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Mass transfer enhancement by suspensions in a shear flow*

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Electrochemical measurement of mass transfer enhancement in a dilute suspension of particles, due to particle rotation in the presence of a shear flow, has been studied with a Couette cell. An effective diffusivity D_e involving the Peclet number Pe of the particles and the molecular diffusivity D of the solute was obtained for low particle volume fraction ϕ as $D_e = D(1 + 3.5\phi Pe^{1/2})$. From steady-state and transient data, it was shown that aggregation may occur with alumina particles and that inertial effects due to centrifugation reveal a marginal layer free of particles near the rotating inner cylinder.

Notation

a	particle radius (cm)
c_0	initial concentration of the solute (mole cm^{-3})
$c(x, t)$	solute concentration at time t and location x (mole cm^{-3})
D	molecular diffusivity of the solute (cm^2 s^{-1})
D_e	effective diffusivity of the solute (cm^2 s^{-1})
e	gap thickness (cm)
$I(t)$	time dependent current (A)
I_∞	steady-state value of the current (A)
J	mass flux (mol cm^{-2} s^{-1})
J_0, J_1	Bessel functions of the first kind
K	coefficient in Equation 11
r	radial coordinate Equation 3 (cm)
R_1, R_2	inner and outer radii of the Couette cell (cm)
S	wall velocity gradient (s^{-1})
t	time (s)
$\mathbf{v}$	local velocity around each particle (cm s^{-1})
V_0	linear velocity of the mobile plane in the plane Couette cell (Fig. 1) (cm s^{-1})
x, y, z	Cartesian coordinate system
Y_0, Y_1	Bessel functions of the second kind

Greek symbols

α_n	roots of Equation 10
β, γ	exponents in Equation 11
δ_r	diffusion layer thickness (Equation 12) (cm)
ν	kinematic viscosity (cm^2 s^{-1})
ϕ	particles volume fraction (%)
ω	angular velocity of particles (rad s^{-1})

1. Introduction

Suspensions in a flowing fluid are known to increase bulk mixing processes. A frequently encountered problem concerns the particle efficiency in strong flows with highly concentrated suspensions. The mechanism involves complex interactions between particles and the fluid, generally in turbulent conditions. Other processes, such as that due to the recurrent disruption of an established diffusion boundary layer by particles near the wall, also lead to mass transfer increase.

Here, we focussed on a very specific process where mass transfer is increased by a rotation motion (single particle) of a small sphere subjected to a shear flow in an otherwise linear concentration gradient. This process is expected to be efficient in creeping flows for species having a very small molecular diffusion coefficient, this mechanism having been invoked in blood medium to explain the transport of platelets to or from walls [1]. An electrochemical technique was used in order to create a linear concentration profile and to accurately measure the overall mass transfer in the bulk.

2. Theoretical analysis

Consider two parallel plates in relative translational motion (parallel Couette cell), the lower one (1) at rest and the upper one (2) at velocity V_0 (Fig. 1). In addition, a solute is initially present at uniform concentration $c = c_0$. At time $t = 0$, boundary conditions, $c = 0$ and $c = 2c_0$, are, respectively, imposed at both plates. A transient regime is observed for which the time-dependent concentration is given by [2]

$$c(x, t) = \frac{2c_0 x}{e} + \frac{4c_0}{\pi}\left\{\sum_{n=1}^{\infty}\left(\frac{\cos n\pi}{n}\right)\left(\sin\frac{n\pi x}{e}\right) \times \exp\left(-\frac{n^2\pi^2 Dt}{e^2}\right) + \sum_{n=0}^{\infty}\left(\frac{1}{2n+1}\right)\right.$$

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$$\times \left(\frac{\sin (2n + 1)\pi x}{e} \right) \times \exp\left(- \frac{(2n + 1)^2 \pi^2 Dt}{e^2} \right) \Bigg\} \quad (1)$$

and the transient flux $J(t)$ by

$$J(t) = -D \left. \frac{\partial c(t)}{\partial x} \right|_{y=0} = J_\infty \left\{ 1 + 2 \sum_{n=1}^{\infty} \exp\left(- \frac{4n^2 \pi^2 Dt}{e^2} \right) \right\} \quad (2)$$

with $J_\infty = -D(2c_0/e)$ and where e is the gap thickness between plates and D is the molecular diffusion coefficient of the solute.

After a large enough time, a steady-state regime is reached with a limiting flux $J = J_\infty$. The concentration gradient is then constant. Considering that the velocity field and the concentration gradient are orthogonal, there is no convective contribution to the flux, which is thus purely diffusional and therefore independent of V_0.

When a small spherical particle is placed between plates, it bears both a translational motion at the local velocity $\mathbf{V}_x = Sy$ with $S = V_0/e$, and a rotational motion at angular velocity $\omega = S/2 = V_0/2e$ due to the shear flow. Then, a local velocity $\mathbf{v}$ relative to the centre of the particle is induced such that [3]:

$$\mathbf{v} = \left(\frac{a}{r} \right)^3 \boldsymbol{\omega} \wedge \mathbf{r} \quad (3)$$

ω is aligned with the z-direction and a is the particle radius. This results in a local mixing which increases the flux between the plates, or in other words, a component of $\mathbf{v}$ along the y-axis gives a contribution of convective diffusion to the overall flux.

Different models have been previously proposed either based on similarity with the so-called Prandtl mixing length in turbulent flow [4, 5], or on a Taylor dispersion model [6, 7]. In general, D is replaced in Equation 2 by an effective diffusivity, D_e, which can be written as

$$D_e = D\{1 + f(Pe)\} \quad (4)$$

where Pe is the Peclet number, equal to $\omega a^2/D$, and which characterizes the effectiveness of convective transport with respect to diffusive transport. This type of analysis was first proposed by Keller [4] who obtained

$$f(Pe) \propto Pe \quad (5)$$

Hyman [5] found the following expression where the Pe exponent is somewhat higher

$$f(Pe) = f^2 Pe^2 \phi^{2/3} (1 - \phi^{2/3})^2 / 192^2 \quad (6)$$

f is a constant of order 1 and ϕ the volume fraction ($\phi \ll 1$). Finally, Antonini *et al.* [6, 7] in two successive analyses, predicted, first, a dependence which did not involve the volume fraction of particles, ϕ:

$$f(Pe) = \frac{Pe}{4\pi} + \left(\frac{Pe}{2\pi} \right)^{1/2} \quad (7)$$

and then a more refined one

$$f(Pe) = \left(\frac{9}{2\pi} \right)^{1/3} Pe^{2/3} \left(\frac{\phi}{1 - \phi^3} \right)^{2/3} \quad (8)$$

In a macroscopic description, Equation 2 is still applicable with a suspension, by substituting D_e in place of D. This affects the asymptotic value J_∞ and also the diffusion time constant.

3. Experimental details

For practical reasons, a plane Couette flow was approximated by a cylindrical Couette flow with a very small gap (inner and outer radii, R_1 and R_2, were, respectively, 1.95 and 2 cm). Only the inner cylinder rotated and was made of nickel over a length of 2.44 cm, constituting the working electrode. In front of it, on the outer cylinder was placed the counter electrode, also made of nickel and with the same length (Fig. 2). The quality of the measurements demands a high degree of concentricity of the cylinders. It is easy to show that this optimal arrangement yields the lowest steady-state current, I_∞, and can be, therefore, experimentally obtained by a mechanical

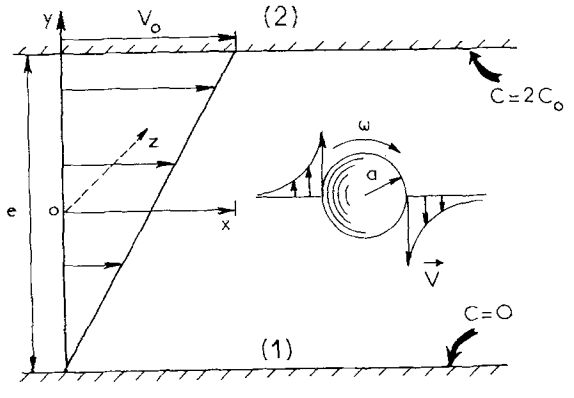

Fig. 1. Principle of mass transfer enhancement by a spherical particle in a simple shear flow (plane Couette cell).

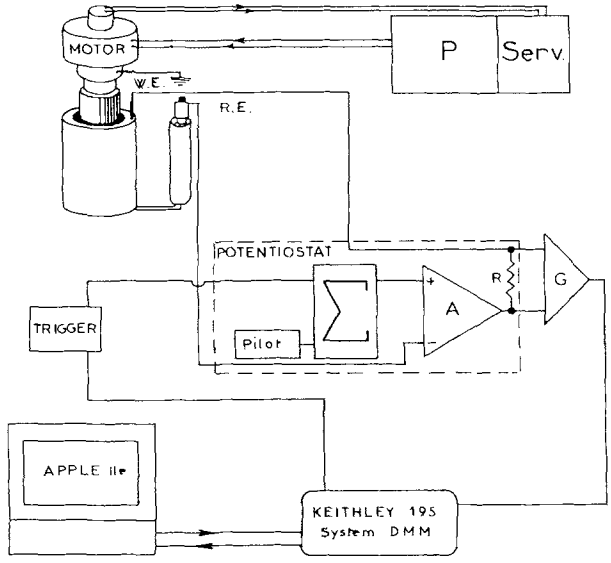

Fig. 2. Experimental arrangement.

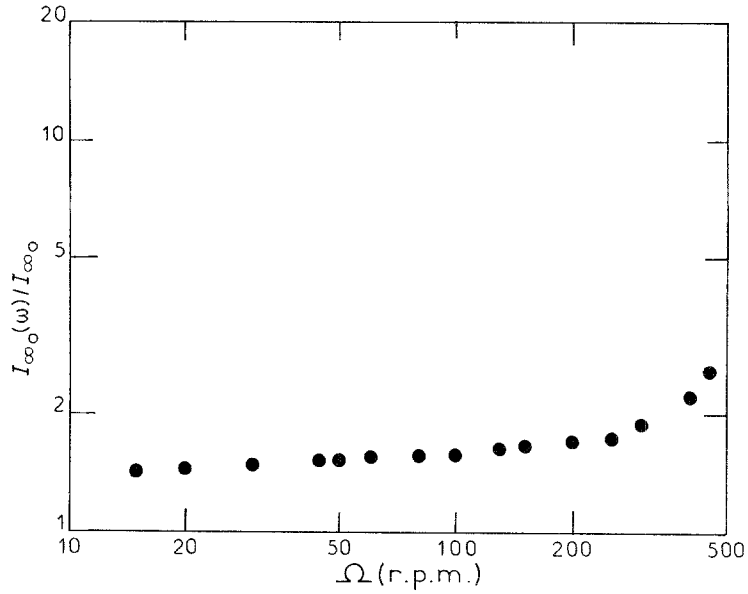

Fig. 3. Steady-state limiting current without suspensions as function of the angular velocity Ω of the inner cylinder, normalized by the current at Ω = 0.

adjustment with a micrometer screw of the outer cylinder.

There remains the eccentricity in rotation of the inner cylinder, estimated as $\sim 10\,\mu$m. This small eccentricity is sufficient to produce a slight increase in the current I_∞ in the order of 30% with the rotation of the inner cylinder without suspensions (see Fig. 3). For a better analysis, the current increase due to suspensions was estimated with respect to the current values without suspensions at the same angular velocity as reported in Fig. 3.

A saturated calomel electrode (SCE) was used as reference electrode. The potential of the working electrode was referred to the SCE potential and controlled by the potentiostat.

The solution was a 30%–70% water/glycerol mixture which also contained $NaNO_3$ (1 M) as supporting electrolyte and potassium ferri/ferrocyanide in equimolar concentration 10^{-2} M. First, the high kinematic viscosity $\nu = 0.282\,\text{cm}^2\,\text{s}^{-1}$ delayed the onset of Taylor vortices to much higher angular velocities. Secondly, it permitted a decrease in the molecular diffusivity by virtue of the Stokes–Einstein relation and, therefore, an increase in Pe, providing a better sensitivity to convective transport. The molecular diffusivity, D, was determined by the EHD impedance technique [8] and found to be $2.8 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$.

Measurements were performed by prompting a trigger signal to the summator of the potentiostat, initially at rest potential (zero net current ensuring $c_{\text{ferro}} = c_{\text{ferri}} = c_0\ \forall x$), with a stepwise potential imposing purely diffusional control of the ferricyanide reduction at the working electrode ($c_{\text{ferri}} = 0$) and hence $c_{\text{ferri}} = 2c_0$ at the counter electrode. The trigger signal also started the acquisition of a sequence of digitized currents (Keithley voltmeter) at time values prescribed by the computer. Time dependent current $I(t)$ and steady asymptotic value I_∞ were both analysed.

For transient conditions, a more accurate expression taking into account the cylindrical geometry was considered [9]:

$$I(t) = I_\infty \left\{ 1 + \frac{e\pi}{2} \sum_{n=1}^{\infty} \frac{\alpha_n}{\left(1 - \dfrac{J_0(\alpha_n R_2)}{j_0(\alpha_n R_1)}\right)} \times [J_1(\alpha_n R_1) Y_0(\alpha_n R_2) - J_0(\alpha_n R_2 Y_1(\alpha_n R_1)] \times \exp(-\alpha_n^2 D t) \right\} \quad (9)$$

where J_0, J_1, Y_0 and Y_1 are Bessel functions of the first and second kind, α_n being the roots of the equations

$$J_0(\alpha_n R_1) Y_0(\alpha_n R_2) - Y_0(\alpha_n R_1) J_0(\alpha_n R_2) = 0 \quad (10)$$

Two types of suspensions were used:

(i) Alumina particles of irregular shape, polydisperse, with average diameters of 1, 3 and 9 μm.
(ii) Hollow glass spheres with narrow fractions around 15 and 40 μm.

4. Results

4.1. *Glass spheres*

Steady-state currents are reported in Fig. 4 as $(I_{\infty_s}/I_{\infty_0}) - 1$, as function of Pe, where I_{∞_s} and I_{∞_0} represent the steady-state current with and without suspensions, respectively. For the different concentrations and the two diameters involved, it can be observed that the data can be reasonably reduced: in fact, considering the "analysis" section, $(I_{\infty_s}/I_{\infty_0}) - 1$ directly represents the quantity $(D_e/D) - 1 = f(Pe)$ and can be put, at the low volume fractions investigated, in the form

$$(D_e/D) - 1 = K\phi^\beta Pe^\gamma \quad (11)$$

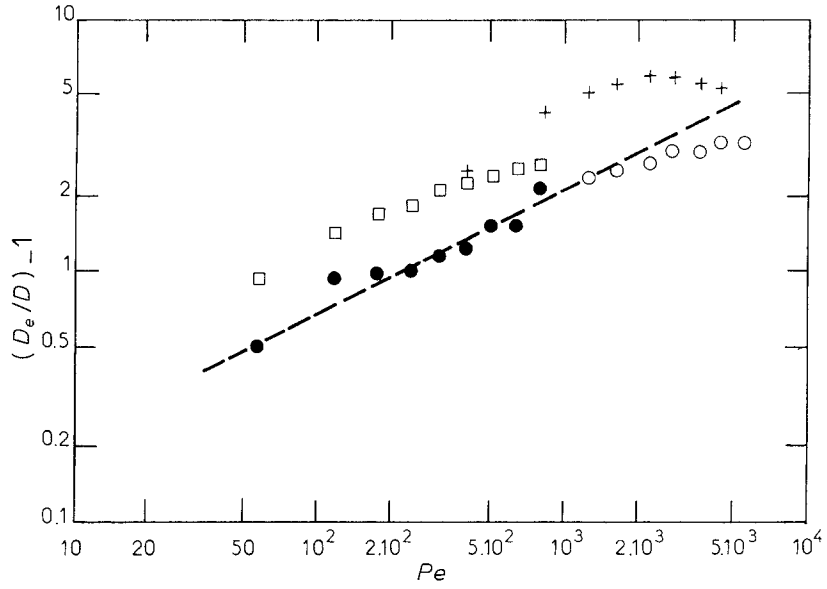

Fig. 4. $(D_e/D) - 1 = f(Pe)$ as a function of the Peclet number (Pe) for glass spheres and for different volume fractions ϕ of particles. Diameter 15 μm, ϕ = 2% (●); 4% (□); diameter 40 μm, ϕ = 2% (○); 5% (+). Solution in this figure and the following ones is a water/glycerol mixture 30%/70% containing $NaNO_3$ 1 M, Fe(III)/Fe(II) 10^{-2} M.

Thus, with the chosen coordinate system, it can be verified that, for a given volume fraction, the data must collapse on a single line whatever the suspension diameter.

A linear fitting procedure provided a coefficient K of ~ 3.5, and exponents β and γ about 1 and 0.5. Some systematic deviations are visible which can be ascribed to sedimentation effects.

We considered this result with glass spheres as a reference since they fulfill the basic hypotheses on some points — low polydispersity, spherical shape, low interactions — and use this correlation to analyse the data with alumina particles.

4.2. *Alumina particles*

Data for the three alumina suspensions (1, 3 and 9 μm) are reported in Fig. 5. It can be seen that, for a given concentration, the diffusivity values at different diameters do not collapse on to a single line. This behaviour is at variance with that for glass spheres. However the γ exponent, expressing the effectiveness of convective transport is confirmed, i.e. is found equal to 0.5 whatever the particle diameter and the concentration.

To explain this fact, we assumed that the Peclet number is only an apparent value and that the real value is obtained by fitting the time constant $(\alpha_n D)^{-1}$ in the theoretical relation to the experimental data. This leads to adjustment of (Equation 10) Pe which provides apparent values of the suspension diameter.

Then, for the 1, 3 or 9 μm values one finds 17, 18 and 26 μm, respectively. Two reasons can be put forward for this result: the first is the high degree of polydispersity which favours the fraction of large diameters, and the second is the formation of aggregates due to the existence of

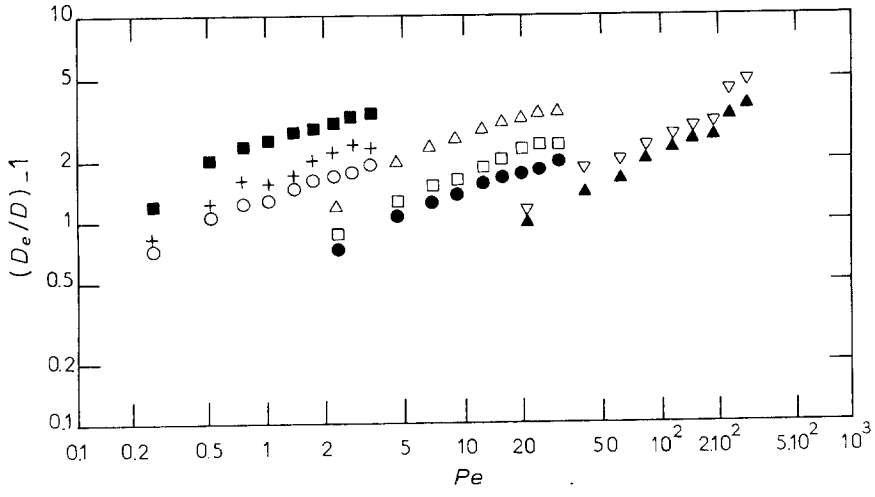

Fig. 5. $(D_e/D) - 1 = f(Pe)$ as function of the Peclet number Pe for alumina particles and for different volume fractions ϕ of particles. Diameter 1 μm, ϕ = 2% (○); 4% (+); 6% (■); diameter 3 μm, ϕ = 2% (●); 4% (□); 6% (△); and diameter 9 μm, ϕ = 2% (▲); 4% (▽).

distributed electric charges over the alumina particle surface while the whole particle is electrically neutral.

Examination of scanning electron microscope photographs suggested rejection of the first explanation.

5. Discussion

The value 0.5 found for the exponent on the Peclet number is not consistent with the theoretical predictions which generally lead to higher values. The models which tend to overestimate the convective transport are based on the analogy with the mixing length concept for which the region around each particle is characterized by infinitely fast mass transport.

Among the available models, that of Antonini *et al.* [7] with the exponent 2/3 is the closest to the experimental results.

The other model of Antonini *et al.* [6] which predicts a contribution in $Pe^{1/2}$ was established from a dimensional analysis, where the maximum thickness of the perturbed diffusion layer due to the particle rotation is of the order of

$$\delta_r \approx 2\pi a/Pe^{1/2} \tag{12}$$

In fact, this effect is similar to that occurring in flows having a stagnation point and must be characteristic of the action of shear on a concentration distribution, and therefore equivalent to a Taylor dispersion.

A more recent model by Nadim, Cox and Brenner [10], describing Taylor dispersion in a concentrated suspension of rotating cylinders, yields the same result.

The intrinsic mass transport properties of this system are basically the same as in the Keller description (see Fig. 1) in that, the fluid being macroscopically at rest, the transport when the cylinders are at rest is only due to molecular diffusion. The cylinders, located at the nodes of a square network, are corotating at the same angular velocity ω. For such a geometry, the flowlines are well defined (Fig. 6) and allow determination of three regions for mass exchange: a zone 'A' close to the cylinders and a zone 'B' where vortices take place, both displaying closed flow lines. Therefore, mass transfer within these zones is minimum but their respective concentrations are different. In fact, mass transfer rate is maximum through the hatched zones 'C' where separation of the flow lines occurs. These zones 'C' reproduce a typical situation of Taylor dispersion. These authors [10] obtained:

$$\frac{D_e}{D} = 4.4Pe^{1/2} \tag{13}$$

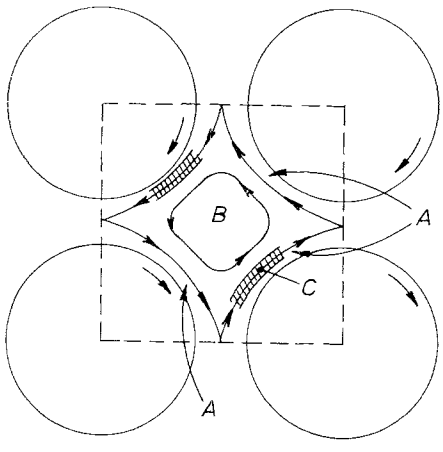

Fig. 6. Convective transport in a quiescent medium with corotating cylinders. Maximum mass transfer occurs in zone C where the flow lines separation occurs (from [10]).

5.1. *Sedimentation effects*

During the time scale of the experiments, no significant sedimentation by gravity occurred over the length of the electrodes (2.44 cm). However, transient measurements revealed some concentration distribution of particles in the radial direction due to inertial effects induced by the density difference between the particles and the fluid.

Without suspensions, the transient response $I(t)/I_\infty - 1$ against t, closely follows the theoretical relation Equation (9) (Fig. 7) and yields a time constant from which the diffusivity value of $2.3 \times 10^{-7}\,cm^2s^{-1}$, through smaller, is consistent with the value determined by the EHD impedance method.

The transient response in the presence of suspensions, gives a large divergence from the theoretical response and also some scattering, especially at long times (Fig. 7). The diffusivity data, adjusted over the whole time response, provide higher values than those determined from the I_∞ values. When a limited time window is analysed, and the diffusivity calculated for

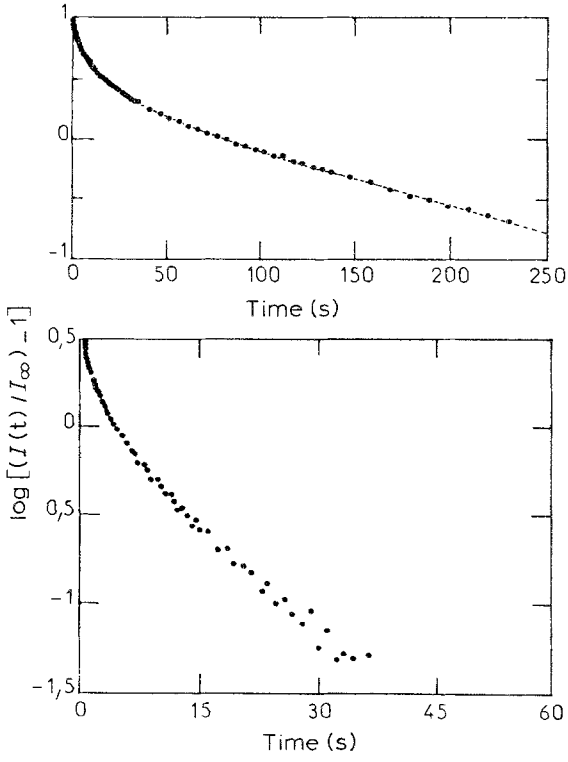

Fig. 7. $\log [I(t)/I_\infty - 1]$ against time. Upper curve corresponds to a solution without suspension at $\Omega = 0$ and the lower curve to a suspension of alumina particles ($2a = 1\,\mu m$, $\phi = 6\%$, $\Omega = 100$ r.p.m.).

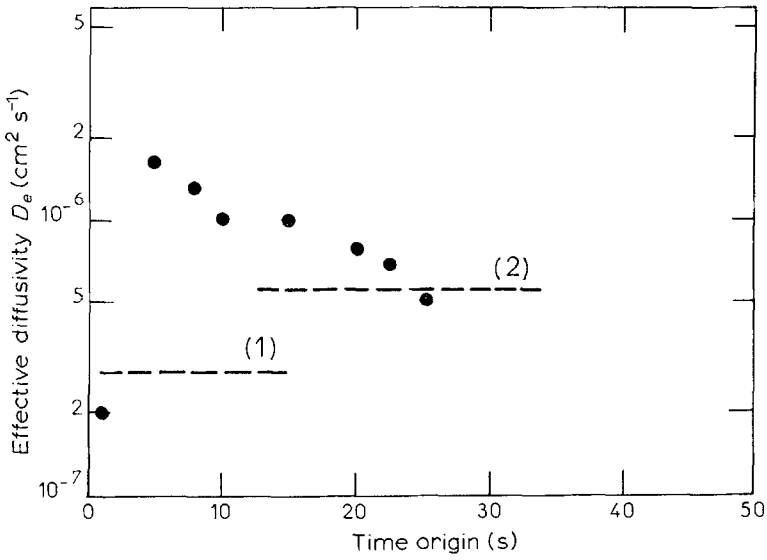

Fig. 8. Effective diffusivity D_e determined from transient response $I(t)$. Fitting procedure is performed over a limited time window by changing the time origin.

different time origins, then the values permit two regions to be distinguished (Fig. 8):

At short time origins, D_e is lower but of the order of magnitude of D without suspensions. At longer times origins, D_e tends to the value deduced from steady-state current (I_∞). These results prove that radial sedimentation is induced by centrifugation, the inner region (inner cylinder) of the gap being a layer without suspension, while, in the outer region (outer cylinder), the average suspension concentration is again found.

6. Conclusion

An electrochemical measurement of mass transfer was performed in a Couette cell for assessing the mass transfer enhancement due to the rotating motion of dilute spherical particles. An effective diffusivity expression $D_e = D(1 + 3.5\phi Pe^{1/2})$ was found, thus corroborating models based on the Taylor dispersion analogy. However, with the particles used, sedimentation by gravity or by centrifugation was shown to bias the results for long time experiments.

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