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P.K. Andersen,* C.W. Tobias, and R.H. Muller
(*Ph.D. Thesis)

November 1987

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The Effect of Suspended Solids on Mass Transfer in Electrochemical Systems

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(Ph.D. Dissertation)

with

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November 1987

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ABSTRACT

The Effect of Suspended Solids on Mass Transfer in Electrochemical Systems

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The enhancement of mass-transfer rates by suspended, inert solid particles was studied using a rotating-disk electrode (RDE). The effects of solids concentration, particle size, and shear rate on limiting currents were measured for the reduction of ferricyanide ion. The suspensions contained glass or polymer particles of various sizes (1 to 100 microns) and concentrations (0 to 40% by volume). To minimize sedimentation of the solid phase, the RDE was placed close to the cell bottom, where the rotation of the disk could keep the solids in suspension.

The data show clear evidence of two different transport mechanisms, which depend on particle size. For particles the same size as, or smaller than, the thickness of the mass-transfer boundary layer, the Sherwood number $Sh$ is a function of a Peclet number $Pe$:

$$Sh = \alpha Pe^m$$

where $\alpha$ and $m$ are experimentally determined functions of the solids volume fraction. To apply this equation to the RDE system, it was necessary first to solve the transport equations assuming that the diffusivity varies with radial position on the disk. The analysis yields

$$\frac{I^*_L}{I_L} \propto \left(\alpha Pe_R^m\right)^{2/3}$$

where $I^*_L/I_L$ is the ratio of limiting current obtained with particles to the limiting current without, and $Pe_R$ is the Peclet number evaluated at the outer radius of the electrode ($r = R$).

For particles much larger than the thickness of the mass-transfer boundary layer, transport enhancement results from the formation of a particle-depleted "slip" layer at the electrode surface.
The shear rate is higher inside the slip layer than would be the case in a homogeneous suspension; this has the effect of thinning the mass-transfer boundary layer. If it is assumed that this layer is of constant thickness, and that the \( r \)- and \( \theta \)-velocity gradients are increased by the same factor, it can be shown that the limiting current is related to the torque required to turn the disk:

\[
\frac{I^*}{I_L} = \left( \frac{T^*}{T} \right)^{1/3}
\]

where \( T^* \) and \( T \) are the torques on the disk with and without particles, respectively. Measurements of the torque show that this equation underestimates the limiting current by as much as 60%, while failing to account for the observed increase in current density with electrode size.

The torque measurements were also useful in estimating the mixing-power requirements. In most cases, the use of suspended solids requires significantly less power to achieve a given increase in limiting current than would an increase in the disk rotation rate.
And further, by these, my son, be admonished: of making many books there is no end; and much study is a weariness of the flesh.

Ecclesiastes 12:12
Acknowledgements

I wish to thank Professor Charles W. Tobias and Dr. Rolf H. Muller for the opportunity to work with them. They allowed me the freedom to plot my own course—then prodded me, when necessary, to follow it.

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Introduction

Many electrochemical processes are limited by the rate at which reactants can be transferred to (and from) the electrodes. In most cases of practical interest, transport in the bulk electrolyte occurs primarily by convection. However, the fluid velocity vanishes at solid boundaries because of the no-slip condition, leaving migration and diffusion as the dominant modes of transport to the electrode surface. Concentration variations tend to occur only within a thin mass-transfer boundary layer, which must be disrupted or reduced in thickness if the rate of mass transfer at the electrode is to be increased.

The addition of inert solid particles to a flowing electrolyte has been found to enhance wall mass-transfer rates significantly. This study was undertaken to elucidate the mechanisms by which this occurs, to determine quantitative relationships that can be used to predict mass-transfer rates, and to discover any connection that may exist between transport enhancement and the rheological properties of suspensions.

Chapter 1 summarizes the technical literature dealing with transport in solid-liquid suspensions. This excludes other kinds of two-phase flow, i.e., solid-gas, liquid-gas, and immiscible liquid-liquid flow. It also excludes work on boiling in suspensions and transport in fluidized beds. Although the focus of this thesis is on mass transfer, relevant studies on heat transfer are also reviewed.

Two mechanisms of transport enhancement are considered in detail in Chapter 2. First, the solid particles are thought to introduce small-scale vortical flows, superimposed on the bulk flow field, that increase the dispersion of solutes. Second, the solid particles may migrate away from the electrode surface, creating a particle-free region in which the shear rate is higher than would otherwise be the case; this has the effect of thinning the mass-transfer boundary layer. Particular attention is paid to the application of these two theoretical models to the rotating-disk electrode (RDE).

Chapter 3 describes the experiments undertaken to confirm the theoretical work outlined in Chapter 2. RDE limiting currents were measured for the reduction of ferricyanide ion in suspensions of glass and polymer particles, 1 to 100 microns in diameter. Similar work had been performed in this
laboratory by Roha (1981), but the experimental apparatus described here incorporated design changes that were intended to improve control of the temperature and suspension of the solid phase, and to permit measurement of the torque on the rotating disk. The results of these experiments are presented in Chapter 4.

The findings of this study are summarized and compared with previously published work in Chapter 5. Also included in Chapter 5 is a discussion of the mixing-power requirements, as well as recommendations for future research.
CHAPTER 1

Literature Review

1.1. Stationary Suspensions

Maxwell (1881) appears to have been the first to treat the problem of transport in a stationary two-phase system. He was interested in electrical conduction in a composite consisting of spheres dispersed randomly in a continuous medium, for which

\[ \sigma^* = \frac{2\sigma_c + \sigma_d - 2\phi(\sigma_c - \sigma_d)}{2\sigma_c + \sigma_d + \phi(\sigma_c - \sigma_d)} \]  

(1-1)

where \( \sigma^* \) is the overall conductivity of the composite, \( \sigma_c \) and \( \sigma_d \) are the conductivities of the continuous and dispersed phases, respectively, and \( \phi \) is the volume fraction of the dispersed phase. Replacing conductivities with diffusivities and setting \( D_d = 0 \) (solute cannot pass through the solid phase), Equation (1-1) becomes

\[ \kappa = \frac{D^*}{D} = \frac{1 - \phi}{1 + \frac{\phi}{2}} \]  

(1-2)

in which \( D^* \) is the effective diffusivity in the composite system, \( D \) is the diffusivity in the pure continuous phase, and \( \phi \) is the volume fraction of solids. Fricke (1924) obtained a similar result for stagnant suspensions of oblate spheroids:

\[ \kappa = \frac{D^*}{D} = \frac{1 - \phi}{1 + \frac{\phi}{1.05}} \]  

(1-3)

Maxwell's derivation applies strictly only in the limit of small values of \( \phi \). Other workers have derived relations intended to cover the entire range \( 0 \leq \phi \leq 1 \). Sides (1980) examined a number of these, and concluded that the equations by Meredith and Tobias (1961) and Prager (1963) agree espe-
cially well with the available experimental data:

\[
\kappa = \frac{8(2 - \phi)(1 - \phi)}{(4 + \phi)(4 - \phi)}
\]  

(Meredith and Tobias)  

\[
\kappa = 1 - \frac{3}{2}\phi + \frac{1}{2}\phi^2
\]  

(Prager)  

Equation (1-5) is plotted in Figure 1-1. As might be expected, the equation predicts a decrease in the effective diffusivity with increasing volume fraction of solids. However, this holds only for suspensions that are not flowing or experiencing shear. Solute transport rates in a flowing suspension may actually be higher than in the pure liquid alone. The remainder of this chapter examines the available literature on this phenomenon.

1.2. Patents

The first patent detailing the use of suspended solids to increase mass-transfer rates was issued to Bixler and Rappe (1970),† who used glass and polymer beads, 10 to 500 microns in diameter, to reduce "concentration polarization" of ultrafiltration membranes. According to data presented in the patent, a 10% suspension‡ of 100-micron glass spheres was found to increase the flux through a commercial polymeric membrane by as much as 112%.

Eisner (1972a) obtained a patent covering the use of suspended solids to increase electrodeposition rates. His plating baths contained particles of hard materials such as glass, sand, ceramics, or abrasives, in concentrations of about 50%. These were placed in vibratory abrasive finishing machines which had been modified to serve as plating cells. The solids increased plating rates by as much as 25

† A number of patents had previously been granted for the use of suspended solids in electrodeposition (Reed 1902; Consigliere 1913; Bugbee 1917; Tomaszewski and Brown 1964; Brown and Tomaszewski 1964) and electropolishing (Pfie1 1946; Olson 1968; Hewins 1970). However, no claim is made in these earlier patents that the solids increased transport rates; instead, the emphasis is on the abrasive or hammering action of the suspended particles on the metal surface. Likewise, a patent for a filter employing suspended particles (Moore 1919) describes the effect of the particles primarily as a mechanical "scrubbing" of the filter medium to prevent clogging.

‡ Unless otherwise noted, all solids concentrations in this chapter are expressed as volume fractions or volume percents.
Figure 1-1. Effective diffusivity of stationary suspensions. The curve is calculated from Prager’s relation, Equation (1-5).
times,† which Eisner attributed to the "mechanical activation" of the cathode surface.

Wisdom (1972) used the same vibratory apparatus and particles as Eisner, but he increased the concentration of solids to about 80%. This greatly improved the throwing power of the bath, although the plating rates were comparable to those of conventional electrodeposition processes. Eisner (1972b) subsequently patented a process which achieved both high deposition rates and good throwing power. The particles used in this process consisted of a cylindrical or annular metallic core partially encapsulated in a hard, nonconducting sheath. According to the patent, "the particles themselves act as bi-polar electrodes, the side of the exposed metal toward the anode at any given instant tending to act as a cathode and having metal deposited on the core, with the side towards the cathode tending to act as an anode and giving up metal ions."

1.3. Engineering and Physical Science Literature

Clough, et al (1962) measured the effective diffusivity of benzoic acid in aqueous kaolinite clay slurries (20% solids) and in aqueous Attaclay slurries (14.2% solids). Their work is unusual in that the solids were found to decrease transport rates by as much as 20%, an effect which appeared to be independent of shear rate.

Collingham (1968) measured the transport of helium and oxygen from suspensions undergoing laminar tube flow. His suspensions contained neutrally-buoyant polystyrene spheres in two diameters (50 microns and 100 microns) and two concentrations (7.5% and 14.6%). The solids increased the effective diffusivity by as much as 500%, with an attendant increase in pressure drop of less than 25%. Collingham attributed the mass-transfer enhancement to the increased local mixing caused by the rotation of the particles. He took high-speed motion pictures of the suspensions, and was able to determine that the particles rotated with an angular velocity one-half that of the local shear rate. Collingham also observed a region of low solids concentration (the "skimming layer") near the tube wall

† These plating baths were probably not operated at limiting current, so this should not be taken to mean that there was a 25-fold increase in limiting current.
Singh (1968) considered the analogous problem of heat transfer to a suspension in tube flow. Using the same polystyrene spheres as Collingham, in concentrations of 3.1% and 8.8%, Singh measured wall heat-transfer rates that were as much as 200% higher than those obtained without suspended particles. Ahuja (1980) showed that the data of both Collingham and Singh can be made to fall on a single curve by plotting \((D^*/D - 1)\) or \((k^*/k - 1)\) versus \(\phi\chi\), where \(\chi\) is given by

\[
\chi = \left( \frac{\omega a^2}{v_f} \right) \left[ \frac{\omega a^2}{\alpha_r} \text{ or } \frac{\omega a^2}{D_r} \right] \left[ \frac{R}{a} \right]^2 \cdot 10^{-8} \cdot f
\]

Here \(a\) is the particle radius; \(\alpha_r\) and \(D_r\) are the thermal and molecular diffusivities, respectively; and \(\omega\) is the angular speed of the particles, taken to be half the local shear rate \(\dot{\gamma}\). Thus, the first factor on the RHS is the rotational particle Reynolds number, while the second factor is the rotational particle Peclet number. The factor \(f\) is the "doublet collision frequency rate", which is supposed to account for the effect of particle collisions on heat or mass transport; it equals the cube of the ratio of the particle diameter to the diameter of an reference sphere, arbitrarily chosen to be 100 microns.

Leal (1973) took a statistical approach to the problem of heat transport in dilute suspensions of spherical drops. First he showed that the bulk heat flux could be expressed in terms of local or microscopic fluxes, averaged over a statistically-significant number of particles. Next he calculated the temperature field near a single sphere in shear flow, assuming high Reynolds and low Peclet numbers. Combining these results, he obtained an effective thermal conductivity \(k^*\) for rigid spheres in simple shear flow:

\[
k^* = k_1 \left[ 1 + \phi \left( \frac{3(k_2 - k_1)}{k_2 + 2k_1} + \left[ \frac{1.176}{(k_2 + 2k_1)^2} - 0.14 \frac{k_2 - k_1}{k_2 + 2k_1} \right] \frac{3}{\text{Pe}^* \phi + O(\text{Pe}^2)} \right) \right]
\]

where \(k_1\) and \(k_2\) are the thermal conductivities of the solid and the liquid phase, respectively. \(\text{Pe}^*\) is the "shear particle Peclet number" for heat transfer.
\[ \text{Pe} = \frac{a^2 \gamma}{\alpha_t} \]

Considering the analogous mass-transfer problem, Leal substituted the molecular diffusivity \( D \) for the thermal diffusivity \( \alpha_t \), and obtained

\[ D^* = D \left[ 1 + \phi(-3/2 + 3.364 \text{Pe}^{3/2}) \right] \]

To test this prediction, Chung and Leal (1982) measured heat fluxes across the gap of a Couette-flow device containing dilute suspensions of polystyrene latex spheres in silicone oil. For \( 0 \leq \phi \leq 0.25 \) and \( 0.01 \leq \text{Pe} \leq 1.28 \), they concluded that Leal's model "could be used for order-of-magnitude estimations of the thermal conductivity of sheared suspensions...in spite of the fact that it obviously does not give a complete physical description of the transport behavior."

McMillen and Leal (1973, 1977) calculated the effective thermal conductivity of dilute suspensions of slightly-deformed spheres, again in the limit of low particle Peclet numbers. They found that the flow-induced component of the conductivity should depend on the Peclet number to the first power, and not to the 3/2 power as predicted for exactly spherical particles. They did not present experimental evidence to support their analysis.

Nir and Acrivos (1976) derived the effective thermal conductivity of sheared suspensions by a statistical method similar to Leal's. Unlike Leal, they considered the limiting case of infinite particle Peclet number, and they treated cylindrical as well as spherical particles. According to their analysis, the flow-induced augmentation of the effective thermal conductivity should depend on \((\ln \text{Pe})^2\) for cylindrical particles, and on \((\text{Pe})^{1/11}\) for spherical particles. Perhaps the most interesting result of this work is the prediction that, at sufficiently high Peclet numbers, closed streamlines around each particle produce regions of infinite effective conductivity.

Watkins, Robertson, and Acrivos (1976) measured heat transfer to suspensions of 580-micron polystyrene spheres \((0 \leq \phi \leq 46\%)\) in the entrance region of a pipe. They confirmed photographically the existence of a thin, particle-depleted layer of fluid at the pipe wall, and proposed that the enhancement of heat transfer might be due entirely to the large velocity gradient within this layer. To account
for this, they modified the classical Leveque solution describing heat transfer in the entrance region:

\[
\frac{\dot{Q}R}{kA\Delta T} = 1.10 \left[ \frac{R/L}{Pe} \right]^{1/3} \left[ (1-\delta)^4 \frac{\mu_w}{\mu} + 1 - (1-\delta)^4 \right]^{-1/3} \left[ \frac{\mu(T_{bulk})}{\mu(T_{wall})} \right]^{0.14}
\]

where \( \dot{Q} \) is the rate of heat transfer through lateral area \( A \), \( k \) is the pure fluid conductivity, \( R \) is the pipe radius, \( 8R \) is the thickness of the wall layer, and \( L \) is the length of the heated section. The factor \( (\mu(T_{bulk})/\mu(T_{wall}))^{0.14} \) corrects for the change in fluid viscosity with temperature across the pipe radius.

The Peclet number used in this case is

\[
Pe = \frac{2\rho C_p RV_{ave}}{k}
\]

where \( V_{ave} \) is the average flow rate, and \( \rho \) and \( C_p \) are the pure fluid density and heat capacity, respectively. The Leveque solution applies where the thermal boundary layer lies entirely within the particle-free layer, which implies that \( \delta > Pe^{-1/3} \). For \( \delta = 0.05 \), this requires \( Pe > 10^4 \). For lower Peclet numbers (<10^4), the authors developed a numerical technique to calculate heat-transfer rates. In all cases, the calculated rates were within 5% of the experimentally-determined rates.

Hsu, et al (1976) measured sodium chloride transport through suspensions of neutrally-buoyant polymer spheres, 37 to 74 microns in diameter, in a flat-plate dialyzer. For solids concentrations of 5% or less, the particles had no effect on transport rates. At 30% solids, the effective diffusivity was twice the molecular diffusivity. The effective diffusivity showed no appreciable dependence on shear rate over the range studied, 12 to 20 sec\(^{-1}\).

Postlethwaite and Holdner (1975, 1976) measured limiting currents for oxygen reduction at electrodes set in the walls of horizontal and vertical slurry pipelines. Their slurries contained sand or iron ore in various sizes (0.04 to 0.21 mm) and concentrations (10 to 23%). The solids increased limiting currents in turbulent flow by as much as 300%, depending on the flow rate, solids concentration, and particle size. This enhancement was attributed to the disruption of the laminar sublayer by the penetration of the solid particles. However, because the particles tended to settle under the influence of gravity, the limiting currents varied from place to place in the pipeline, making it difficult to interpret the
results quantitatively.

Pini and DeAnna (1977) studied the effect of 40- to 70-micron silicon carbide particles on transport at a rotating-cylinder electrode in turbulent flow. Using a reversible iodine/iodide redox couple, they obtained limiting currents in the presence of the solid particles that were as much as twice those measured without particles. Unfortunately, they reported their solids concentrations in “parts per million,” without specifying whether this was on a weight or a volume basis.

Chen and Sohn (1980) investigated heat transport in suspensions undergoing laminar shear flow. They considered the effective thermal conductivity \( k^* \) to be the sum of the true conductivity \( k \) (i.e., the conductivity of the stationary suspension) and a “microconvective conductivity” \( k_{mc} \):

\[
k^* = k + k_{mc}
\]

They derived the following relation for the microconvective term:

\[
k_{mc}/k_f = f(\phi) \text{Pe}^{1/3}
\]

where \( k_f \) is the thermal conductivity of the suspending fluid, \( f(\phi) \) is an empirical function of the volume fraction of solids, and \( \text{Pe} \) is the shear particle Peclet number. Chen and Sohn measured heat transfer through suspensions of polymer particles in oil in a Couette-flow device and confirmed that for \( \phi = 0.15 \) and 0.3, the transport augmentation depended on \( (\text{Pe})^{1/3} \).

Working in this laboratory, Roha (1981) investigated the effects of suspended glass spheres, 4 to 75 microns in diameter, on the rate of ferricyanide reduction at a rotating-disk electrode. In a 40% suspension of 8.4-micron particles, he obtained limiting currents at 2870 rpm that were nearly three times those observed in the absence of particles. The effect was especially pronounced with particles whose diameter was slightly greater than the thickness of the mass-transfer boundary layer as calculated from classical RDE theory. Transport enhancement increased with the diameter of the RDE, an effect that Roha did not explain. The functional dependence of limiting current on the electrode rotation rate was observed to change from the classical 1/2-power relation to a nearly linear one as both the solids concentration and rotation rate were increased. Roha proposed two theoretical models, both
of which assume that the motion of the particles near the electrode surface causes mixing of fresh solution with the depleted solution of the boundary layer. In the "Surface-Renewal Model", this increased mixing is attributed to the wakes left by the particles as they skim across the electrode surface. In the "Particle-Film Model", the mixing is assumed to result from particle rotations. Neither model proved entirely adequate to describe the experimental results.

Caprani and coworkers (1984) measured limiting currents for the reduction of ferricyanide at a rotating disk electrode in suspensions of Al₂O₃ (1 to 40 microns) and SiO₂ (120 microns). Their mathematical analysis indicated that the limiting current at low rotation rates should depend on \((\text{rpm})^{1/2}\), which was confirmed experimentally. However, their analysis also predicted that at high rotation rates the current should depend on \((\text{rpm})^{7/6}\), whereas the actual dependence was closer to \((\text{rpm})^{0.6}\). The discrepancy was attributed to blockage of the active electrode area by particles trapped in surface irregularities.

1.4. Biological Studies

The papers described in this section are concerned with transport in blood, a complex suspension of pliable particulates in an aqueous solution of salts and proteins. The liquid phase, called plasma, accounts for about 55% of the total volume; its density and viscosity are similar to those of pure water. Most of the remaining 45% of the blood volume consists of red blood cells (erythrocytes), which are biconcave disks, typically about 8 microns in diameter and 2 microns at their thickest. They contain hemoglobin, giving them their red color and a high affinity for oxygen and carbon dioxide. Other constituents of blood include various kinds of white blood cells (leukocytes) and platelets (thrombocytes). The latter are thin, biconvex disks, approximately 3 microns in diameter, which take part in the clotting process.

It should be noted that blood differs in important ways from the suspensions considered in the previous section. Blood cells, unless "hardened" artificially, are not rigid solids. They swell or shrink in response to changes in plasma composition, and they deform when subjected to hydrodynamic

...
forces. Blood consequently displays fairly complicated rheological behavior (Goldsmith and Skalak 1975; Chien 1979). Furthermore, red blood cells are not chemically inert, but act as carriers of oxygen and carbon dioxide. This tends to obscure relatively minor effects of diffusion and convection in the plasma, and may explain why published values of the oxygen diffusion coefficient differ by nearly an order of magnitude (Colton and Drake 1969). Nevertheless, measurements of oxygen transport in blood are useful in understanding, if only qualitatively, transport in suspensions of inert, rigid solids.

Keller (1971) hypothesized that blood oxygen transport might be enhanced by the shear-induced rotations of red blood cells. He defined an "eddy diffusion coefficient" $D_{\text{eddy}}$, similar to the eddy diffusivity encountered in turbulent transport problems:

$$D^* = D_{\text{eddy}} + D$$

where $D^*$ is the total or effective diffusion coefficient and $D$ is the molecular diffusivity of the solute. The quantity $D_{\text{eddy}}$ was assumed to depend only on the state of motion of the fluid, and not on the physical properties of the fluid or solute. For a suspension of neutrally-buoyant spheres of radius $a$, $D_{\text{eddy}} = 0.18 a^2 (du/\text{dy})$

where $du/\text{dy}$ is the bulk fluid velocity gradient, ignoring secondary flows caused by the spheres themselves. Keller measured oxygen uptake in saline solutions (meant to simulate blood plasma), with and without red blood cells, using a Couette-flow blood oxygenator. At a shear rate of 2000 sec$^{-1}$, the blood cells increased the rate of $O_2$ uptake nearly fourfold, corresponding to a $D_{\text{eddy}}$ approximately twice Keller's predicted value.

Colton, et al (1971) studied the transport of urea in blood, using a continuous-flow, flat-plate dialyzer. They found that the effective diffusivity decreased with increasing cell concentration, the results correlating well with a Fricke's relation for diffusion in a stagnant suspension of oblate spheroids, Equation (1-3). Only at the lowest solids concentration (16%) was there any evidence of transport augmentation: at a wall shear rate of 50 sec$^{-1}$, the effective diffusivity was about 24% higher than predicted by the Fricke model.
Turitto, Benis, and Leonard (1972) measured effective diffusivities for platelets in flowing blood, by recording the change in the platelet concentration as a platelet-rich solution was displaced from a tube by a platelet-poor solution. Platelet transport was enhanced by one to two orders of magnitude for the range of cell concentrations and shear rates studied \((0 \leq \phi \leq 0.5\) and \(40 \leq \gamma \leq 440 \text{ sec}^{-1}\)). These results agree with measurements made under similar conditions by other workers (Grabowski, Friedman, and Leonard 1972; Dosne, et al. 1977; Antonini, et al. 1978). It should be pointed out that platelets are much larger than the soluble components of blood, and therefore have much lower Brownian diffusion coefficients \((= 10^{-9} \text{ cm}^2/\text{sec})\). This in turn implies that the particle Peclet number will be large even at fairly modest shear rates.

Caprani and Nakache (1983) measured limiting currents for the oxidation of ferrocyanide ion at a rotating disk electrode in whole blood, in aqueous suspensions of red blood cells, and in aqueous suspensions of 5-micron alumina. They treated these suspensions as power-law fluids, obeying the relation

\[
\tau = K (\dot{\gamma})^n
\]

where \(\tau\) is the shear stress, \(\dot{\gamma}\) is the shear rate, and \(K\) and \(n\) are constants. For such a fluid, Greif and Paterson (1973) had shown that the limiting current density is given by

\[
i_L = 6.85 FC_b D^{2/3} R^{(1-n)} \left[ \frac{(1+n)}{(7+5n)} \right]^{2/3} \left[ \frac{\rho \Omega^3}{K} \right] \]

where \(C_b\) and \(D\) are the bulk concentration and diffusivity of ferrocyanide, \(R\) is the electrode radius, and \(\Omega\) is the disk rotation rate. Caprani and Nakache obtained the following results:

<table>
<thead>
<tr>
<th>Suspension</th>
<th>(K)</th>
<th>(n)</th>
<th>(D^*/D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole blood</td>
<td>4.8 cP·s^{-0.12}</td>
<td>0.88</td>
<td>1.46</td>
</tr>
<tr>
<td>Blood cells</td>
<td>7.07 cP·s^{-0.135}</td>
<td>0.865</td>
<td>1.26</td>
</tr>
<tr>
<td>Alumina</td>
<td>277 cP·s^{-0.52}</td>
<td>0.48</td>
<td>1.42</td>
</tr>
</tbody>
</table>
Wang and Keller (1985) measured limiting currents for ferricyanide reduction in suspensions of red blood cells in Couette flow. Using normal, hardened, and "ghost" (hemolyzed) cells, at volume fractions up to 0.4 and shear rates up to 3680 sec\(^{-1}\), they found that the effective diffusivity \(D^*\) obeyed the relation

\[
\left( \frac{D^*}{D} - 1 \right) \times 100\% = \alpha Pe^m
\]

where \(\kappa\) is calculated from Fricke's relation, Equation (1-3). The quantities \(\alpha\) and \(m\) were found to depend on the cell rigidity and solids volume fraction: for a 40% suspension of normal human red cells, \(\alpha = 6.1\) and \(m = 0.89\). In dilute suspensions, the hardened cells and the normal cells produced the same degree of transport enhancement. In concentrated suspensions (\(\phi > 0.1\)), the hardened cells produced limiting currents approximately double those obtained with normal cells. Wang and Keller concluded that transport enhancement in dilute suspensions primarily involves particle rotations, whereas the dominant mechanisms in concentrated suspensions are particle collisions and deformations.

Studies of heat transfer in flowing blood (Ahuja 1975; Victor and Shah 1976) have shown no cell-induced augmentation under conditions commonly encountered in vivo. This is consistent with the mass-transport work reviewed here, since the Peclet number for heat transfer may be orders of magnitude smaller than the Peclet number for transport of a solute such as oxygen.

1.5. Summary

There appear to be two distinctly different mechanisms involved in transport enhancement in suspensions. First, the particles introduce local flows that tend to increase both the dispersion of solutes and the dissipation of energy. Chen and Sohn use the term "microconvection" to describe these local flows, which may result from particle rotations, collisions, etc. Second, transport to solid surfaces is greatly influenced by the presence of a thin layer of particle-free liquid, over which the bulk suspension appears to "slip". The increased shear within this slip or skimming layer reduces the
thickness of the wall diffusion layer, thereby increasing transport to the wall.

Microconvection, as the name implies, occurs over distances that are much shorter than the scale of the bulk flow, generally on the order of the particle size. It is customary to account for microconvection by defining an effective diffusivity $D^*$, which, like the eddy diffusivity of turbulent transport problems, involves both convective and diffusive effects. Dimensional analysis suggests that the effective diffusivity depends on the shear particle Peclet number:

$$\text{Pe} = \frac{a^2 \gamma}{D}$$  \hspace{1cm} (1-7)

While there is little agreement on the exact functional form relating $D^*$ and Pe, most investigators have obtained relations in which $\text{Pe}$ is raised to a power $m$. Some proposed values of $m$ are given in the following table:

<table>
<thead>
<tr>
<th>Investigator</th>
<th>$m$</th>
<th>Pe</th>
<th>$\phi$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leal (1973)</td>
<td>$3/2$</td>
<td>low</td>
<td>high</td>
<td>theoretical only</td>
</tr>
<tr>
<td>Nir &amp; Acrivos (1976)</td>
<td>$1/11$</td>
<td>high</td>
<td>low</td>
<td>theoretical only</td>
</tr>
<tr>
<td>Chen &amp; Sohn (1980)</td>
<td>$1/3$</td>
<td>5 to 500</td>
<td>0.15, 0.30</td>
<td></td>
</tr>
<tr>
<td>Chung &amp; Leal (1982)</td>
<td>1.34 to 1.91</td>
<td>&lt;1</td>
<td>0.01 to 0.25</td>
<td></td>
</tr>
<tr>
<td>Wang &amp; Keller (1985)</td>
<td>0.89</td>
<td>4 to 100</td>
<td>0.40</td>
<td></td>
</tr>
</tbody>
</table>

Microconvection occurs throughout the bulk of the suspension, but slip layers affect transport only near solid surfaces—precisely the region of greatest interest in an electrochemical system. Of the investigators mentioned in this chapter, only Watkins, Robertson, and Acrivos (1976) explicitly considered transport enhancement by slip layers. In some cases they found that the particle-free region extended far enough from the wall that the suspended solids could not interact directly with the much thinner mass-transfer boundary layer. In the absence of microconvective effects, transport enhancement was caused entirely by an increase in the wall shear rate.

It is possible that slip effects were important in some of the other experiments, but were simply not taken into account. Neglecting slip could lead to serious errors. Mashelkar and Dutta (1982) examined the literature on transport in "structured fluids" (including suspensions) and concluded that
“even a minor violation of the no-slip condition can sometimes have a profound effect on transport rates. . . . [Consequently], serious doubts are cast on a number of flow techniques which have been proposed to evaluate the apparent transport coefficients (such as diffusivity, thermal conductivity, etc.) . . . in non-homogeneous flows of structured fluids.”
CHAPTER 2

Theory of Transport Enhancement

2.1. Governing Equations

The complete dynamical description of transport in a suspension of $N$ particles requires $6N + 6$ coupled, nonlinear partial differential equations: three convection-diffusion equations, three equations for fluid motion, $3N$ equations for particle translations, and $3N$ equations for particle rotations. Furthermore, it is necessary to specify initial and boundary conditions on all $N$ particles. When $N$ is on the order of $10^8$ per milliliter, as it may be for the typical suspension used in this work, the resulting system of equations presents a formidable computational challenge indeed.

A more practical approach is to ignore the microscopic details of the flow and treat the suspension as if it were a single-phase fluid. This eliminates the $6N$ equations governing individual particle motions, and leaves six equations with greatly simplified boundary conditions. The problem remains far from trivial, however, because the effective viscosity, density, and diffusivity (denoted $\mu^*$, $\rho^*$, and $D^*$) will in general depend on the distribution of the solids and the local flow field, as well as the physical properties of the two phases. The complexity of the problem is such that there is yet no generally accepted theory of multiphase flow. Nevertheless, it may be possible in some cases to make reasonable simplifying assumptions.

It will be assumed throughout this chapter that the suspended particles are spherical and of uniform size, that the solids are distributed uniformly (except possibly for thin wall layers), and that the resulting suspensions are Newtonian. Furthermore, only systems at steady state will be considered. Under these conditions, the transport equations become

$$\nabla \cdot (cv) = \nabla \cdot (D^* \nabla c)$$

(2-1)
\[ \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \mu^* \nabla^2 \mathbf{v} + \rho^* \mathbf{g} \]  
(2-2)

where \( \mathbf{v} \) is the suspension velocity, \( c \) is the concentration of the chemical species of interest, \( p \) is the pressure, and \( \mathbf{g} \) is the acceleration due to gravity. The suspension density \( \rho^* \) is calculated from

\[ \rho^* = \phi \rho_s + (1 - \phi) \rho_f \]  
(2-3)

where \( \rho_s \) and \( \rho_f \) are the material densities of the solid and fluid phase, respectively. Here it is assumed that \( \rho_s \) and \( \rho_f \) are constants, although not necessarily equal. (Note that if \( \rho_f \neq \rho_s \) and \( \phi \) is not constant—i.e., if the solids are distributed nonuniformly—then \( \rho^* \) will not be constant either, and the suspension cannot be treated as an incompressible fluid. This is true even if the constituent phases are themselves incompressible.)

The effective viscosity \( \mu^* \) depends most strongly on \( \phi \), but it may also depend on such factors as the shear rate and the sizes and shapes of the solid particles. Thomas's correlation (1965) is often used to estimate \( \mu^* \) in the absence of experimental data:

\[ \frac{\mu^*}{\mu} = 1 + 2.5 \phi + 10.05 \phi^2 + 0.00273 e^{16.6\phi} \]  
(2-4)

2.2. Microconvective Transport

Transport enhancement in suspensions is commonly attributed to particle rotations. It is well known that an isolated solid particle immersed in a viscous fluid will tend to rotate with an angular speed one-half the bulk shear rate \( \dot{\gamma} \). However, except in the most dilute suspensions, the particles are not isolated from each other; even at \( \phi = 5\% \), nearly a third of the particles exist as "collision doublets" at any one time (Goldsmith and Skalak 1975). As \( \phi \) increases, each particle comes into more frequent contact with its neighbors, and is consequently unable to rotate freely. Studies of erythrocyte suspensions have shown that the cells rotate erratically or not at all for \( \phi \geq 20\% \) (Goldsmith and Marlow 1979).

Nevertheless, even when the particles themselves are not free to rotate, the liquid filling the space between particles may rotate. Davis and coworkers (1976) solved the Navier-Stokes equations
for creeping flow around two equal spheres. They discovered that when the gap between the spheres is less than 1.57 times their radius, the flow separates from the spheres and forms vortex rings in the gap (Figure 2-1). Flow visualization studies by Taneda (1979) confirmed that such vortices do indeed form as predicted. If, in addition, the spheres also rotate, the vortices may become detached from the spheres (Smith 1979). The combined effects of particle rotation, flow separation, and vortex shedding make for an extremely complicated flow field.

When faced with a problem that is not amenable to an analytical solution, the engineer typically attempts to discover a correlation based on dimensionless groups. Such an approach will be taken here. Figure 2-2 shows a section of a hypothetical electrode surface exposed to the steady laminar flow of a suspension. Two boundary layers form at the electrode: a hydrodynamic boundary layer of thickness $\delta_h$, and a mass-transfer boundary layer of thickness $\delta_{mt}$. It is assumed that no slip layer is present. If there were no microconvection, the mass flux to the wall would be entirely by diffusion:

$$\text{diffusive flux} = \kappa D \Delta c / \delta_{mt}$$

where $\kappa$ is given by Prager's relation, Equation (1-4). Since $0 \leq \kappa \leq 1$, the solid particles of the suspension can only reduce the diffusive flux. But the particles also give rise to a microconvective mass flux, which increases the overall flux to the electrode:

$$\text{total flux} = D^* \Delta c / \delta_{mt}$$

It should be noted that the effective diffusivity $D^*$ is not a true diffusivity, but is in fact a mass-transfer coefficient accounting for the combined effects of diffusion and microconvection.
Figure 2-1. Confined viscous vortices before, during, and after coalescence (Davis, et al. 1976).
Figure 2-2. Boundary layers in steady laminar flow (from left to right). $c$ is the concentration of the reactant, $\delta_{mt}$ is the thickness of the mass-transfer boundary layer, and $\delta_h$ is the thickness of the hydrodynamic boundary layer. In general, $\frac{\delta_{mt}}{\delta_h} \sim Sc^{1/3}$. 
The ratio of the total flux to the diffusive flux is the Sherwood number (also called the mass-transfer Nusselt number):

\[ Sh = \frac{D^* \Delta c/\delta_{ml}}{\kappa D \Delta c/\delta_{ml}} = \frac{D^*}{\kappa D} \]

In most forced convection problems, the Sherwood number is found to depend on the Reynolds and Schmidt numbers, or on their product, the Peclet number:

\[ Pe = Re \text{ Sc} = \frac{vL}{D} \]

Here, L is a characteristic length, and v is a characteristic velocity. For transport in boundary layers, an appropriate choice for the characteristic length is the boundary-layer thickness $\delta_{ml}$. In the case of suspension transport, v is not the bulk fluid velocity but rather the product of the bulk shear rate and a linear dimension related to the size of the microconvective vortices:

\[ v = \gamma l \]

Since a vortex cannot be larger than the gap between adjacent particles, it seems reasonable to identify l as the average gap width $\varepsilon$. It can be shown that

\[ \varepsilon = 2a \left[ (\phi_{\text{max}}/\phi)^{1/3} - 1 \right] \tag{2-5} \]

where 2a is the particle diameter, and $\phi_{\text{max}}$ is the volume fraction of solids at the closest possible packing of the particles (Bagnold 1954). Thus, the characteristic vortex size is the particle diameter multiplied by a function of $\phi$. Since the Peclet number is to be multiplied by another function of $\phi$—and it is convenient that the Peclet number itself not be a function of $\phi$—the factor in square brackets in Equation (2-5) is dropped, leaving $l = 2a$. The Peclet number then takes the form

\[ Pe = \frac{2a \gamma \delta_{ml}}{D} \]

The Peclet number proposed here involves two length scales, namely, the boundary-layer thickness and the particle size. In contrast, the conventional shear particle Peclet number, Equation (1-5), is
formed with only the particle size as a characteristic length because no other reasonable length scale is apparent in the bulk suspension.

In the particular case of the rotating disk, Levich (1962) gives

$$\gamma \approx r \left( \frac{\Omega^3}{v} \right)^{1/2}$$  \hspace{1cm} (2-6)

$$\delta_{\text{mot}} = \left[ \frac{D}{v} \right]^{1/3} \delta_h = \left[ \frac{D}{v} \right]^{1/3} \left( \frac{v}{\Omega} \right)^{1/2}$$  \hspace{1cm} (2-7)

(These are expressed as approximations because numerical coefficients on the order of unity have been neglected.) Hence, the Peclet number becomes

$$\text{Pe} = \frac{2a r \Omega}{(D^2 v)^{1/3}}$$  \hspace{1cm} (2-8)

Dimensional analysis alone cannot establish the functional relationship between the variables. As outlined in the previous chapter, a number of different functions have been proposed, all of which have proven to be more or less unsatisfactory. The rotating-disk work of Roha (1981) suggests that a power function might be suitable:

$$\frac{D^*}{\kappa D} = \alpha(\phi) \text{Pe}^{m(\phi)} = \alpha(\phi) \left( \frac{2a r \Omega}{(D^2 v)^{1/3}} \right)^{m(\phi)}$$  \hspace{1cm} (2-9)

2.3. The Rotating Disk with Shear-Dependent Diffusivity

The rotating-disk electrode (RDE) is popular in electrochemical studies because it is simple to construct and to operate, and because it is one of the few systems for which exact solutions of the Navier-Stokes equations are available. The major drawback to its use with suspensions is that the shear rate—and hence the effective diffusivity—varies radially on the disk. Previous theoretical treatments of the RDE have assumed a diffusivity that is independent of radial position on the disk. It is therefore necessary to solve the transport equations assuming that the diffusivity depends on the shear rate according to Equation (2-9).
Cylindrical polar coordinates are defined as in Figure 2-3, and the following additional assumptions are made:

(1) the suspension is homogeneous, with constant $\rho^*$ and $\mu^*$;

(2) the mass-transfer boundary layer is much thinner than the hydrodynamic boundary layer;

(3) $D^*$ varies only in the radial direction;

(4) The boundary conditions are $c = 0$ at $z = 0$, and $c \to c_\infty$ as $z \to \infty$.

Assumption (1) implies that the solution to the hydrodynamic problem is the same as in the classical case, with the suspension properties $\rho^*$ and $\mu^*$ being substituted for the pure liquid properties $\rho$ and $\mu$. Assumption (2) implies that radial diffusion can be neglected, and that the velocity components in the diffusion layer can be approximated by the first terms of their infinite-series representations (Newman 1973):

\[
 v_r = 0.51023 rz \frac{\Omega^3}{v_*} \quad \text{and} \quad v_z = -0.51023 z^2 \frac{\Omega^3}{v_*}.
\]

Assumption (3) implies that $D^*$ is independent of $z$ and $\theta$. Under these conditions, Equation (2-2) can be written

\[
 0.51023 z \Omega \left( \frac{\Omega^3}{v_*} \right)^{1/2} \left[ r \frac{\partial c}{\partial r} - z \frac{\partial c}{\partial z} \right] = D^* \frac{\partial^2 c}{\partial z^2} \quad (2-10)
\]

The next step is to define a dimensionless concentration $\Theta$, and a dimensionless axial distance $\zeta$:

\[
 \Theta = \frac{c}{c_\infty} \quad \text{and} \quad \zeta = z \left[ \frac{0.51023 v_*}{3D^*} \right]^{1/3} \left[ \frac{\Omega}{v_*} \right]^{1/2}
\]

In terms of these new variables, Equation (2-10) becomes

\[
 0 = 3f_D \zeta^2 \frac{\partial \Theta}{\partial \zeta} + \frac{\partial^2 \Theta}{\partial \zeta^2}, \quad f_D = \left[ \frac{r}{3D^*} \frac{dD^*}{dr} + 1 \right] 
\]

The boundary conditions are $\Theta = 0$ at $\zeta = 0$ and $\Theta \to 1$ as $\zeta \to \infty$. 
Figure 2-3. Coordinate system applied to RDE. Origin is at center of electrode.
Because $f_D$ remains a function of $r$ rather than $\zeta$, the change of variables that converts Equation (2-10) to Equation (2-11) is called a *pseudo-similarity transformation* (Seshadri and Na 1985). Equation (2-11) can be integrated twice to obtain

$$\Theta = \frac{f_D^{1/3}}{\Gamma(4/3)} \int_0^\xi \exp(-f_D x^3) dx$$

which is plotted in Figure 2-4 for various values of $f_D$. Clearly, Equation (2-12) represents not a single solution but a family of solutions; this is typical of pseudo-similarity transformations.

What is of interest here is not the reactant concentration itself but the concentration gradient at $z = 0$. Given this gradient and the diffusivity $D^*$ at the electrode, the local current density can be calculated:

$$i_L^* = -nF D^* \frac{\partial c}{\partial z} \bigg|_{z=0} = 0.62048 n F c_m f_D^{1/3} (D^*)^{2/3} \Omega^{1/2} (\nu^*)^{-1/6}$$

This may be compared to the classical solution derived by Levich (1962):

$$i_L = 0.62048 n F c_m D^{2/3} \Omega^{1/2} \nu^{-1/6}$$

Dividing Equation (2-13) by Equation (2-14) yields

$$\frac{i_L^*}{i_L} = f_D^{1/2} \left(\frac{\nu^*}{\nu}\right)^{-1/6} \left(\frac{D^*}{D}\right)^{2/3}$$

Equation (2-15) remains completely general because no particular functional form has been assumed for the effective diffusivity. If $D^*$ depends on $\text{Pe}$ as in Equation (2-9), then

$$\frac{dD^*}{dr} = \alpha \kappa D m \text{Pe}^{m-1} \frac{\text{Pe}}{r} = D^* \frac{m}{r}$$

† If it were a true similarity transformation, neither of the original independent variables would appear explicitly in the transformed equation or boundary conditions.
Figure 2-4. Dimensionless concentration profiles, from Equation (2-12).
The diffusivity function \( f_D \) becomes

\[
f_D = \left[ \frac{r}{3D^*} \frac{dD^*}{dr} + 1 \right] = \left[ \frac{m}{3} + 1 \right]
\]

Substituting for \( D^* \) and \( f_D \) in Equation (2-15), and integrating over the disk yields

\[
\frac{I_0^*}{I_L} = \left[ \frac{\nu^*}{\nu} \right]^{-1/6} \left[ \kappa \alpha \left( \frac{\text{Pe}_R}{m/3 + 1} \right)^{2/3} \right],
\]

where \( \text{Pe}_R \) is the particle Peclet number calculated at the outer radius of the electrode:

\[
\text{Pe}_R = \left( \frac{2a R \Omega}{(D^2 \nu)^{1/3}} \right)
\]

According to Equation (2-16), the increase in the suspension limiting current depends on the particle size \( 2a \), the disk radius \( R \), and the disk rotation rate \( \Omega \), all raised to the same power \( \left( \frac{2}{3} m \right) \). In contrast, the conventional definition of the Peclet number given by Equation (1-7) implies a dependence on \( a^3 \), \( R^3 \), and \( \Omega^m \). Experimental measurements of the RDE limiting currents should establish which of the two Peclet numbers is the more suitable for describing mass transfer in suspensions. Experiments are also needed to determine the values of \( \alpha \) and \( m \) in Equation (2-16) because, as explained in the first section of this chapter, it is not practical to calculate the microconvective flow field for a large number of particles. Once determined for the rotating disk, these values should be applicable to other geometries as well.
2.4. Wall Slip Layers

It has been assumed to this point that a well-mixed suspension can be treated as a homogeneous fluid. However, as was pointed out in Chapter 1, this assumption may fail to hold at solid boundaries because of the formation of particle-depleted liquid layers. Lateral migration of particles away from confining walls was first noted by Poiseuille (1836) in his studies of blood flow. Saffman (1956, 1965) showed theoretically that a rigid sphere moving slowly in a shear field experiences a lateral force that is inertial in origin:

\[ F = 6.45 \mu \left[U_{\text{sphere}} - U_{\text{fluid}}\right] a^2\left(\frac{\gamma}{\nu}\right)^{1/2} \]

Segre and Silberberg (1961, 1962) studied laminar Poiseuille flows of dilute suspensions, and found that the particles tended to move across streamlines to take up a preferred position at \( r = 0.6R \) (where \( R \) is the tube radius). Numerous other studies have confirmed and extended these observations; Brenner (1966) gives an excellent review of the early work in this field.

The paper by Watkins, Robertson, and Acrivos (1976), already mentioned in Chapter 1, is one of the few to examine wall layers in concentrated suspensions. These authors estimated the slip-layer thickness \( \delta_s \) to be on the order of 1 to 2 particle radii. This agrees with the theoretical work of Vand (1948), who obtained \( \delta_s = 1.301a \) for plane Couette flow. If in fact the slip-layer thickness increases with increasing particle size, then sufficiently large particles may be offset from the wall so far that they cannot penetrate the diffusion layer. In that case microconvection can have little direct effect on transport to the wall, and any transport enhancement that occurs will be entirely the result of the higher velocity gradient inside the slip layer.

The influence of the slip layer on the wall shear rate can be illustrated by a simple example. Figure 2-5 shows a Couette-flow device, which produces a constant shear stress in the fluid at steady state:

\[ \tau_{xy} = \tau_{yx} = \text{constant} = \tau_w \]

where \( \tau_w \) is the wall shear stress. The resulting velocity profile depends on the fluid's rheological
Figure 2-5. Plane Couette flow of a homogeneous suspension. At steady state, the shear rate is constant across the gap; if the suspension is Newtonian, the velocity profile will be linear.
properties and the boundary conditions. For a homogeneous Newtonian suspension, assuming no slip at the wall,

\[ \tau_w = \mu^* \frac{du^*}{dy} \rightarrow u^* = \frac{\tau_w}{\mu^*} y \]

Figure 2-6 shows the same system, but with a particle-free slip layer of thickness \( \delta_x \) along the upper plate. As before, the shear stress is maintained constant at \( \tau_w \):

\[ \tau_w = \mu^* \frac{du^*}{dy} = \mu \frac{du}{dy} \rightarrow \frac{du}{dy} = \frac{\mu^*}{\mu} \frac{du^*}{dy} \]

Thus, the velocity gradient in the slip layer is \( \mu^*/\mu \) times the gradient in the bulk. To maintain the same shear stress as before, the plate speed must be increased from \( U_{old} \) to \( U_{new} \):

\[ \frac{U_{new} - U_{old}}{U_{old}} = \left( \frac{\mu^*}{\mu} - 1 \right) \frac{\delta_x}{L} \]
Figure 2-6. The effect of slip. The system is the same as in Figure 2-5, but a slip layer of thickness δ occurs at the upper plate.
2.5. The Rotating Disk with Slip

Figure 2-7 depicts laminar flow over a generalized axisymmetric electrode. The limiting current at such an electrode depends on the wall velocity gradient \( \beta \) (Newman 1973):

\[
i_L = \frac{nFDc_m}{\Gamma(4/3)} (R \beta)^{1/2} \left[ 2D \int_0^x R (R \beta)^{1/2} \, dx \right]^{-1/3}
\]  

(2-17)

Here, \( x \) is the distance along the electrode from the stagnation point, \( y \) is the perpendicular distance from the surface, and \( R(x) \) is the distance from the axis of symmetry to the electrode surface. In the case of the rotating disk, \( x = r = R, y = z \), and \( \beta \) is the gradient of the radial velocity at the disk:

\[
\beta = \frac{\partial v_r}{\partial y} \bigg|_{y=0} = \frac{\partial v_r}{\partial z} \bigg|_{z=0}
\]

Assuming that the effect of the slip layer is to increase \( \beta \) by a constant factor \( \zeta \), Equation (2-17) becomes

\[
i_{L*} = \frac{nFDc_m}{\Gamma(4/3)} (R \zeta \beta)^{1/2} \left[ 2D \int_0^x R (R \zeta \beta)^{1/2} \, dx \right]^{-1/3}
\]  

(2-18)

Bringing \( \zeta \) out of the integral and dividing by Equation (2-17) yields

\[
\frac{i_{L*}}{i_L} = \zeta^{1/3}
\]  

(2-19)

If the slip-layer thickness \( \delta_s \) were accurately known, \( \zeta \) could be obtained by solving the equations of motion for the suspension. Even when \( \delta_s \) remains unknown, as in the present case, it may be possible to estimate \( \zeta \) from measurements of the viscous drag on the rotating disk. According to Schlichting (1979), the torque on a rotating disk is given by

\[
T = -2\pi \int_0^R r^2 (\tau_{sr}) \, dr = 2\pi \int_0^R r^2 \mu \frac{\partial \nu_r}{\partial z} \, dr
\]
Figure 2-7. Axisymmetric electrode, showing boundary-layer coordinates $x$ and $y$. Flow is from left to right.
If the slip layer increases \( (\partial v_\theta / \partial z) \) by the factor \( \zeta \), as before, then

\[
\frac{T^*}{T} = \frac{2\pi}{2\pi} \left[ \int_0^R r^2 \mu \left( \frac{\partial v_\theta}{\partial z} \right) dr \right] = \zeta
\]

and Equation (2-19) becomes

\[
\frac{i_{L^*}}{i_L} = \left( \frac{T^*}{T} \right)^{1/3}
\]  

(2-20)

It should be emphasized that this equation depends on the assumptions that both the \( r \)- and \( \theta \)-velocity gradients are increased by the same factor \( \zeta \), and that this factor is independent of the radial position on the disk. Experimental measurements of the limiting current and torque will readily show whether these assumptions hold in real suspensions.

2.6. Summary

The effects of microconvection and slip on transport to a rotating disk have been considered in this chapter. Perhaps the most serious weakness in the analysis is the tacit assumption that the two mechanisms can be treated separately—i.e., that microconvection is important for small particles, while slip is important for large particles. This follows from the observation that slip layers generally tend to be about 1 or 2 particle radii in thickness, placing the large particles too far outside the wall diffusion layer to have any direct interaction with it. But there are three reasons why this inference must be viewed with some caution.

First, no one has measured the thicknesses of slip layers on rotating, axisymmetric bodies in concentrated suspensions at high shear rates. Most of experiments have involved dilute suspensions of relatively large particles flowing through tubes at low shear rates.

Second, while the slip layer has been described as being “particle-free”, this is almost certainly an oversimplification. Given the chaotic conditions in a concentrated suspension, it is to be expected
that solid particles will at least occasionally be forced into the slip layer. Therefore, microconvection involving large particles cannot be ruled out entirely.

Finally, there is no reason to believe that slip effects are ever completely absent, even when the dominant transport mechanism is microconvection. Small particles probably come closer to solid surfaces than large particles—close enough to penetrate the diffusion layer—but a slip layer is formed in any case.
CHAPTER 3

Experimental Apparatus and Procedures

3.1. Solid Particles

Most of the experiments in this study were carried out using soda-lime glass beads, having a
density of 2.48 gm/cm³, which had previously been obtained by Roha (1981) from the manufacturer.†
Scanning-electron micrographs (Figures 3-1 through 3-6) show that most of the particles were spheri­
cal, or nearly so, although each sample included a number of elongated, fractured, or otherwise irregu­
lar shapes. As described in Appendix 2, particle sizes were determined from measurements of the
micrographs, and a volume-weighted average diameter \( \bar{2a} \), standard deviation SD, and mean deviation
MD were calculated for each sample:

<table>
<thead>
<tr>
<th>( \bar{2a} ) (microns)</th>
<th>SD</th>
<th>MD</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.55</td>
<td>0.67</td>
<td>0.95</td>
<td>3-1</td>
</tr>
<tr>
<td>5.14</td>
<td>1.41</td>
<td>1.52</td>
<td>3-2</td>
</tr>
<tr>
<td>7.09</td>
<td>2.73</td>
<td>2.50</td>
<td>3-3</td>
</tr>
<tr>
<td>9.05</td>
<td>1.82</td>
<td>1.39</td>
<td>3-4</td>
</tr>
<tr>
<td>37.4</td>
<td>3.99</td>
<td>3.91</td>
<td>3-5</td>
</tr>
<tr>
<td>57.3</td>
<td>6.88</td>
<td>6.52</td>
<td>3-6</td>
</tr>
</tbody>
</table>

The glass beads are referred to as "large" or "small" depending on their size relative to the
thickness of the mass-transfer boundary layer. According to the estimates presented in Appendix 4, \( \Delta = 4.5 \times 10^{-6} \) cm²/s, and \( \nu = 0.014 \) cm²/s; Equation (2-7) then gives \( \delta_{mt} = 9 \) microns at 2000 rpm.
Therefore, the two largest fractions (37.4 and 57.3 microns) fall into the "large" category, while the
other beads are considered "small".

† A complete list of suppliers is given in Appendix 1.
Figure 3-1. Scanning-electron micrograph (1270x) of "small" glass beads. Volume-weighted average diameter: 2.55 microns.
Figure 3-2. "Small" glass beads (1270×). Volume-weighted average diameter: 5.14 microns.
Figure 3-3. "Small" glass beads (1270×). Volume-weighted average diameter: 7.09 microns.
Figure 3-4. "Small" glass beads (1270×). Volume-weighted average diameter: 9.05 microns.
Figure 3-5. "Large" glass beads (255×). Volume-weighted average diameter: 37.4 microns.
Figure 3-6. "Large" glass beads (115x). Volume-weighted average diameter: 57.3 microns.
Glass particles, being relatively dense, tend to settle out of suspension. One way to avoid this is to use neutrally-buoyant solids. Polymethylmethacrylate (PMMA) was chosen for this purpose because it is fairly resistant to chemical attack, and because its density (1.18 gm/cm$^3$) is close to that of the electrolyte solutions (1.13 gm/cm$^3$). PMMA particles were made by pulverizing Plexiglass shavings in a planetary ball mill. As shown in Figures 3-7 and 3-8, the resulting particles were very irregular in shape, making it impractical to determine a meaningful average diameter from the SEM photographs. Instead, the particles were classified using standard Tyler sieves to obtain a rough estimate of the particle-size distributions. The “coarse” PMMA particles were all found to be in the range 88-105 microns (+170-150 mesh). The “fine” PMMA sample contained a much broader range of particle sizes:

<table>
<thead>
<tr>
<th>Sieve Size</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>+150</td>
<td>&gt;105</td>
</tr>
<tr>
<td>+170-150</td>
<td>88-105</td>
</tr>
<tr>
<td>+200-170</td>
<td>74-88</td>
</tr>
<tr>
<td>+270-200</td>
<td>52-74</td>
</tr>
<tr>
<td>+325-270</td>
<td>44-52</td>
</tr>
<tr>
<td>-325</td>
<td>&lt;44</td>
</tr>
</tbody>
</table>

The nonuniformity of the PMMA particles makes any quantitative comparison with the glass beads highly problematical. It is not clear how best to define an average Peclet number for the fine PMMA sample, and the formation of wall slip layers has not been studied for irregularly-shaped particles. Nevertheless, the PMMA particles were included to verify that transport enhancement is not somehow just a consequence of particle sedimentation.
Figure 3-7. "Fine" PMMA particles (635x).
Figure 3-8. “Coarse” PMMA particles (90x).
3.2. Electrode Design and Construction

Two types of disk electrodes were made for use in these experiments. The first type is shown in cross-section in Figure 3-9. Three such electrodes were made, having active areas of 1, 2, and 5 cm$^2$. Each comprised a short piece of nickel rod attached with conductive silver epoxy to a brass shaft; the upper part of the shaft was tapered to fit inside a Pine Model ASR-2 rotator, where it could be secured by a threaded rod. The rest of the electrode assembly was encased in insulating epoxy, leaving exposed only the nickel electrode face. (The preparation of the epoxy is described in Appendix 3.) Unfortunately, these cylindrical electrodes caused severe vortexing which limited their use to rotation speeds less than about 2000 rpm.

The second type of electrode, shown in Figure 3-10, was based on a design by Selman (1971). The nickel electrode piece was attached to the brass core by a threaded joint, which was secured by spreading silver epoxy in the threads before assembly. Epoxy was cast around the metal, and machined to shape. Two such electrodes were made (A = 0.5156 cm$^2$ and 1.267 cm$^2$); one of Selman’s original electrodes (0.123 cm$^2$) was also used in the experiments. These electrodes could be used at rotation speeds up to 5000 rpm.
Figure 3-9. First RDE design. (Shown approx. 90% of full size; dimensions in centimeters.) Electrodes made to this pattern suffered from vortexing at speeds greater than 2000 rpm.
Figure 3-10. Second RDE design, patterned on an original by Selman. (Shown full size; dimensions in centimeters.) Electrode of this type were usable to 5000 rpm.
3.3. Electrochemical Cell and Circuit

Limiting-current measurements were carried out in the jacketed Pyrex cell depicted in Figure 3-11. The cell was equipped with four Teflon baffles, which fit into slots in the acrylic cell lid. The cell lid was also drilled to accept a glass thermocouple well and a nitrogen gas inlet. A 4-cm by 6-cm piece of nickel foil was placed against the cell wall to serve as a counter electrode. The cell temperature was maintained by circulating water from a constant-temperature bath (not shown) through the jacket of the cell. A thermocouple probe connected to a digital meter displayed the cell temperature to within ±0.1°C.

Figure 3-12 shows the modifications made to the Pine RDE rotator to accommodate a "Bexometer", a device for measuring running torque.† A rigid bracket was constructed of brass, consisting of a horizontal circular plate attached to two vertical arms that were spaced to fit around the body of the rotator. The lower face of the horizontal plate was covered by an acrylic disk, milled so as to mate with the cell lid; this served both to center the cell and to protect the brass from the caustic electrolyte. Figure 3-13 is a photograph of the assembled cell and rotator.

The electrical circuit is diagrammed in Figure 3-14. Current was supplied to the cell by a PARC (Princeton Applied Research) Model 173 potentiostat. A PARC Model 175 universal programmer was used to ramp the applied potential, and the resulting current was read off the potentiostat’s built-in digital meter. Currents and voltages were also plotted on an X-Y recorder. Figure 3-15 is a photograph of the entire RDE system and the associated electronic equipment.

† The upper and lower sections of the Bex-meter are joined internally by a pair of precision springs. Torque displaces the two sections relative to each other; the degree of displacement is indicated by a scale which is read with the aid of a strobe lamp. The particular Bex-meter used in this work was calibrated in ounce-inches (1 oz-in = 7.96 mN-m). It had a maximum capacity of 5 oz-in (35.3 mN-m), and a sensitivity of ±0.01 oz-in (±0.071 mN-m).
Figure 3-11. Jacketed Pyrex cell and acrylic cell lid, showing position of disk electrode (approx. 70% of full size). Not shown are the cooling-water connections, thermocouple, or nitrogen gas inlet. The distance from the face of the electrode to the cell bottom is 1.2 cm.
Figure 3-12. Modified Pine rotator with Bex-ometer for measuring torque on the RDE shaft. (Shown approx. 70% of full size; dimensions in centimeters.)
Figure 3-13. Electrochemical cell, RDE rotator, and Bex-ometer. The hose shown leaving the top of the photograph supplies nitrogen to the cell; the other two hoses circulate water from the constant-temperature bath.
Figure 3-14. Schematic of electrical circuit. ("R", "C", and "W" on the potentiostat refer to the reference electrode, counter electrode, and working electrode.) For most measurements, a low-pass signal filter was placed in the line leading to the XY-recorder to reduce noise.
Figure 3-15. Experimental apparatus. (A) Programmer; (B) Potentiostat; (C) X-Y recorder; (D) Rotor and cell; (E) Digital thermometer; (F) Low-pass signal filter; (G) Rotator speed control; (X) Equipment not used in these experiments.
3.4. Limiting-Current Measurements

Limiting currents were measured for the reduction of ferricyanide to ferrocyanide:

$$\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-}$$

This was carried out in solutions that were typically 2.0 N in sodium hydroxide, 0.2 N in potassium ferrocyanide, and 0.04 N in potassium ferricyanide. (Details of the preparation, storage, and analysis of these solutions are presented in Appendix 4.) The procedure for making limiting-current measurements was as follows:

1. Make up alkaline ferro/ferricyanide solution. Pipette required amount of solution into cell. Open valves on N\(_2\) line and begin circulation of water from constant-temperature bath.
2. Polish RDE on 0000-grit (8-micron) emery paper using kerosene as a lubricant. Clean thoroughly with acetone, methanol, and distilled water.
3. Rotate RDE in auxiliary cell filled with 2 N NaOH solution and evolve hydrogen for 5 minutes.
4. Transfer RDE to main cell. When temperature has stabilized, ramp potential of RDE (e.g., 0 to -1.1 V at 20 mV/sec) and measure limiting current. Repeat at various rotation rates.
5. Weigh out solids and transfer to main cell. Mix well with RDE at 2000 rpm or higher.
6. Make limiting-current measurements as before (Step 4).

A digital strobe lamp was used to set disk rotation rates and to read the Bex-ometer scale in Steps 4 and 6.

3.5. Electrode Placement

The double-walled design of the cell made it impractical to use a conventional magnetic stirrer because the stirring bar was raised too far from the driver to permit effective magnetic coupling. It was therefore decided to use the disk itself to stir the suspensions. For this to be effective, the disk had to be moved closer to the bottom of the cell, and the amount of fluid had to be reduced.
Although RDE theory presupposes that the disk is to be placed in a semi-infinite expanse of fluid, experience has shown that the location of the disk in the cell and the total fluid volume are relatively unimportant (Pleskov and Filinovskii, 1976; Bruckenstein, 1984; Newman, 1984). To test this, limiting-current measurements were made (without suspended solids) with the RDE positioned at various distances from the cell bottom. Even when the disk was placed as close as 0.5 mm to the bottom, the measured limiting currents agreed closely with the theory. A disk-to-bottom distance of 1.2 cm was chosen for all subsequent work.
CHAPTER 4

Experimental Results

4.1. Introduction

This chapter presents the results of the experiments described in Chapter 3. Disk-torque measurements are discussed in Section 4.2. Limiting-current work with small and large glass beads is summarized in Sections 4.3 and 4.4; work with PMMA particles is summarized in Section 4.5.

The limiting currents obtained without solid particles invariably agreed closely with classical RDE theory. The current-voltage curves were smooth, with long, flat plateaux that made determination of the limiting current very simple (Figure 4-1). In contrast, the current-voltage curves obtained using the suspensions exhibited rapid, random fluctuations about the average limiting current which became more pronounced as the disk rotation rate was increased (Figure 4-2). Unfortunately, the X-Y recorder was not sufficiently responsive to allow quantitative measurements of the amplitude or frequency of these fluctuations. No comparable fluctuations were observed in the torque measurements, possibly because the Bex-ometer was too insensitive to register them.

The average limiting current itself also appeared to vary randomly over time. Repeated measurements, made minutes apart under identical conditions, would sometimes differ by ±5% or more. These variations were not artifacts of the instrumentation, since they did not occur when limiting currents were measured in the absence of the suspended solids.

Despite the placement of the RDE near the cell bottom, mixing of the suspension remained a problem in some cases. When working with the larger glass beads, a settled bed of solids would often remain on the bottom of the cell at disk rotation rates of 1000 rpm or more. The PMMA particles tended to clump together when first introduced into the electrolyte, and considerable agitation was required to disperse them completely.
Figure 4-1. Current-voltage curves made in the absence of suspended solids.
Figure 4-2. Current-voltage curves obtained with 20% fine PMMA particles, showing rapid current fluctuations.
4.2. Disk-Torque Measurements

As expected, suspended solids were found to increase the drag on the rotating disk. For example, Figure 4-3 is a log-log plot of the torque $T^*$ versus the rotation rate for 5.14-micron glass beads. Increasing the solids volume fraction $\phi$ has the effect of raising the $T^*$-rpm line without changing its slope. This is consistent with a simple increase in the effective viscosity $\mu^*$. According to Schlichting (1979), the torque on a rotating disk is given by

\[
T^* = \frac{3.87}{2} \left( \frac{v^*}{R^2 \Omega} \right)^{1/2} \rho^* \Omega^2 R^5 = \frac{3.87}{2} (\mu^* \rho^*)^{1/2} R^4 \Omega^{3/2}
\]  

(4-1)

This equation does not take into account the drag on the shaft attached to the disk. However, the small diameter of the shaft makes for a very short moment arm, and the net effect on the torque is small. Dividing by the corresponding equation for $\phi = 0$ yields

\[
\frac{T^*}{T} = \left( \frac{\mu^* \rho^*}{\mu \rho} \right)^{1/2} \quad \rightarrow \quad \frac{\mu^*}{\mu} = \left( \frac{\rho^*}{\rho} \right)^{-1} \left( \frac{T^*}{T} \right)^{2}
\]  

(4-2)

The reduced viscosity $\mu^* / \mu$ is plotted against $\phi$ in Figure 4-4. Considerable scatter is evident in the data; this is not unusual in suspension rheology work. In general, the measured effective viscosities were higher than predicted by the Thomas's relation. The following relation, obtained by a polynomial least-squares curve fit to the 5.14-micron data, will be used to represent all of the data:

\[
\frac{\mu^*}{\mu} = 1 + 5.4132 \phi - 24.6141 \phi^2 + 169.825 \phi^3
\]  

(4-3)
Figure 4-3. Bex-ometer readings for suspensions of 5.14-micron glass beads.
Figure 4-4. Reduced viscosity $\mu/\mu_0$ as a function of the solids volume fraction $\phi$. The solid curve is calculated from the Thomas correlation, Equation (2-4); the dashed curve is a third-order polynomial [Equation (4-3)] fitted to the 5.14-micron data.
4.3. Limiting Currents—Small Glass Beads

The experiments described in this section involved glass beads whose diameters \((2\bar{a} = 2.55, 5.14, 7.09,\) and 9.05 microns), were less than the thickness of the mass-transfer boundary layer. As discussed in Sections 2.2 and 2.3, the following equation is presumed to hold for these particles:

\[
\frac{D^*}{\alpha D} = \alpha \text{Pe}^m = \alpha \left[ \frac{(2\alpha) R \Omega}{(D^2 \nu)^{1/3}} \right]^m
\]

where \(\alpha\) and \(m\) are to be found experimentally. According to this equation, the RDE limiting-current ratio \(i_i^* / i_L\) should be proportional to \([(2\alpha)R\Omega]^{2m/3}\). Therefore, a log-log plot of limiting current versus rotation rate should produce a straight line of slope \(\frac{2}{3}m + \frac{1}{2}\), from which \(\alpha\) and \(m\) can determined.

Figures 4-5, 4-6, and 4-7 are log-log plots of limiting current versus rotation rate, obtained using various glass beads and rotating disks. As expected, the data produce straight lines on these plots. At low rotation rates, the solids reduce the limiting current because microconvection cannot offset the obstruction of the diffusion path by the inert solids. As the rotation rate is increased, transport by microconvection becomes more important. Eventually, the suspension limiting-current line crosses over the particle-free \((\phi = 0)\) line; further increases in rotation rate result in a positive enhancement of transport rates. A comparison of Figures 4-5 through 4-7 also shows that transport enhancement increases with disk radius and particle diameter, in accordance with Equation (4-4).

Approximately 900 limiting-current measurements were obtained using the small glass beads. Six different RDEs were used, the smallest having an active area of 0.123 cm\(^2\), the largest, 5.00 cm\(^2\). Thirty-seven experimental runs were made, each run comprising ten or more limiting-current measurements over a range of rotation rates (typically, 200 to 5000 rpm). The data from each run were fitted to a relation of the form†

† All calculations were done on a Macintosh Plus personal computer using "Statworks", a general statistics program from Cricket Software.
where \( \Omega \) is the disk rotation rate in sec\(^{-1}\). The regression coefficient \( b_1 \) provides an estimate of the exponent \( m \):

\[
m = \frac{3}{2} b_1
\]

Substituting this into Equation (2-15) and rearranging yields the Sherwood number \((D^*/\kappa D)\):

\[
\frac{D^*}{\kappa D} = \frac{1}{\kappa} \left( \frac{i_i^*}{i_L} \right)^{3/2} \left( \frac{v^*}{v} \right)^{1/4} (b_1/2 + 1)^{-1/2}
\]

For each limiting-current measurement, the Sherwood number was calculated and plotted against the Peclet number; these plots are shown in Figures 4-8 through 4-13. Each figure includes the line obtained by fitting the data to the relation

\[
\log(D^*/\kappa D) = \log \alpha + m \log Pe
\]

The values of \( \alpha \) and \( m \) are presented in Table 4-1, which also gives the standard deviations in \( \alpha \) and \( m \).

Figures 4-14 and 4-15 are plots of \( \alpha \) and \( m \) as functions of the volume fraction of solids. Included in these figures are error bars indicating the 95\% confidence intervals \((\alpha \pm 2 \times SD \text{ or } m \pm 2 \times SD)\).
Figure 4-5. Limiting current densities measured with the smallest glass particles (2.55 microns) and the smallest RDE ($R = 0.198$ cm). Below 2500 rpm, the solids reduce the limiting current.
Figure 4-6. Limiting current densities. Measured with same RDE as in Figure 4-5, but with larger glass beads (9.05 microns). Positive transport enhancement occurs above 900 rpm.
Figure 4-7. Limiting current densities. The same 9.05-micron beads were used as in Figure 4-6, but the RDE was larger (R = 0.6351 cm). Transport was enhanced at all measured rotation rates.
Figure 4-8. Sherwood number (D*/kD) as a function of the Peclet number for 40% suspensions of small glass beads. A total of N = 332 points are shown. The line represents a least-squares fit to the data.
Figure 4-9. Sherwood number ($D^*/kD$) as a function of the Peclet number for 30% suspensions of small glass beads. $N = 114$ points. The line represents a least-squares fit to the data.
Figure 4-10. Sherwood number ($D^*/xD$) as a function of the Peclet number for 20% suspensions of small glass beads. N = 189 points. The line represents a least-squares fit to the data.
Figure 4-11. Sherwood number (D*/κD) as a function of the Peclet number for 15% suspensions of small glass beads. N = 57 points. The line represents a least-squares fit to the data.
Figure 4-12. Sherwood number (D*/κD) as a function of the Peclet number for 10% suspensions of small glass beads. N = 101 points. The line represents a least-squares fit to the data.
Figure 4-13. Sherwood number ($D^*/kD$) as a function of the Peclet number for 5% suspensions of small glass beads. $N = 104$ points. The line represents a least-squares fit to the data.
<table>
<thead>
<tr>
<th>φ</th>
<th>Pc</th>
<th>N</th>
<th>α</th>
<th>(SD)</th>
<th>m</th>
<th>(SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>16-5540</td>
<td>332</td>
<td>0.0869</td>
<td>(0.0033)</td>
<td>0.6361</td>
<td>(0.0058)</td>
</tr>
<tr>
<td>0.30</td>
<td>67-2620</td>
<td>114</td>
<td>0.1921</td>
<td>(0.0146)</td>
<td>0.4645</td>
<td>(0.0113)</td>
</tr>
<tr>
<td>0.20</td>
<td>16-2620</td>
<td>189</td>
<td>0.3121</td>
<td>(0.0087)</td>
<td>0.3347</td>
<td>(0.0046)</td>
</tr>
<tr>
<td>0.15</td>
<td>40-2460</td>
<td>57</td>
<td>0.3640</td>
<td>(0.0120)</td>
<td>0.2694</td>
<td>(0.0051)</td>
</tr>
<tr>
<td>0.10</td>
<td>33-3460</td>
<td>101</td>
<td>0.6898</td>
<td>(0.0266)</td>
<td>0.1321</td>
<td>(0.0057)</td>
</tr>
<tr>
<td>0.05</td>
<td>16-3110</td>
<td>104</td>
<td>0.7857</td>
<td>(0.0311)</td>
<td>0.0670</td>
<td>(0.0064)</td>
</tr>
</tbody>
</table>

Table 4-1. Summary of log(D*/KD)-log(Pc) data for small glass beads. α and m are defined in Equation (4-4). The quantities in parentheses are the standard deviations (SD) in α and m.
Figure 4-14. Coefficient $\alpha$ as a function of solids volume fraction $\phi$. Error bars indicate 95% confidence intervals ($\pm 2 \times SD$).
Figure 4-15. Exponent m as a function of solids volume fraction $\phi$. Error bars indicate 95% confidence intervals ($\pm 2 \times SD$).
4.4. Limiting Currents—Large Glass Beads

The experiments summarized in this section involved glass beads larger than the thickness of the mass-transfer boundary layer \( (2\alpha = 37.4 \text{ and } 57.3 \text{ microns}) \). Transport enhancement with these beads is expected to depend on the formation of a particle-depleted slip layer at the electrode surface. According to the analysis presented in Chapter 2, the increase in RDE limiting current is related to the increase in the torque on the disk:

\[
\frac{i^*_L}{i_L} = \left( \frac{T^*}{T} \right)^{1/3}
\]  

(4.5)

The torque data discussed in Section 4.2 produce straight, parallel lines when plotted against the rotation rate on log-log paper; if Equation (4.5) holds, a log-log plot of limiting current versus rotation rate should also consist of straight, parallel lines (of slope 1/2). Figure 4-16 shows that this is indeed the case, if the low-rpm (<1500 rpm) data are omitted.

However, Figures 4-17 and 4-18 show that Equation (4.5) underestimates the limiting currents, while failing to account for the dependence of current density on disk size. It is interesting to note that although higher current densities were obtained with the 0.5156-cm\(^2\) than with the 0.123-cm\(^2\) RDE, there was no significant difference between the 0.5156-cm\(^2\) and the 1.267-cm\(^2\) electrodes. This contrasts with the results obtained with the small glass beads, for which a larger disk invariably produced higher current densities (all other things being equal).
Figure 4-16. Limiting current densities obtained with 57.3-micron glass beads, showing the effect of particle sedimentation. Below 900 rpm, most of the solids were on the bottom of the cell.
Figure 4-17. Reduced current density $i_L^*/i_L$ as a function of the solids concentration, for 37.4-micron glass beads.
Figure 4-18. As in Figure 4-17, but for 57.3-micron beads.
4.5. Limiting Currents—PMMA Particles

As explained in Section 3.1, polymethylmethacrylate (PMMA) particles were included in this study primarily to verify that transport enhancement is not caused by the relatively high density of the glass beads. In other words, the PMMA experiments were meant only to provide a semiquantitative check on the work of the previous sections.

A total of 205 limiting-current measurements were made using fine PMMA particles. Figure 4-19 shows some typical PMMA results, which closely resemble those obtained with small glass beads. These data were fitted to the relation

\[
\log \left( \frac{i^*}{i_L} \right) = \log b_0 + b_1 \log \Omega
\]

As was mentioned in Section 4.3, the regression coefficient \( b_1 \) provides an estimate of \( m \), the exponent on the Peclet number in Equation (4-4). The values estimated from the PMMA work agree quite well with those obtained with the small glass beads:

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( m ) (PMMA)</th>
<th>( m ) (glass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.6503</td>
<td>0.6361</td>
</tr>
<tr>
<td>0.30</td>
<td>0.4442</td>
<td>0.4645</td>
</tr>
<tr>
<td>0.20</td>
<td>0.2837</td>
<td>0.3347</td>
</tr>
<tr>
<td>0.10</td>
<td>0.0960</td>
<td>0.1321</td>
</tr>
</tbody>
</table>

Figures 4-20 and 4-21 present the limiting-current data obtained using coarse PMMA particles and two different disk electrodes. The PMMA particles had a slightly greater specific gravity than the suspending liquid (1.19 versus 1.13), so some particle sedimentation occurred at low rotation rates. Nevertheless, the PMMA particles remained well suspended at rotation rates as low as 800 rpm, whereas the glass particles began to settle out of suspension at about 1500 rpm. Otherwise, there was little difference between the behavior of the two types of particles. In both cases, the suspended solids raised the limiting-current lines without greatly changing their slopes.
Figure 4-19. Limiting current densities in fine PMMA suspensions. (R = 0.198 cm.) The dashed line represents a logarithmic least-squares fit to the 40% data.
Figure 4-20. Limiting-current densities in suspensions of coarse PMMA particles. (R = 0.198 cm.) Sedimentation occurs below 800 rpm.
Figure 4-21. As in Figure 4-20, but for larger RDE (R = 0.635 cm.)
CHAPTER 5

Discussion and Conclusions

5.1. General Conclusions

According to the theoretical analysis presented in Chapter 2, suspended solids may enhance mass transfer to a surface in two very different ways, depending on whether the particles are smaller or larger than the thickness of the mass-transfer boundary layer. Small particles \((2a \leq \delta_{ml})\) penetrate the boundary layer, causing microconvective secondary flows. Large particles \((2a > \delta_{ml})\) tend to migrate away from the surface, creating a particle-free slip layer that increases the wall shear rate.

The experiments discussed in the foregoing chapter demonstrate that transport enhancement in suspensions does indeed occur by at least two different mechanisms. Transport by particles the same size as, or smaller than, the thickness of the mass-transfer boundary layer can be described in terms of an effective diffusivity \(D^*\), which depends on the particle diameter \(2a\), the shear rate \(\gamma\), and the boundary-layer thickness \(\delta_{ml}\):

\[
\frac{D^*}{\kappa D} = \alpha \left( \frac{(2a) \gamma \delta_{ml}}{D} \right)^m, \quad (2a) \leq \delta_{ml}
\]  

(5-1)

The experimentally-determined values of \(\alpha\) and \(m\) are given in Table 1 of Chapter 4 (p.71); \(\kappa\) can be estimated from Equations (1-3) or (1-4). It should be noted that since \(\kappa \leq 1\), the solids may decrease the effective diffusivity when the particles are small or the shear rate is low.

As expected, particles significantly larger than than the mass-transfer boundary layer behave differently. Such particles increase the RDE limiting current without altering its dependence on the square root of the disk rotation rate. This is consistent with Equation (2-20), which relates the increase in limiting current to the increase in the torque needed to turn the disk:
\[
\frac{i^*}{i_L} = \left( \frac{T^*}{T} \right)^{1/3}
\] (2-20)

However, this equation not only tends to underestimate the limiting current, it also fails to account for the observed increase in limiting current with disk radius.

The latter point deserves some comment. If the larger beads enhanced mass transfer by microconvection, a shear-dependent process, the limiting current would increase with the electrode size. Although the current density did increase when the 0.5156-cm\(^2\) RDE was substituted for the 0.123 cm\(^2\) RDE, no further increase was observed with the 1.267-cm\(^2\) electrode. This rather peculiar dependence on disk size may reflect the development of the slip layer near the center of the disk. The lateral forces that cause the large particles to migrate away from the disk depend on the local shear rate. Because the shear rate vanishes at the center of the disk, suspended particles experience no lateral forces in this region. Moving outward from the center, the shear rate increases, and the particles begin to be forced away from the disk surface. Eventually, a slip layer of more or less constant thickness is formed; but on a small electrode, the slip layer might not develop fully before the edge of the active area is reached.

5.2. Comparisons with Other Work

Of the published studies reviewed in Chapter 1, only Roha's (1981) work in this laboratory employed glass beads with the rotating-disk electrode. Typical data from Roha's thesis are plotted in Figures 5-1 and 5-4, along with the lines calculated from the present study. In most cases, the agreement is excellent. This would seem to indicate that Roha's experimental apparatus was better suited for suspending the glass beads than was previously thought. The discrepancies observed at high solids concentrations and high rotation rates can be attributed to viscous heating: Roha had no way to control or even to measure the temperature inside his cell.

Caprani and Nakache (1983) also used rotating disks in their experiments, but because their suspensions behaved as non-Newtonian fluids, their work has little relevance to the present study.
Figure 5-1. Comparison of Roha’s data with Equation (5-1), for 4.0-micron glass beads.
Figure 5-2. Comparison of Roha's data with Equation (5-1), for 8.4-micron glass beads.
Caprani, et al. (1984) used an RDE to study mass transfer in Newtonian suspensions of alumina and silica powders. Unfortunately, it is difficult to compare their results with the models proposed in this thesis because their paper does not include their original data. The solid particles were probably large relative to the mass-transfer boundary layer (e.g., the silica particles were 120 microns in diameter), and the limiting current varied with (rpm)\(^{1/2}\) or (rpm)\(^{0.6}\). This is consistent with the slip-layer transport model discussed in Chapter 2.

A number of workers have used Couette-flow devices to study heat and mass transfer in suspensions (Keller 1971, Chen and Sohn 1980, Chung and Leal 1982, Wang and Keller 1985). There is no true boundary layer in slow, laminar Couette flow; the concentration or temperature gradient is constant across the annular gap. Accordingly, the old definition of the particle Peclet number does not involve the boundary-layer thickness as a characteristic length:

\[
P_{\text{e,old}} = \frac{a^2 \gamma}{D} \quad (1-7)
\]

When applied to a rotating disk, this becomes

\[
P_{\text{e,old}} = \frac{a^2 R}{D} \left( \frac{\Omega^3}{\nu} \right)^{1/2} \quad \text{(rotating disk)}
\]

Thus, the conventional Peclet number is proportional to \(a^2, R^1, \) and \(\Omega^{3/2}\). But the experimental data of Chapter 4 clearly support the alternative definition of the Peclet number, in which the disk radius, particle radius, and rotation rate are raised to the same power:

\[
P_{\text{e,new}} = \frac{(2a) \gamma \delta_{\text{m}}}{D} = \frac{2a R \Omega}{(D^2 \nu)^{1/3}} \quad \text{(rotating disk)}
\]

The two definitions differ by a factor \((\delta_{\text{m}})/a\):

\[
P_{\text{e,new}} = \frac{\delta_{\text{m}}}{a} P_{\text{e,old}}
\]

In slow Couette-flow problems, it is customary to take as the boundary-layer thickness half the annular gap width, making \(\delta_{\text{m}}\) a constant for a given instrument. Both Peclet numbers are then dependent on
the first power of the shear rate, and should give essentially equivalent results. In particular, transport enhancement might be expected to depend on \( \text{Pe}^m \cdot \phi \), where \( 0.07 \leq m \leq 0.64 \) for \( 0.05 \leq \phi \leq 0.40 \) (cf. Table 4-1).

The published Couette-flow studies generally do not support these conclusions. Wang and Keller (1985), for example, discovered that the effective diffusivity varied with \( \text{Pe}^{0.89} \) at \( \phi = 0.40 \). Chung and Leal (1982) found \( 1.21 \leq m \leq 1.91 \) for \( \phi \leq 0.25 \). Chen and Sohn (1981) estimated the exponent to be nearly 1/3, which is closer to the results of this thesis; however, they also found \( m \) to be independent of \( \phi \). Obviously, more work is needed to resolve these differences.

5.3. Power Requirements

Suspended solids may be used to increase mass-transfer rates, but only at the cost of increased viscous dissipation. The power needed to drive a rotating disk equals the product of the torque and the rotation rate. Therefore, at a given rotation rate \( \Omega \),

\[
\frac{P^*}{P} = \frac{T^*\Omega}{T\Omega} = \frac{T^*}{T} \tag{5-2}
\]

The torque ratio \( T^*/T \) is given by Equation (4-2); hence

\[
\frac{P^*}{P} = \left( \frac{\mu^* \rho^*}{\mu \rho} \right)^{1/2} \tag{5-3}
\]

Dividing this equation into Equation (2-16) yields

\[
\left[ \frac{I_1^*}{I_1} \right] \left( \frac{P^*}{P} \right)^{-1} = \left[ \left( \frac{k \alpha}{m/3 + 1} \right)^2 \left( \frac{\mu^*}{\mu} \right)^{-2} \left( \frac{\rho^*}{\rho} \right)^{-7} \right]^{2/3} \text{Pe}_R^{2m/3} \tag{5-4}
\]

The quantity on the left is a dimensionless "benefit-cost" ratio; it is plotted as a function of the Peclet number in Figure 5-3. Except at the highest Peclet numbers, this ratio is less than 1, indicating that the increase in limiting current is less than the increase in power dissipation. This would seem to suggest that the use of suspended solids to enhance mass transfer would not be economical.
Figure 5-3. Dimensionless benefit/cost ratio. The quantity plotted along the vertical axis is given by Equation (5-4); a value less than 1 indicates that the increase in limiting current is proportionally less than the increase in the mixing-power requirements.
However, Equation (5-4) compares limiting currents and power dissipation at a fixed rotation rate. It may be that a given current density could be achieved more economically without suspended solids by simply rotating the disk faster. The Levich equation, (2-14), shows that the current depends on the square root of the disk rotation rate. Therefore,

$$\frac{I^+_n}{I_n} = \left(\frac{\Omega^+}{\Omega}\right)^{1/2}$$

(5-5)

where the superscript cross (+) indicates a quantity obtained at a higher rotation rate $\Omega^+$, but in the absence of suspended solids. According to Equation (4-1), the torque depends on the 3/2-power of the rotation rate, giving

$$\frac{P^+}{\Omega^+} = \left(\frac{\Omega^+}{\Omega}\right)^{3/2}$$

(5-6)

Dividing (5-5) by (5-6) yields

$$\frac{I^+_n/I_n}{P^+/\Omega} = \left(\frac{\Omega^+}{\Omega}\right)^{-2}$$

(5-7)

Thus, doubling the rotation rate increases the current by a factor $2^{1/2}$, and the power dissipation by a factor of $2^{3/2}$; this reduces Equation (5-7) by $2^{-2} = (1/4)$.

Dividing Equation (5-4) by (5-7) gives

$$\left[\frac{I^+_n}{I^+_n}\left(\frac{P^+}{P^*}\right)^{-1}\right] = \left[\left(\frac{\kappa \alpha}{m/3 + 1}\right)^{2} \left(\frac{\mu^+}{\mu}\right)^{-2} \left(\frac{\rho^+}{\rho}\right)^{-1}\right]^{2/3} \text{Pe}_R^{3/2} \left(\frac{\Omega^+}{\Omega}\right)^{+2}$$

(5-8)

This equation indicates the advantage of using suspended solids instead of a higher disk rotation rate to achieve a given increase in the limiting current. Figure 5-4 presents the results obtained from a sample calculation ($\phi = 0.40$, $2a = 8$ microns, $R = 1$ cm, $D = 4.5 \times 10^{-6}$ cm$^2$/s, and $v = 0.014$ cm$^2$/s). Obviously, substantial increases in the limiting current ($I^+_n/I_n > 1.4$) require far less power using the suspended solids.
Figure 5-4. Dimensionless benefit-cost ratio. The quantity plotted along the vertical axis indicates the relative advantage of using a 40% suspension of glass beads (denoted by *) instead of a higher disk speed without solids (+), to achieve a given increase in limiting current.
Nevertheless, it should be noted that the added expenses associated with handling solid-liquid suspensions might well outweigh any advantage gained from their use. Such suspensions are often abrasive, requiring special (and expensive) vessels, piping, slurry pumps, etc. Equipment has to be redesigned to eliminate dead spots, sharp corners, gaps, and other places where solid particles can lodge. On the other hand, suspended solids might prove to be useful even when they offer no net reduction in operating or equipment costs. For instance, Wisdom (1972) and Eisner (1972b) found that suspended solids greatly improved the throwing power of electroplating baths, thereby producing more uniform deposits. Other workers used solid particles to improve the surface finish of electroplated objects (cf. footnote, p. 4).

5.4. Recommendations

This study suggests a number of possible directions for future research on transport in suspensions. Perhaps the most pressing need is to understand the process of slip-layer formation. Useful information on the radial distances required for the development of these layers could be obtained by employing electrodes intermediate in size between those described in Section 3.2. Even better would be to make high-speed motion pictures of the developing slip layer. This would be difficult or impossible to do using the rotating disk; more convenient for this purpose would be a Poiseuille-, Couette-, or channel-flow device. Once the structure of the slip layer is known, it should be possible to solve the equations of motion for flow to a rotating disk with slip.

The present cell-and-disk arrangement, in which the disk electrode is placed very close to the bottom of the cell, reduces but does not eliminate the problem of particle sedimentation. Therefore, more work should be done with neutrally-buoyant polymer particles. (This would be especially important in Couette-flow studies, where the motion of the electrode provides no vertical flow to counter the influence of gravity.) Polymethylmethacrylate (PMMA) appears to have good chemical resistance to the caustic electrolyte solutions. However, the method of making PMMA powders by milling and grinding is not entirely satisfactory because the resulting particles are highly irregular. It should be
possible to make uniform, spherical polymer beads by suspension or emulsion polymerization.

This study has focussed exclusively on the enhancement of mass-transfer rates for a redox reaction. Future studies might also consider the influence of suspensions on electrodeposition. Barkey (1987) studied high-rate electrodeposition of copper on a rotating cylinder; he also performed a few preliminary experiments using suspended glass beads. Other workers in this laboratory (Faltemier and Tobias 1983; Mc Vay, Muller, and Tobias 1986) have examined striations that occur on electrodeposited zinc. It would be interesting to see what effect, if any, suspended solids would have on the formation and morphology of such surface features.

Most of the published work on suspension mass transport has been limited to laminar flows. (Barkey's experiments, just mentioned, are an exception.) The influence of suspended particles on transport in turbulent flows certainly should be investigated.

The rapid current fluctuations described in Section 4.1 were something of a nuisance when it came to measuring the average current. Yet these fluctuations, if properly measured and analyzed, might provide important insight into the processes occurring at the electrode surface. For example, it might be possible to record the signal caused by the passage of a single solid particle over a microelectrode. Work along these lines would require rapid signal acquisition and analysis.

Suspension mass-transfer work may ultimately prove useful in the development of a general theory of multiphase flow. Passman, Nunziato, and Walsh (1984) describe such a theory, which is based on the idea that each phase of the mixture separately obeys the usual equations of motion if additional terms are included to account for the exchange of energy and momentum between the phases. Since microconvection results from the interaction between phases, mass-transfer measurements might provide some clue as to the proper forms of the energy- and momentum-exchange terms.
### NOTATION

#### Roman Letters

<table>
<thead>
<tr>
<th>Letter</th>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>particle radius, cm</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>area, cm²</td>
<td></td>
</tr>
<tr>
<td>b₀, b₁</td>
<td>regression coefficients (Chapter 4)</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>concentration, moles/liter</td>
<td></td>
</tr>
<tr>
<td>Cₚ</td>
<td>heat capacity, ergs gm⁻¹ degree⁻¹</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>particle diameter, cm or microns</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>diffusivity, cm²/s</td>
<td></td>
</tr>
<tr>
<td>f_D</td>
<td>dimensionless diffusivity function, Equation (2-11)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Faraday's constant, 96,487 C/equiv.</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>gravitational force vector, dynes</td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>current density, A/cm²</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>current, A</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>thermal conductivity, erg s⁻¹ gm⁻¹ degree⁻¹</td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>characteristic dimension of microconvective vortices, cm</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>characteristic length, cm</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>exponent on Peclet number, Equation (2-9)</td>
<td></td>
</tr>
<tr>
<td>MD</td>
<td>mean deviation</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>number of electrons in electrode reaction, equiv./mole</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>pressure, dynes/cm²</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>mixing power, ergs/s</td>
<td></td>
</tr>
<tr>
<td>Pe</td>
<td>Peclet number</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>rate of heat transfer, ergs/s</td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>radial coordinate, cm</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>tube or disk radius, cm</td>
<td></td>
</tr>
</tbody>
</table>
$R$ distance from axis of symmetry, Equation (2-17)

Sc Schmidt number

SD standard deviation

Sh Sherwood number

T torque, dyne-cm

U velocity, cm/s

$v$ velocity vector, cm/s

$x$ tangential boundary-layer coordinate, cm

$y$ normal boundary-layer coordinate, cm

$z$ axial coordinate, cm

**Greek Letters**

$\alpha$ thermal diffusivity, cm$^2$/s (Chapter 1 only)

$\alpha$ empirical coefficient, Equation (2-9)

$\gamma$ shear rate, cm$^{-1}$

$\Gamma$ gamma function

$\beta$ gradient of radial velocity at wall, s$^{-1}$

$\delta$ thickness of boundary layer or slip layer, cm

$\epsilon$ average width of gap between particles, cm

$\zeta$ dimensionless axial coordinate

$\theta$ angular coordinate

$\Theta$ dimensionless concentration

$\kappa = D^*/D$ for stationary suspensions

$\mu$ viscosity, gm/cm-s

$\nu$ kinematic viscosity, cm$^2$/s

$\omega$ angular rotation rate of particles, s$^{-1}$

$\Omega$ angular rotation rate of disk electrode, s$^{-1}$
\( \pi \) 3.14159...
\( \rho \) density, gm/cm\(^3\)
\( \sigma \) electrical conductivity, mho/cm
\( \zeta \) dimensionless slip factor, Equation (2-18)
\( \tau \) shear stress, dyne/cm\(^2\)
\( \phi \) volume fraction (or volume percent) of dispersed phase
\( \omega \) angular rotation rate of particles, s\(^{-1}\)
\( \Omega \) angular rotation rate of disk electrode, s\(^{-1}\)

Subscripts
- c continuous phase
- d dispersed phase
- f pure fluid
- h hydrodynamic
- L limiting value
- mt mass-transfer
- s solid or slip
- w wall value
- \( \infty \) bulk value (far from electrode)

Superscripts
- * suspension property
- + property measured at increased rotation rate (no solids)
APPENDIX 1

Equipment Manufacturers and Suppliers


(2) **Sodium hydroxide, Analytical Reagent Grade.** Mallinckrodt, Inc., Paris, KY 40361.

(3) **Potassium ferricyanide, potassium ferrocyanide “Baker Analyzed” Reagent Grade.** J.T. Baker Chemical Company, Phillipsburg, NJ 08865.

(4) **RDE Rotator, Model ASR.** Pine Instrument Company, P.O. Box 429, Grove City, PA 16127.

(5) **Potentiostat/Galvanostat, PARC Model 173.** Princeton Applied Research, P.O. Box 2565, Princeton, NJ 08540.

(6) **Programmer, PARC Model 175.** Princeton Applied Research.

(7) **X-Y recorder Model 7044B.** Hewlett-Packard Company, Palo Alto, CA 94304.

(8) **“Bex-ometer” Model 38.** The Bex Company, 1500 17th Street, San Francisco, CA 94107.

(9) **Digital thermometer, “Trendicator” Model 410A.** Doric Scientific Division, Emerson Electric Company, 3883 Ruffin Road, San Diego, CA 92123.

(10) **Strobe lamp “Digistrobe”.** Power Instruments, 7360 N. Lawndale Ave., Skokie, IL 60076.
APPENDIX 2

Particle Size Analysis

The sizes of the glass particles were determined by scanning-electron microscopy (SEM). Representative particle samples were attached to standard SEM sample holders with double-sided adhesive tape, then sputter-coated with gold to make them conductive. Each sample was photographed at a magnification that produced easily measured images (2 to 20 mm) while still showing a large number of particles (>100). The true particle size \( d \) is related to the image size \( d_{\text{image}} \) by

\[
d = \frac{d_{\text{image}}}{(\text{magnification})}
\]

Non-spherical particles in the samples were characterized in terms of a volume-equivalent diameter, defined as the diameter of a sphere having the same volume as the particle in question:

\[
d_{\text{eq}} = (\frac{6V}{\pi})^{1/3}
\]

For each sample, a volume-weighted average diameter was calculated:

\[
\bar{d} = \frac{\sum \frac{\pi}{6} d_i^3 d_i}{\sum \frac{\pi}{6} d_i^3} = \frac{\sum d_i^4}{\sum d_i^3}
\]

This quantity was used as a measure of central tendency because the usual arithmetic average gives undue weight to very small particles, which may be present in great numbers while still accounting for a minor fraction of the total volume of solids.

Two measures of dispersion were calculated for each sample, the volume-weighted standard deviation \( SD \), and the mean deviation \( MD \):

\[
SD = \left[ \frac{\sum d_i^3 (d_i - \bar{d})^2}{\sum d_i^3} \right]^{1/2}
\]
where $\bar{d}$ is the volume-weighted average diameter, and $N$ is the total number of particles measured. The mean deviation $MD$ is to be preferred over the standard deviation when the sample size is small and the extreme values are suspect (Sachs 1984).
APPENDIX 3
Preparation of Insulating Epoxy

Epoxy resin was used to make the electrically-insulating parts of the rotating-disk electrodes. The following recipe was found to give good results:

(1) Weigh out approximately 70 parts Shell "826" epoxy resin, 12.5 parts "736" epoxy resin/thinner, and 17.5 parts "D-40" hardener. (The exact proportions are not critical; slight changes in formulation seem to affect only the final color.) Mix well.

(2) Place resin mixture in vacuum oven at room temperature. Pump down and leave under vacuum until all air bubbles are removed. The mixture tends to foam, expanding to several times its original volume. The foam can be suppressed by increasing the pressure (e.g., by cracking open the oven's vent).

(3) Pour resin mixture into clean, dry mold. The mold should be designed so as to provide sufficient space for foam expansion in the next step.

(4) Remove air bubbles again, as in step 2.

(5) Cure for 24 hours at 60°C and atmospheric pressure. Continue curing for another 24 hours at 45°C. Allow to cool slowly to room temperature. Remove mold for further machining, etc.

The removal of air in Steps 2 and 4 is especially important, and requires some care to prevent loss of resin due to foaming. The curing temperatures specified in Step 5 are approximate. Increasing the temperature speeds up the process, but at the risk of cracking the epoxy upon cooling.
APPENDIX 4
Preparation and Analysis of Electrolyte Solutions

Alkaline ferricyanide solutions were prepared by dissolving 40.0 gm NaOH, 42.24 gm K₃Fe(CN)₆·3H₂O, and 6.5852 gm K₃Fe(CN)₆ in distilled water to 500 ml. These solutions remain usable for several weeks if kept in a tightly stoppered flask away from light. (Nevertheless, it is a good practice—generally followed in these experiments—to discard solutions that are more than a week old.) The solutions were analyzed according to the procedure outlined below:

1. Pipette 10-ml sample into 500-ml flask.

**NaOH determination**

2. Add 50 ml distilled water and 4 or 5 drops of phenolphthalein indicator solution.
3. Titrate with standard 1.0N HCl to disappearance of phenolphthalein color.

**Ferrocyanide determination** (Sutton 1955)

4. Add 10 ml concentrated HCl and 5 drops 1% diphenylamine indicator solution.
5. Titrate with 0.2N standard dichromate solution.

**Ferricyanide determination** (Kolthoff & Belcher 1942; Sutton 1955)

6. Add 20 ml 1F KI and 0.11F ZnSO₄; stopper flask and let stand in the dark for 5 minutes.
7. Titrate with 0.15N standard thiosulfate solution, stopping just before the equivalence point.
8. Add 5 ml starch indicator solution.
9. Continue titrating with thiosulfate until blue starch-iodine color disappears.

Once the composition of the solution is known, its density and viscosity can be calculated from the empirical equations of Boeffard (1966):

\[ \rho (\text{gm/cm}^3) = 0.99702 + 0.04423 C_{\text{NaOH}} + 0.17118 C_{\text{Ferri}} + 0.23119 C_{\text{Ferro}} \]
\[ \mu(\text{cP}) = 0.96714 + 0.09622C_{\text{NaOH}} - 0.20528C_{\text{Ferri}} + 0.090255C_{\text{Ferro}} \\
+ 0.05404C_{\text{NaOH}}^2 + 0.53303C_{\text{Ferri}}^2 + 0.43505C_{\text{Ferro}}^2 \\
+ 0.23546C_{\text{NaOH}}C_{\text{Ferri}} + 0.302585C_{\text{NaOH}}C_{\text{Ferro}} + 0.99923C_{\text{Ferro}}C_{\text{Ferri}} \]

For the electrolyte solutions used in this study, \( C_{\text{NaOH}} = 2\text{M}, \) \( C_{\text{Ferri}} = 0.2\text{M}, \) and \( C_{\text{Ferro}} = 0.04\text{M} \), giving a density of 1.13 gm/cm\(^3\) and a viscosity of 1.55 cP.

The diffusivity of ferricyanide ion can be determined from the empirical equation of Gordon, Newman, and Tobias (1966):

\[ \frac{D\mu}{T} = (0.234 + 0.0014I) \times 10^{-9} \text{ cm}^2\text{ poise s degree} \]

Here, \( T \) is the absolute temperature (degrees Kelvin), and \( I \) is the ionic strength, defined by

\[ I = 1/2 \sum_{i}^{m} c_i z_i^2 \]

where \( c_i \) is the concentration of the \( i \)th species, \( z_i \) is the charge on the ion, and the summation is taken over all solutes. In the present case, \( T = 298\text{K}, I = 3.85, \) and \( D = 4.5 \times 10^{-6} \text{ cm}^2/\text{s}. \)
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