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Electrochemical measurements of mass transfer between a sphere and liquid in motion at high Péclet numbers

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Experimental studies of the effect of a transverse velocity gradient on the mass transfer between a fixed solid spherical particle and liquid and of the mass-transfer intensity between solid sphere and liquid in a uniform flow have been carried out. Both types of flow were formed between two rotating circular cylinders parallel to each other and separated by a distance of 10 mm. The following experimental procedures were applied: a method of stroboscopic visualization to measure velocity profiles, and an electrochemical method to measure the mass-transfer intensity between sphere and liquid.

Results were obtained for a wide range of the relevant dimensionless parameters, viz the Reynolds and Péclet numbers specified for each case appropriately. In the case of simple shear flow these ranges are: $0{\cdot}03 < Re^* < 1$, $150 < Pe^* < 13000$, and for the mass-transfer intensity $5 < Nu < 24$. It is shown that the experimental data agree fairly well with the approximation formula $Nu = 1{\cdot}134 Pe^{*\frac{1}{3}}$ obtained theoretically by Batchelor (1979) for an ambient pure straining motion with the assumptions that $Re^* \ll 1$ and $Pe^* \gg 1$. In the case of a uniform flow the ranges of the dimensionless parameters are $0{\cdot}4 < Re < 20$, $3000 < Pe < 40000$; and $13 < Nu < 35$. The experimental data are here in good agreement with theoretical dependences of the type $Nu \propto Pe^{\frac{1}{3}}$ obtained by Aksel'rud (1953) and Acrivos & Taylor (1962).

1. Introduction

Mass-transfer intensity between a solid sphere and liquid depends on many factors including radial diffusion, forced and free convection, particle shape, hydrodynamic pattern of a liquid flow round the particle, physical properties of liquid and particle, etc. In practice these factors are present simultaneously, and the study of this process consequently presents some difficulties. Most research workers have restricted themselves to investigations of the mass-transfer process in plane parallel liquid flows in which the greatest contribution to the mass transfer is made by the forced convection. This is explained by the relative simplicity of theoretical and experimental studies of this type of process rather than by a traditional approach to these studies.

For the last 30 years a great number of works have been devoted to studies of the intensity of mass transfer between a fixed sphere and liquid with a uniform ambient velocity. As a rule, these studies were performed in flows with $Re \gg 1$ and are mainly experimental, which is not surprising since these are the flow regimes realized in many practical technological systems. Although the Stokes particle flows are not so important in practical problems, they are of fundamental importance for understanding the mass-transfer mechanism in 'solid–liquid' systems. Aksel'rud (1953) used the concentration boundary-layer approximation for high Péclet numbers (the Levich approach) and obtained an expression for the mass-transfer intensity between a sphere and liquid in uniform flows in the form $Nu = 1{\cdot}075Pe^{\frac{1}{3}}$. Here $Pe = Vd/D$. In the same study he obtained experimental confirmation of this relation in the range $Re = 0{\cdot}1$–$2{\cdot}5$, where $Re = Vd/\nu$, by dissolving a ball of pressed benzoic acid in oil. The experimental coefficient was 1·10, rather close to the theoretical value of 1·075, and was almost unchanged with increase of Re. For similar conditions Acrivos & Taylor (1962) obtained theoretically a relation of the same type in which the above coefficient was equal to 0·991. Experimental data reported by Sandoval-Robles, Riba & Couders (1980) cover the much wider range $Re = 2$–23000. Here the Prandtl number is about 2000. The empirical curve representing data for $2 < Re < 20$ and having the form

$$Nu = 1{\cdot}032Re^{0{\cdot}385}\,Pr^{\frac{1}{3}}$$

is in good agreement with the theoretical curves of Aksel'rud and Acrivos & Taylor. The analysis of this data suggests that the numerical coefficient decreases with increasing Re and the exponent of Re increases.

Unfortunately, studies performed at $Re < 1$ are limited in number, whereas only in these conditions can a comparison be made with the available theoretical curves.

More interesting are the mass-transfer studies in the 'solid–liquid' systems with a transverse velocity gradient in the ambient flow. As a first step, this process should be studied in the simplest case of a constant velocity gradient. Novikov (1958) considered and solved the problem of mass diffusion from a point source in a parallel flow whose velocity changes linearly. His final result concerned the concentration distribution near the source. Frankel & Acrivos (1968) solved the problem of heat and mass transfer from a sphere and a cylinder suspended in a simple shear flow. Acrivos (1971) obtained an expression for the heat-transfer intensity between liquid and a sphere freely rotating in the velocity-gradient flow and found $Nu = 9{\cdot}0$ for high Péclet numbers. Gupalo & Ryazantsev (1972) considered the problem of a freely suspended rigid sphere in a steady axisymmetric pure straining flow, and derived an analytical expression for the mass-transfer intensity between particle and liquid at high Péclet numbers of the form $Nu = 1{\cdot}134Pe^{*\frac{1}{3}}$, where the Péclet number is based on the sphere diameter. Batchelor (1979) solved a similar problem in more general form and concluded that the same expression is valid at high Péclet numbers for any ambient steady pure straining motion provided the Péclet number is defined appropriately.

As seen from the above survey, the available theoretical studies provide a rather clear picture of the regularities in the mass transfer from a sphere to liquid at high Péclet numbers. However the experimental data in this field are scanty. Therefore, it is difficult to judge the validity of the reported theories. The analytical equations obtained should be thoroughly tested experimentally. We have carried out mass-transfer-intensity measurements between a sphere and liquid by an electrochemical technique.

2. Experiment and experimental setup

The main difficulty in planning the experiment was the choice of the method of obtaining uniform and simple shear flows with small fluid volumes and somewhat simple configuration of the experimental setups. The known methods could not be

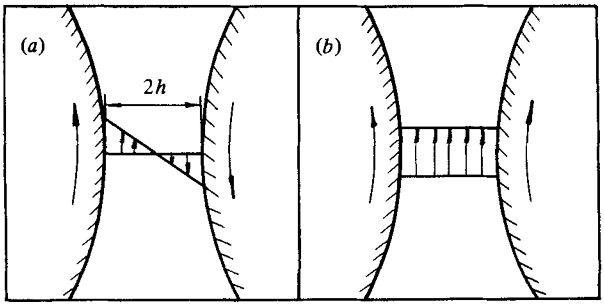

FIGURE 1. Types of flows utilized in experiment: (*a*) simple shear flow with cylinders rotating in the same direction; (*b*) uniform flow with cylinders rotating in the opposite directions.

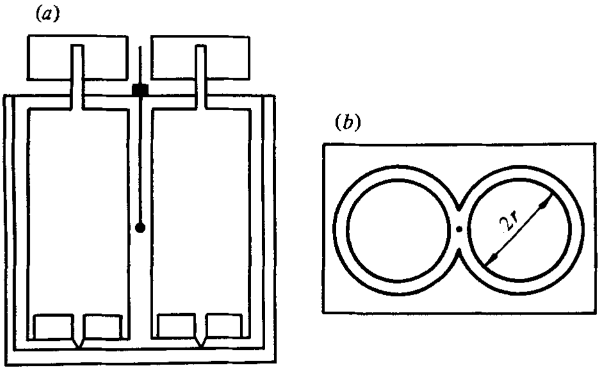

FIGURE 2. Schematic diagram of the arrangement: (*a*) side view; (*b*) top view.

used because of their cumbrous structure and technological complexity; in any event they are not sufficiently versatile. As a result the following concept has been utilized: if two circular cylinders are positioned at a small distance from each other (the distance should be much less than their radii) so that their axes are parallel, and are rotated in the same direction, the liquid-velocity profile formed in the gap between the cylinders should be similar to the velocity profile for plane Couette flow with walls moving in opposite directions. It is evident that this is valid only in some vicinity of the gap whose size can be increased by increasing the diameter of the rotating cylinders. This scheme is very convenient since it permits us to obtain a uniform liquid flow in the same region. For this purpose the cylinders are rotated in opposite directions. Flow patterns realized in the experiment are illustrated in figure 1.

A practical experimental setup is schematically shown in figure 2. The total experimental setup, except for a few components, was made of Plexiglas to ensure transparency and stability to active media (test liquids). The cylinders are 200 mm in height, 100 mm in diameter and the minimum gap between them is 10 mm. Periods of their rotation were recorded by using a photodiode and were varied in the range $t = 7{\cdot}0$–$130{\cdot}0$ s. The measurement error was 3 % at the largest periods and did not exceed 1 % at small t. To eliminate the effect of free convection due to the temperature gradients in the lower and upper layers of liquid, the test section was completely immersed in a tank with water where the temperature was maintained at 20 °C accurate to 0·1 °C by using a thermostat. To eliminate the effect of the bottom, the lower part of the cylinders was made with cavities which remain filled with air when the test volume is filled by liquid, i.e. the effect was created as if underneath there were a free surface as well, whence the source of perturbations is only the fine edge rather than the overall bottom part of the cylinder.

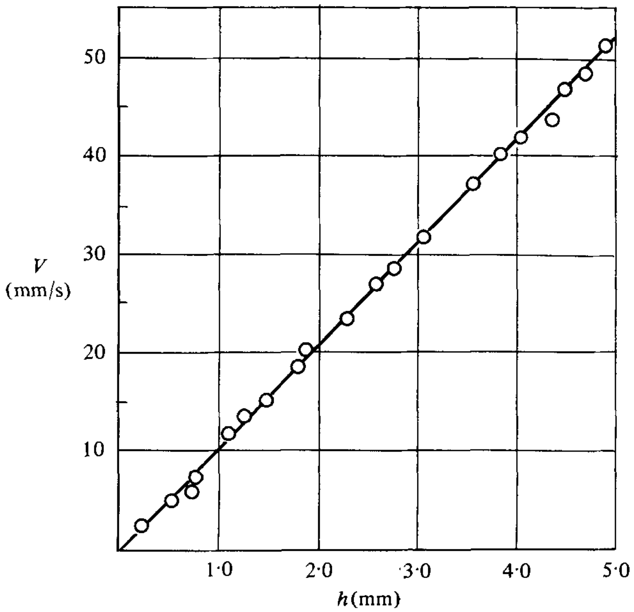

FIGURE 3. Velocity profile in a simple shear flow with cylinders rotating in the same direction. Velocity value at $h = 5{\cdot}0$ mm for the rotation period $t = 6{\cdot}0$ s can be determined from the formula $V = 2\pi r/t$.

An important factor is the feasibility of obtaining the required hydrodynamic conditions between the rotating cylinders, i.e. to verify the validity of the hypotheses applied to construct the setup. For this purpose the profiles of unperturbed liquid velocity were obtained by the stroboscopic visualization technique. One of them is shown in figure 3. To obtain each velocity profile, approximately 200 measurements were required. The tracks from the particles were taken from a square region with a side of 10 mm. Since the measured velocities from both sides of the profile are shown in the same plot, one can conclude that the flow pattern between the cylinders is symmetrical and the zero streamline for any plane cross section is localized at the gap centre. The mean relative error of velocity measurements by the above method in a given experiment was less than 3 %. It should be noted that in certain conditions stability is lost and Taylor vortices form in the system, as in the case of flow between coaxial cylinders. When vortices form the intensity of mass transfer between sphere and liquid sharply increases, but measurements under these conditions are beyond the scope of our present study. The transition is readily recorded and no mistake in the determination of the measurement regime can arise. In the case when the cylinders rotate in opposite directions, the mass-transfer intensity for the sphere in different positions along the line connecting their centres was measured. For each given regime the *Nu* values were sufficiently close to constant; hence a conclusion can be drawn that between the cylinders a uniform liquid flow is obtained.

It should be noted that the streamlines round the cylinders are approximately circular; therefore the required conditions are met only in the limited region. But we are helped by the fact that the ratio between the size of the cylinders and the solid spherical particle is very large and, depending on the probe-sphere size, it lay within 100 and 200. Therefore, in quite a large region compared with the sphere diameter, the streamlines can be considered as straight lines. The experiment indicates that this assumption has been completely justified.

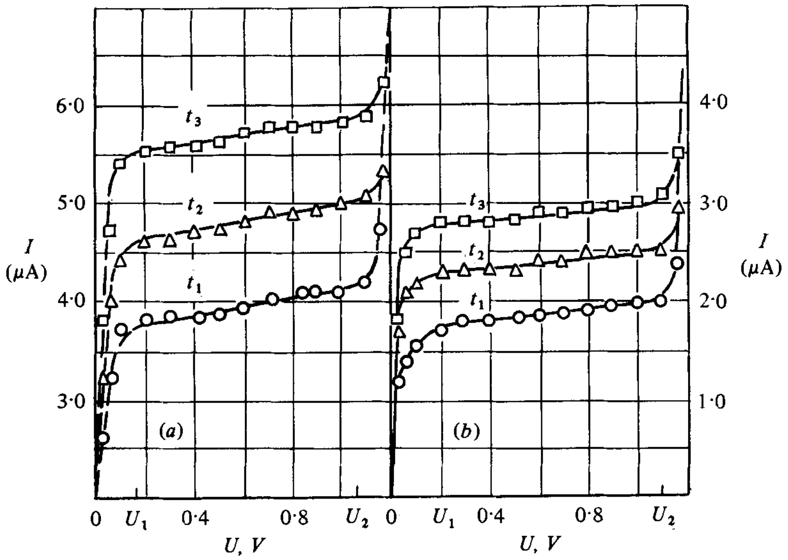

FIGURE 4. Current–voltage characteristics of electrochemical transducer: (*a*) uniform flow, $t_1 = 72$ s, $t_2 = 36$ s, $t_3 = 19{\cdot}2$ s; (*b*) simple shear flow, $t_1 = 57{\cdot}6$ s, $t_2 = 31{\cdot}2$ s, $t_3 = 23$ s.

3. Experimental procedure

The intensity of the sphere–liquid mass transfer was measured by an electrochemical method, consisting of measurements of the oxidation–reduction reaction rate on the metal electrode in the diffusion regime. The diffusion regime corresponds to the current–voltage characteristics of the electrochemical transducer in the range between U_1 and U_2 (figure 4). As a rule, all electrochemical measurements were carried out at a potential difference between the electrodes of $\frac{1}{2}(U_1 + U_2)$. When operating in the diffusion regime, the flux of ions to the electrode is assumed to be independent of the applied potential and is determined by the hydrodynamic conditions round the electrode. If the cathode area S is much smaller than that of the anode, the mass-flow density on the cathode is much higher than on the anode, it is already detectable and can be recorded on recording devices. Most extensively used is a solution of sodium hydroxide and potassium ferri- and ferrocyanides in distilled water, in which under the effect of electric current there occurs the redox reaction

$$\mathrm{Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-}}.$$

We have used an aqueous solution of 0·01 N potassium-, ferri- and ferrocyanide and 0·5 N sodium hydroxide with glycerol additives to vary the kinematic viscosity coefficient.

An electrochemical method is very convenient for studies of mass-transfer processes since the electrolyte consists of components such that after the above reaction the concentration of $\mathrm{Fe(CN)_6^{3-}}$ on the cathode is equal to zero; hence the transducer surface is always clean. In addition, the object under study is the transducer itself and therefore the construction is significantly simplified. An electrochemical cell used in experiments is schematically represented in figure 5 (*a*). A spherical transducer was positioned at the centre of the gap between the cylinders, i.e. on a zero streamline. The position of the centre was determined from the minimum mass-transfer intensity by moving the transducer along the line connecting the cylinder centres. The electrochemical transducer was made of pure platinum as follows. A platinum wire of 150 μm diameter was fused at the end using a gas jet till a sphere of the required

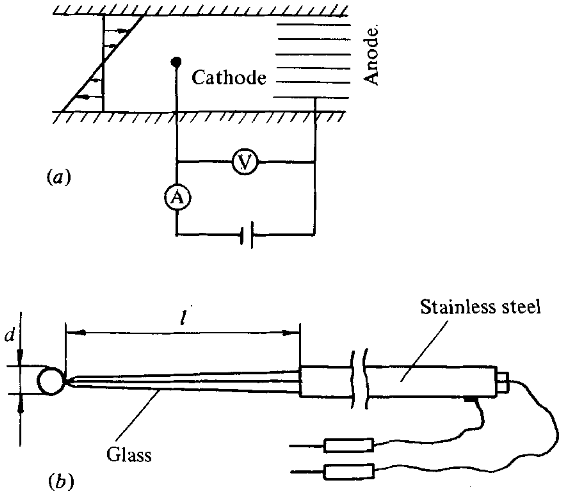

FIGURE 5. Measuring part of the experimental arrangement: (a) schematic representation of electrochemical cell; (b) electrochemical transducer, $d = 0{\cdot}5$–$0{\cdot}6$ mm, $l = 30$ mm.

size was formed. Then the wire, which in this case serves as a conducting contact, was coated by chemical glass with the thickness of about several tens of microns and was gradually thickened to a diameter of 1·5 mm at a distance of 20–30 mm. Then the transducer was cemented into a stainless-steel tube used as the anode with an outer diameter of 2·5 mm and the electric contact was well insulated. A schematic representation of the apparatus is shown in figure 5(*b*). The transducers had the diameter $d = 500$–$600\,\mu$m. The ratio of the anode and cathode surfaces was varied depending on the transducer sizes between 100 and 500.

The intensity of mass transfer was determined as

$$Nu = \frac{Id}{F\mathcal{S}C_f D},$$

where I is the diffusion current, d is the spherical transducer diameter, F is the Faraday constant, $\mathcal{S}$ is the area of the sphere surface, C_f is the concentration of potassium ferricyanide and D is the diffusion coefficient of potassium ferricyanide ions. C_f was measured using the potentiometric titration technique and the C_f value was calculated according to the formula $C_f = \mathcal{V}_c C_c/\mathcal{V}$, where $\mathcal{V}$ is the volume of the titration solution and $\mathcal{V}_c$ is the volume of cobalt solution added to the point of equivalence at the concentration C_c. This method is sufficiently accurate, its accuracy being as high as 0·5 %. The kinematic viscosity ν of the solution was measured in a standard viscometer. Values of the diffusion coefficient were found from the formula $\mu D/T = 2{\cdot}36 \times 10^{-15}$ kg m/s^2 K, obtained by Gordon, Newman & Tobias (1966) for the same electrolyte. Here T is the Kelvin temperature. The accuracy of the above calculation is within 4 %. This relation was also used for the solutions with weight concentration of glycerol in the electrolyte of up to 40 %. The addition of glycerol to the electrolyte solution makes it possible to vary the value of ν in the range $1{\cdot}06 \times 10^{-6}$–$3{\cdot}4 \times 10^{-6}$ m^2/s; the Prandtl numbers were respectively within the range 1700 to 18400. The diameter of the spherical transducer was measured using a microscope calibrated to 1 μm. The difference between the maximum and the minimum values of any of the fabricated transducers was no more than 10 μm. For subsequent calculations we took the average value as the actual diameter.

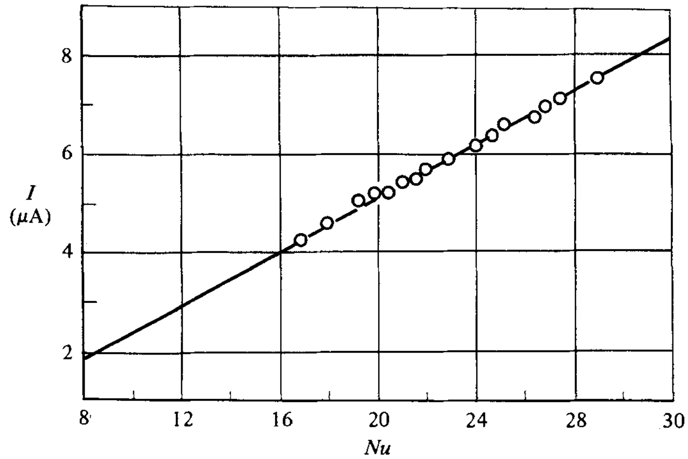

FIGURE 6. Calibration curve obtained in a uniform flow for the transducer with $d = 0{\cdot}53$ mm.

In carrying out the experiments, it is important to confirm that the results obtained represent correctly the physical process. Therefore the results should be compared with the data of other authors or the experimental results should be obtained by several independent methods. In the uniform-flow measurements we followed the first route, since here there are data from several authors, whereas for the velocity-gradient flows the literature lacks such data and we used the second method. The first method is the application of the theory of the electrochemical technique which permits us to measure the mass-transfer intensity via the transformation of the experimental electric values. The other applied method consists in the application of the theoretical relations for other hydrodynamic conditions supported experimentally many times for the transducer calibration. Thus, for a uniform flow the curves $Nu = f(I)$ were plotted, then in a flow with a transverse velocity gradient the mass-transfer intensity was determined according to the diffusion-current values. For the uniform flow the formula obtained by Acrivos & Taylor (1962) was used in the form

$$Nu = 0{\cdot}991 Pe^{\frac{1}{3}}.$$

The calibration straight line is illustrated in figure 6.

4. Discussion

The present study is devoted to the experimental investigation of the effect of a transverse velocity gradient on the mass transfer between a stationary fixed (i.e. non-rotating) solid spherical particle and liquid. We have also measured the mass-transfer intensity between a sphere and liquid in a uniform flow. Results for the uniform flow are given in figure 7 in the range of Reynolds numbers $Re = 0{\cdot}4$–20, where $Re = Vd/\nu$. The plot demonstrates their good agreement with the Aksel'rud and Acrivos & Taylor theoretical relationships for the Stokes particle flow. All experimental data lie within the interval between these theoretical curves, and no explicit trend to an increase or a decrease in the constant of proportionality (to $Pe^{\frac{1}{3}}$) has been revealed. Therefore it can be concluded that in practical calculations both formulas can be successively used accurately to ±4 %. Figure 8 shows our measurements of the intensity of the mass transfer between a fixed solid sphere and liquid in a simple shear flow. Also shown in the figure is the theoretical relation

$$Nu = 1{\cdot}134 Pe^{*\frac{1}{3}}$$

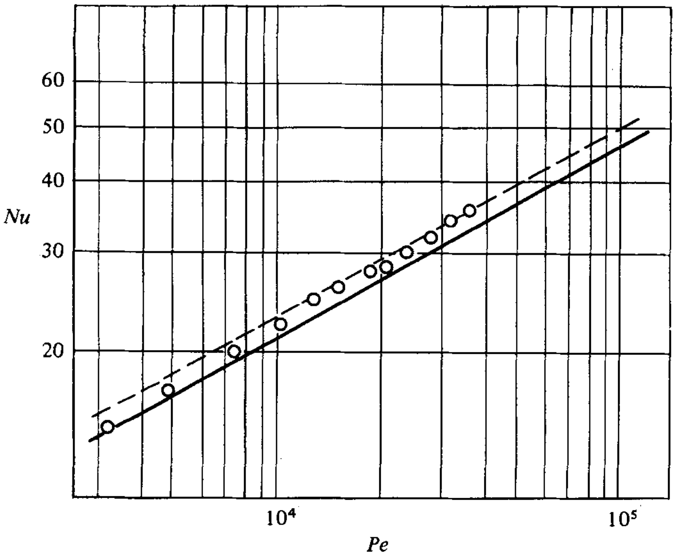

FIGURE 7. Mass-transfer intensity between solid spherical particle and liquid in uniform flow. Heavy line corresponds to $Nu = 0{\cdot}991Pe^{\frac{1}{3}}$, dashed line corresponds to $Nu = 1{\cdot}075Pe^{\frac{1}{3}}$. Dimensionless parameter $Pe = Vd/D$, where $V = 2\pi r/t$. ○, data of the present study.

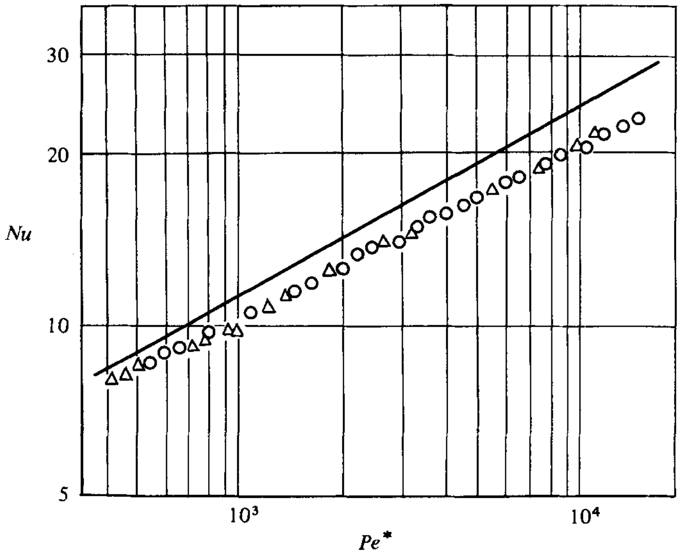

FIGURE 8. Mass-transfer intensity between a fixed solid spherical particle and liquid in simple shear flow. Heavy line corresponds to $Nu = 1{\cdot}134Pe^{*\frac{1}{3}}$, where $Pe^* = \epsilon d^2/D$ and $\epsilon = V/h$ (velocity gradient). ○, data obtained according to the calibration curve; △, data obtained from $Nu = Id/FSC_f D$.

obtained by Batchelor (1979) for the case of a sphere in a steady pure straining motion of the liquid. Our data show the same dependence on Péclet number but a value of the proportionality constant which is about 10 % smaller would give a better fit with the data. There is no *a priori* reason why values of the constant should be exactly the same for an ambient pure straining motion and for a fixed sphere in an ambient simple shearing flow. We may conclude that the ranges of Pe^* and Re^* realized in the experiment are such that the mass transfer between the fixed solid sphere and

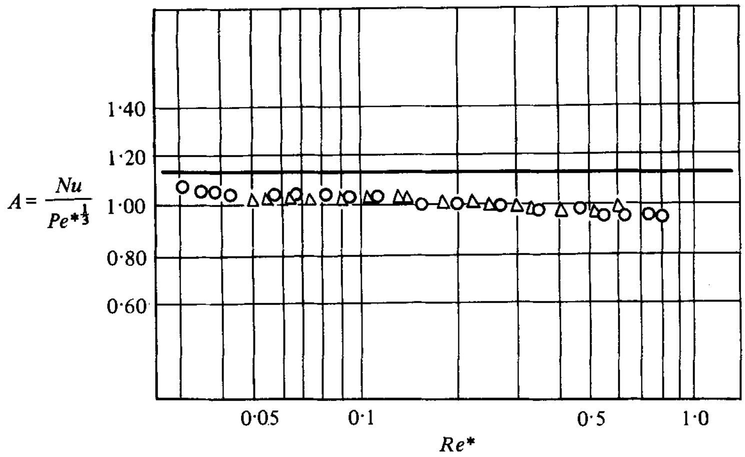

FIGURE 9. Evolution of value of A as $Re^* \rightarrow 0$. The straight line corresponds to $A = 1{\cdot}134$. ○, data obtained from the calibration curve; △, data obtained according to $Nu = Id/FSC_f D$.

liquid in a simple shear flow is also described by a relation of the type $Nu = A\,Pe^{*\frac{1}{3}}$, which results from the convective-diffusion equation with a boundary-layer approximation.

A tendency for the experimental and approximate curves to come together as $Re^* \rightarrow 0$ is evident in figure 9. For $Re^* < 0{\cdot}1$ the mean deviation of A from the straight line corresponding to $A = 1{\cdot}134$ is below 6–7 %. This deviation is within the experimental error. Unfortunately, we cannot extend the range owing to the further decrease of Re^*, since a glycerol content above 40 % leads to solution instability. In addition the size of the transducer cannot be decreased any more either, since the conducting leads have finite diameters and their disturbing influence increases with decrease of the sphere size. In the applied transducers the area of the conducting leads and of the spherical transducer did not exceed 2 % of the total sphere surface.

As noted above, for the velocity-gradient flows the measured values were processed by two independent methods; therefore in figures 8 and 9 two types of points are represented. The plots indicate that both types of point lie on the same curve to a high degree of accuracy. Hence, the experimental results are in good agreement with the theoretical approximate expressions of the mass-transfer intensity from a sphere to liquid in uniform and simple shear flows obtained from the approximation of a concentration boundary layer at the surface of the sphere.

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