RESULTS AND DISCUSSION

Solubility data for the chlorobenzene isomers were obtained from the Dow Chemical Company via a private communication. At a solution concentration of 60% para- and 40% orth-dichlorobenzene, by weight, a slight variation was noted between the solubility data provided by Dow and the solubility data observed by the authors of this paper. The solubility data obtained by the authors were about 0.8°C higher than the data provided by Dow for the aforementioned concentration. This discrepancy was carefully investigated using a calibrated thermometer with an accuracy of ±0.05°C. This observation was important, since a supersaturation level of 0.6°C was the largest supersaturation level the solution would support before spontaneous, homogeneous nucleation would occur.

Although the organic solution, in the absence of any seed crystals, could be supercooled 0.6°C before any homogeneous nucleation would occur, crystallization occurred at lower levels of supersaturation if a crystal were present but uncontacted in the solution.

Using the experimental procedure previously described, a crystal attached to a stirring rod could be placed without contact into a solution supersaturated from about 0.3° to 0.6°C with the result that many nuclei would be formed; however, if the same procedure is repeated at a lower supersaturation level (less than about 0.3°C), no nuclei are formed. What was observed to happen was that at the higher supersaturation level (0.3° to 0.6°C), the crystal growth rate was quite great with dendritic growth occurring. Being mechanically weak, these dendrites, owing to their mass, broke away from the parent crystals and fell to the bottom of the vessel giving birth to a host of progeny. This phenomenon was described as needle breeding by Mason and Strickland-Constable (1963). At supersaturation levels less than about 0.3°C, the growth rate was reduced and dendritic growth didn't occur, so no nucleation of the noncontacted crystal occurred.

Experiments performed at a supersaturation level of about 0.2°C with no crystal contact resulted in no nuclei being formed. If at this same supersaturation level the seed was slid along or tapped softly against the bottom of the vessel or carefully rubbed with another glass rod, formation of new crystals always resulted. Qualitatively, it was observed that the greater the force of contact between the crystal and the solid object it was being contacted with, the larger the number of crystals formed. Generally, the number of crystals produced by the gentle contacting procedures were in the range of two to six.

It can therefore be concluded that para-dichlorobenzene crystals in solutions of para- and ortho-dichlorobenzene do exhibit the phenomena of initial breeding, needle breeding, and contact nucleation similarly to aqueous solutions of inorganic salts, aqueous solutions of citric acid, and benzophenone from its melt.

ACKNOWLEDGMENT

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The Effect of Single Stationary Objects Placed in the Fluid Stream on Mass Transfer Rates to the Tube Walls

SLOBODAN K. KONČAR-DJURDJEVIĆ and ALEKSANDAR P. DUDUKOVIĆ

Department of Chemical and Metallurgical Engineering Faculty of Technology and Metallurgy, Beograd, Yugoslavia

Mass transfer rates to tube walls or to single spheres, cylinders, and other objects suspended in the flowing stream have been studied extensively. However, the effect of objects placed in tubes on mass transfer to the walls, to our knowledge, has not been investigated. The interaction of the wake formed by the body with the boundary layer at the tube wall affects the local mass transfer rates and deserves further attention. This phenomenon of wake —boundary layer interaction is interesting from the fundamental point of view. At the same time, its better understanding may lead to improved performance (design) of related process equipment.

The objective of this work was to investigate the effect of stationary geometrical objects placed into a fluid stream on the mass transfer rates to the wall of a cylinder through which the fluid is flowing. The presence of a single stationary body in the fluid is reflected on mass transfer due to the reduction of the free cross section, that is, increase of the flow velocity around the body, and due to the wake formed beyond the body. Both effects should increase the mass transfer rate. By applying the adsorption method to the study of mass transfer in such cases, one could expect to obtain not only discrete, local values of mass transfer, but also a complete image of this complex diffusion field.

Correspondence concerning this note should be addressed to Aleksander P. Dudukovic, Department of Chemical Engineering, Facuity of Technology, 21000 Novi Sad, Yugoslavia.

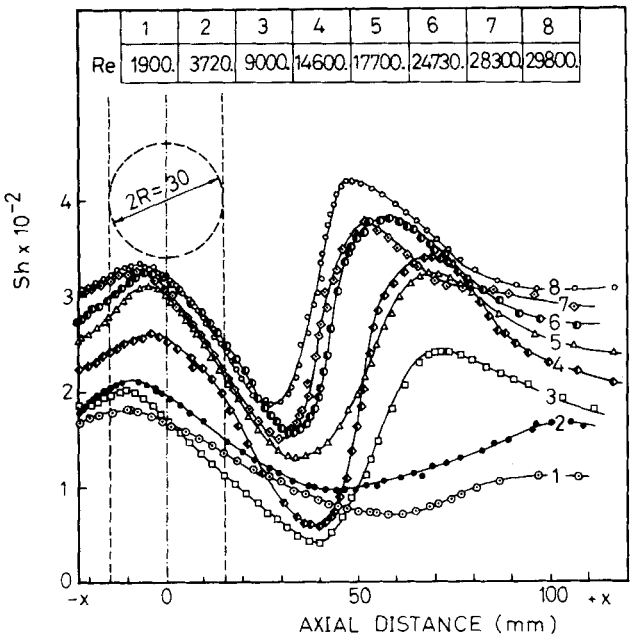

Fig. 1. Local Sherwood number vs. tube wall length. Coaxially sphere of 1/2 *d*.

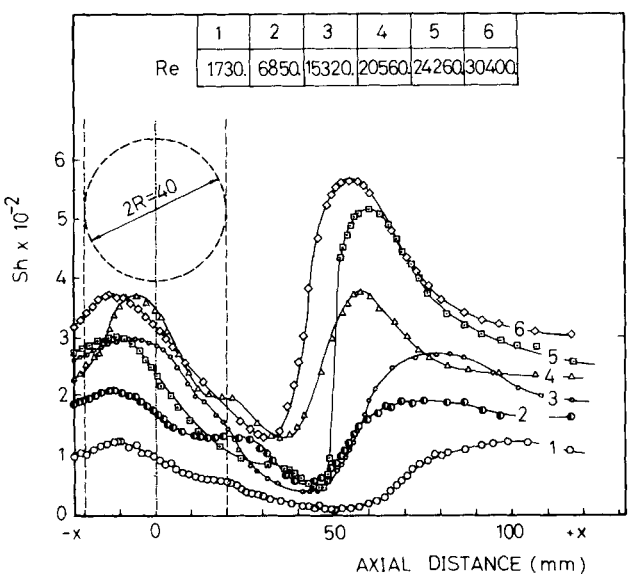

Fig. 2. Local Sherwood number vs. tube wall length. Coaxially sphere of 2/3 *d*.

EXPERIMENTAL METHOD

The mass transfer to tube walls was measured by the adsorption method developed at the Faculty of Technology and Metallurgy in Belgrade by Končar-Djurdjević (1949, 1953, 1956) and Mitrović (1965). This method has been previously utilized for similar investigations (Popović and Končar-Djurdjević, 1963; Mitrović and Končar-Djurdjević, 1963; Duduković, 1974; Vuković and Končar-Djurdjević, 1975). The method is based on adsorption of a dye from aqueous solutions on the walls or bodies coated with white adsorbents. The resulting colorings on the bodies (adsorption spectra) are proportional to the mass transferred. By colorimetric measurements of the colored areas it is possible to determine the amount of transferred dye per unit of surface area. The transfer parameters can be obtained as shown below.

The method is based on the assumption that under specific conditions and over defined time intervals, mass transfer by adsorption may be considered as a stationary isothermal process with constant concentration gradients

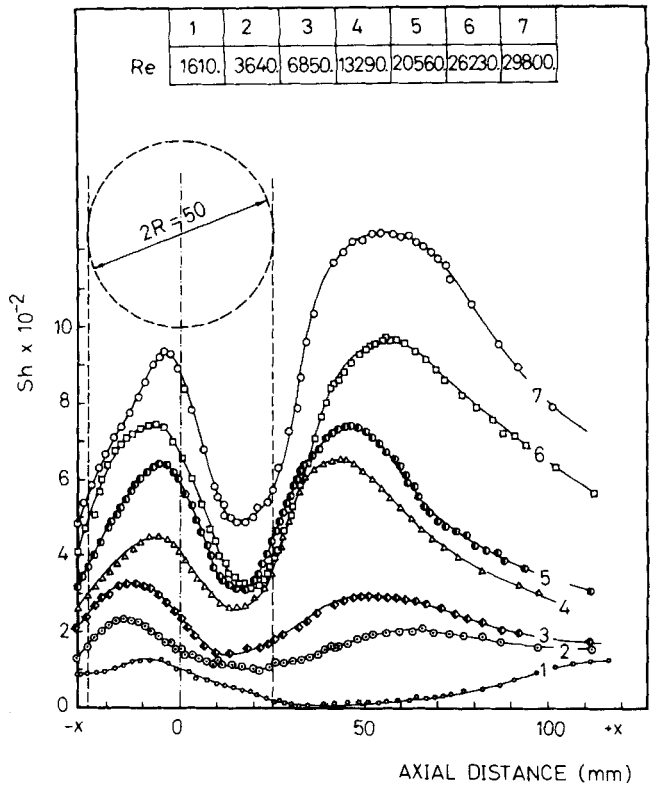

Fig. 3. Local Sherwood number vs. tube wall length. Coaxially sphere of 5/6 *d*.

which depend only on the characteristics of the boundary layer. With short times of adsorption from highly dilute solutions, the overall transfer rate is controlled by the rate of diffusion through the boundary layer. Under such conditions, the concentration of the adsorbing species immediately above the adsorbent surface is essentially zero.

Silica gel deposited as a thin film on aluminium foils (Merck, DC-Alufolien Kieselgel, Art. 5553) was used as the adsorbent; methylene blue (Merck, Methylenblau B, Art. 1283) dissolved in water was used as the adsorbing species. The intensity of silica gel coloration is a function of the transferred methylene blue mass and consequently of the thickness of the boundary layer above the surface over which the solution flowed.

Quantitative results of mass transfer were obtained by reflected light intensity measurements. The dependence of the reflection on mass transferred per unit surface area was determined earlier by Cvijović and Mitrović (1969).

The concentration of methylene blue aqueous solution was $2.5 \cdot 10^{-3}$ g/l, and the total adsorption time was 6 min. It was previously determined by Končar-Djurdjević and Duduković (1975) that the equilibrium methylene blue surface concentration on silica gel with solution concentration of 10^{-4} g/l is $1.084 \cdot 10^{-6}$ g/cm^2. This solution concentration is only 4% of the concentration of the solution we worked with in the present study, and the mass transferred per unit surface area in this work was much lower than the above mentioned. Therefore, in our experiments it may be considered, with satisfactory accuracy, that the concentration immediately above silica gel surface is equal to zero.

The Schmidt number for this system is $2.12 \cdot 10^3$.

APPARATUS

A single body was placed coaxially in a Plexiglas tube of 60 mm diameter. Three sizes of spheres, a hemisphere, and a disk were used. The object was always placed 35

tube diam from the entrance so that the flow in the tube was fully developed prior to reaching the obstruction. The spheres were fixed by a steel shaft, 1.8 mm thick, mounted perpendicular to the flow direction. Other bodies had an additional support for maintaining the desired position. It was found that the supporting shafts interfered with the flow only slightly and affected the adsorption spectrum only within several millimeters of the shafts.

The diameters of the spheres were 30, 40, and 50 mm and of the hemisphere and disk 40 mm. The hemisphere was mounted so that the spherical part faced the upstream direction. The 3 mm thick disk, tapered around the circumference at a 45 deg. angle in the downstream direction, produced an effect analogous to that of an extremely thin disk placed in the fluid stream.

Silica gel coated foils were placed on the tube wall around the body. Owing to their flexibility, the foils fully adhered to the tube wall.

RESULTS

Experiments were made of local mass transfer as a function of the distance along the tube at different Reynolds numbers, and for the sphere, a dependence on the ratio of sphere and tube diameters was also investigated.

The total adsorption time was 6 min; 1 min was required for filling and emptying the operating tube and 5 minutes for adsorption at stationary flow conditions. Independent measurements were made of the mass transferred per unit surface area during tube charge and discharge. This was subtracted from the total mass transferred per unit surface area during the experiment, yielding the mass transferred per unit area during stationary flowing under desired conditions.

When the conditions under which mass transfer by adsorption may be considered stationary are satisfied, the coefficient of mass transfer may be determined. Since the methylene blue concentration in the fluid immediately above silica gel surface, as demonstrated, may be considered in our case as approximately equal to zero, a simplified equation is obtained:

$$k = \frac{C_p}{\theta \cdot c_o}$$

Local Sherwood numbers were calculated as

$$Sh = \frac{k \cdot d}{D}$$

and are presented as a function of the distance along the tube, where $x = 0$ is the normal projection of the body center on the tube wall. The positive direction of the x axis is in the direction of fluid flow. Individual curves in Figures 1 to 5 correspond to different values of Reynolds numbers.

Figures 1, 2, and 3 show the effects of the 30, 40, and 50 mm spheres on the local mass transfer along tube wall for different ratios of sphere and tube diameters (1/2, 2/3, 5/6).

Figure 4 shows the effect of the 40 mm diameter hemisphere on local mass transfer and Figure 5 the effect of the 40 mm diameter disk.

DISCUSSION

The curves in Figures 1 through 5 which show the dependence of the local Sherwood number on the distance along the tube have several common characteristics for all bodies and all Reynolds numbers. At larger distances in front of and behind the body, all curves tend to reach some

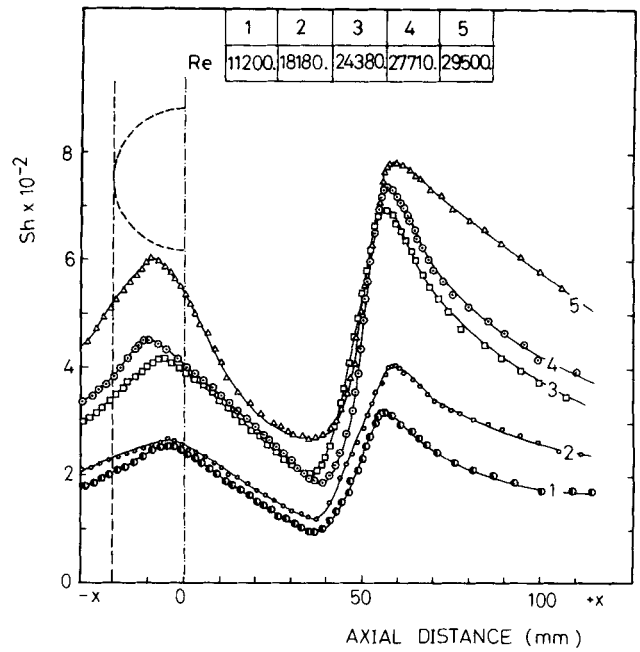

Fig. 4. Local Sherwood number vs. tube wall length. Coaxially hemisphere of 2/3 *d*.

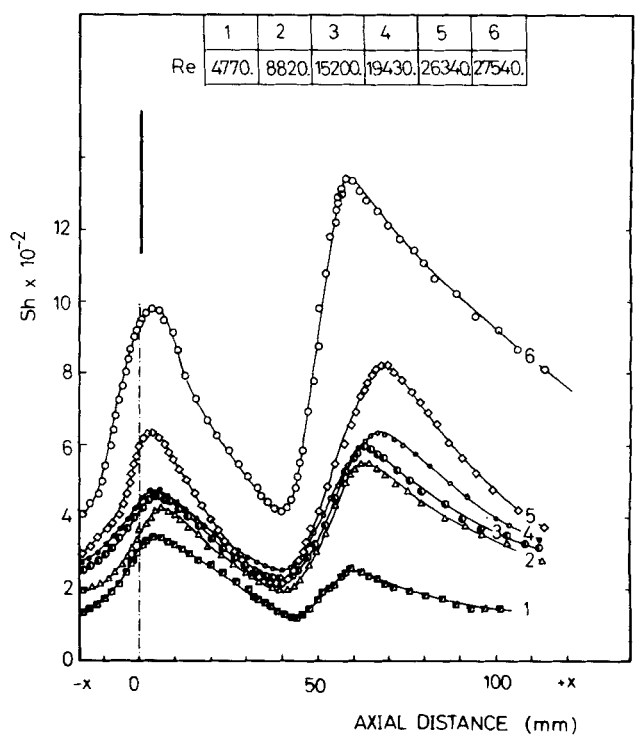

Fig. 5. Local Sherwood number vs. tube wall length. Coaxially disk of 2/3 *d*.

constant value of Sherwood number, characteristic for the undisturbed flow through an empty tube at that Reynolds number. In addition, one immediately observes two maxima and one minimum, where the first maximum is lower than the second one. The sudden rise of the curves between the minimum and second maximum is also characteristic.

The first maximum is due to two effects. An increase of the velocity gradient in the axial direction results from the

narrowing of the effective cross section available for flow because of the presence of the body. This causes a decrease in boundary-layer thickness at the wall. In addition, the fluid obtains, owing to the deflection by the body, a velocity component perpendicular to the tube wall that also decreases the boundary-layer thickness. The first effect is most intense at $x \approx 0$ and the second at $x \approx -R$. Owing to the superposition of the two effects, the first maximum for the Sh number occurs for $-R < x < 0$. Exceptions are the curves for the disk, because in this case the deflection occurs only at $x \approx 0$. Consequently, the first maximum is immediately behind the point $x = 0$.

The minimum and second maximum for the curves are due to the annular wake, formed behind the body, and its effect on the fluid flow. Fluid behind the body is sucked into the wake, causing an increase of boundary-layer thickness at the wall. This leads to the decrease of the local Sherwood number.

Owing to the instability and separation of the wake beyond the body, the turbulence intensity increases in the zone beyond the wake. The turbulent pulsations penetrate deeper into the laminar sublayer, causing a reduction of the diffusion sublayer thickness. This leads to the increase of the local Sherwood number.

For bodies of identical diameters, the difference between the minimum and second maximum is the smallest for the sphere, larger for a hemisphere, and the largest for a disk, because the wake beyond the bodies of these geometries gains intensity in the same order. This also applies to the values of the Sherwood number at the second maximum. The difference in the Sh number between the minimum and second maximum, as well as the value at the second maximum, increases with increasing Reynolds number for the same reasons.

The analysis of the results for spheres of different diameters indicates an increase in the Sh number at both maxima and an increase of the difference between the minimum and second maximum with the increase of sphere diameter. This is due to the decrease of the free cross section between the sphere and the wall, as well as between the wake and tube wall, resulting in a higher influence of the sphere and wake beyond it on the velocity gradients along the walls.

NOTATION

c_o = bulk methylene blue concentration in the fluid
C_p = surface concentration of methylene blue on the silica gel transferred during stationary flow
d = tube diameter
D = diffusion coefficient
k = mass transfer coefficient
R = body radius
Re = Reynolds number
Sh = local Sherwood number
x = distance along the tube
θ = stationary adsorption time

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Prediction of Heat Transfer Coefficients in Drag Reducing Turbulent Pipe Flows

AFSHIN J. GHAJAR and WILLIAM G. TIEDERMAN

Oklahoma State University
Stillwater, Oklahoma 74074

In this prediction method, an eddy diffusivity model proposed by Cess (1958) and the Reynolds analogy are used to integrate the momentum and energy equations for the case of constant heat flux in fully developed, turbulent pipe flows. The unique feature is that in drag reducing flows, it is not possible to determine one of the constants in the eddy diffusivity model a priori. An iterative scheme proposed by Tiederman and Reischman (1976) is used to determine the constant A^+ which characterizes the thickness of the near-wall region of the flow. This iterative scheme requires as inputs an experimental value for the von Karman constant K and some initial guess for A^+. The procedure then determines an exact value for A^+ and integrates the equations to yield velocity and temperature profiles. From this point, heat transfer calculations are straightforward, as the heat transfer coefficient is then determined by evaluating the temperature gradient at the wall and the mixed mean or bulk temperature of the flow.

ANALYSIS

The eddy diffusivity expression proposed by Cess (1958) is

$$E = \frac{\epsilon_M}{\nu} = \frac{1}{2}\left\{1 + \frac{K^2 r_o^{+2}}{9}[1 - (r/r_o)^2]^2\right.$$