/s
$\hat{\mathcal{D}}_i$ = dimensionless diffusivity of species i
E = constant in Eq. 4
$\mathcal{F}$ = Faraday's constant, 96,487 C/eq.
$G = (1 - \beta)/(1 + 2\beta)$
i_L = limiting electric current, A
i_{Lm} = limiting electric current for the solution, A
K = effective suspension conductance, *Mho*
K_b = beads conductance, *Mho*
K_m = solution conductance *Mho*
l_0 = characteristic length, m
n = number of electrons transferred in a red/ox reaction
Pe = Péclet number
$\bar{P}$e = modified Péclet number
r = distance from axis of rotation of RDE, m
Re = Reynolds number
S = cell constant, m^{-1}
Sc = Schmidt number
t = time, s
$\hat{t}$ = dimensionless time
u_i = mobility of species i, $m^2 \cdot mol/J \cdot s$
v_0 = characteristic velocity, m/s
$\mathbf{v}$ = convection velocity m/s
$\hat{\mathbf{v}}$ = dimensionless convection velocity
$\hat{\mathbf{x}}$ = dimensionless position
z_i = charge number on species i

Greek letters

α = ratio of particle to solution conductivities
$\beta = (\alpha - 1)/(\alpha + 2)$
δ = thickness of hydrodynamic boundary layer, m
δ_m = thickness of mass-transfer boundary layer, m
$\dot{\gamma}$ = shear rate, s^{-1}
κ = conductivity, *M*ho · cm^{-1}
κ_b = conductivity of the particles, $Mho \cdot cm^{-1}$
κ_m = conductivity of the matrix, $Mho \cdot cm^{-1}$
ν = kinematic viscosity of suspension, m^2/s
ν_m = kinematic viscosity of suspending solution, m^2/s
ϕ = solid volume fraction
Φ = electrical potential, V
ρ_e = electrical charge density, C/m^3
ω = rotation rate, *rpm*

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