INTERFACIAL HEAT AND MASS TRANSFER
IN THE TURBULENT FLOW AND ITS EXPERIMENTAL VERIFICATION

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Various methods have been discussed of experimental measurement of interfacial mass transfer under the turbulent flow in a tube at high values of the Schmidt number. Difficulties and short-comings have been discussed of the determination of the mass transfer coefficient k_∞^+, *i.e.* the quantity necessary for experimental verification of theoretical models. Necessity has been stressed of devising special experiments to further elucidate the mechanism of interfacial heat and mass transfer in the turbulent flow.

Interfacial heat and mass transfer in the turbulent flow remains in the focus of attention as may be documented by updated reviews[1-11] of models. Increasing number of these models testifies to the fact that few, if any, of the so far published models are capable, on the basis a single concept, of describing satisfactorily the mechanism of turbulent heat transfer between two immiscible phases in the whole real range of the Prandtl (Schmidt) number Pr (Sc). This situation is a consequence of the following reasons. It has been generally known that hydrodynamic conditions at the interface play a major role in affecting the transport phenomena. The formulation of the model must therefore start from the knowledge of the hydrodynamics in the close proximity of the interface. Its description, however, is usually very difficult. The difficulties are circumvented by application of various simplifications which limit the validity of the given model. This can be documented by a series of models (the film, penetration, surface renewal, surface rejuvenation, turbulent diffusivity and other models). Attempts for a more detailed description of the situation at the interface have lead, apart from frequent inveritability, to mathematical complexities of the models, which strongly limits their application.

Criteria for verification of a formulated model are suitable experimental data. The term suitable means such data, for which all necessary parameters and experimental conditions are known, experimental errors are well established and systematic errors eliminated. The mechanism of heat or mass transfer has been verified almost always by an experimental technique using a smooth tube and the usual result has been the dependence of the coefficient of heat or mass transfer on the Prandtl or the Schmidt number, eventually on the Reynolds number or the L/d ratio. The coefficient of heat and mass transfer has been usually presented in the dimensionless form in terms of the friction velocity $k^+ = k/u^*$. One has to carefully distinguish between dimensionless heat or mass transfer coefficients defined differently. From local values of the coefficient of mass transfer, k_x^+, one can derive both the average (averaged over the tube length, L), k^+, and the steady state value, k_∞^+. The local value, k_x^+, is obtained by averaging the mass transfer coefficient over a period of time and an infinitesimal surface along the circumference of the tube at a distance x measured from the inlet into the heat or mass transfer section. In the literature most often exa-

mined region falls between $Sc \approx 1$ and $Sc \sim 10^3$. From the comparison of the experimental data k_{∞}^{+} with the values predicted from various models it follows that the agreement between the theory and experiment is satisfactory. A different situation occurs in region of very low values of Sc ($Sc \ll 1$) and also very high values of Sc ($10^3 < Sc < 10^6$). It is particularly the region of extremely high values of Sc where we find not only considerable discrepancies between experimental data as well as between theoretical models[12,13]. It is therefore useful to examine this region in more detail.

The aim of this work is to critically review methods of obtaining and processing experimental data in region of very high Sc values, to review methods of verifying theoretical models as well as shortcomings that may be possibly encountered.

EXPERIMENTAL

Since thermal conductivities do not reach values as low as molecular diffusivities, experiments used to obtain data are based on mass transfer. For the verification of the dependence of the mass transfer coefficient on Sc, Re, L/d the model experiment is based on the observation of the rate of mass transfer from the internal surface of a poorly soluble tube into a turbulently flowing liquid (the method of soluble wall). As an advantage of this system appears the fact it is well defined. For the manufacture of the soluble section of the wall various materials have been employed e.g. cinnamic acid, β-naphthol, oxalic acid and natrium chloride, but the most frequently used substance is benzoic acid. Used solvents involve water, methocell and others. The widest application, however, received glycerol, aqueous solutions of which enable easy variations of Sc in the range of several orders of magnitude. A detailed description of this system is given e.g. by Harriot[14] or Vašák[13].

It is a well-known fact that in the region of high Sc numbers all resistance to mass transfer is concentrated into a thin film along the interface, the concentration boundary layer. As the thickness of the concentration boundary layer markedly decreases with increasing Sc (Vieth, Porter and Sherwood[15] report estimates of the thicknesses for $Re = 30\,000$ and $Sc = 9\,000$ $\delta_c = 0.019$ mm and for $Sc = 27\,000$ already as little as 0.012 mm), the requirements on the quality of the internal surface of the soluble experimental section increase proportionally. The effect of gradual improvement of the quality of the internal surface of the soluble section on the course of the experimental dependence of the dimensionless mass transfer coefficient on the Schmidt number is shown in Fig. 1. Certain scatter, of course, is the result of not entirely identical experimental conditions. The highest of the experimental points were measured on experimental sections manufactured by casting[16,17] (○). It has been found out, however, that solidification gives rise to cracks in the internal surface of the experimental section and these cracks increase the mass transfer coefficient. The next stage in the development of the technique of preparation of the experimental section was a section assembled of individual segments prepared by pressing[14,18] (●).

The quality of the surface of these segments was already good, free of the cracks. This method appears in principle very advantageous, for the loss of weight of a segment permits determination of the average coefficient of mass transfer (averaged over the length of the segment) in dependence on the distance from the inlet end of the experimental section. Unless the value of k^+ on the following segments further decreases, the obtained k^+ is regarded to be k_∞^+, i.e. the steady state value. Vašák[13], however, found that due to the effect of the tolerance of the size of individual molded segments, the internal and external surface of the segments after assembly are not precisely coaxial (see Fig. 2 showing exaggerated flaws of alignment). This disalignment, after fitting the external surfaces of the segments, brings about flaws of smoothness of the internal surface. These imperfections need not be very large in order to partially or totally homogenate the liquid in the thin laminar sublayer. On the leading edge of every segment, and particularly that part of the circumference that protrudes toward the axis of the tube, thus appears a new concentration boundary layer. The experimental values of the mass transfer coefficient then do not correspond to the sought values k_∞^+ but, instead a higher pseudo-steady state value affected by the suggested mechanism. From Fig. 1 it is apparent that data obtained in this
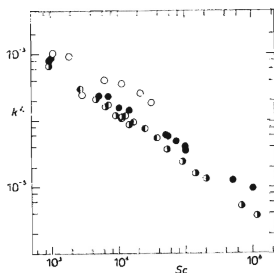

FIG. 1

Effect of gradual improvement of the quality of internal surface of a soluble tube on the course of the experimental dependence of k^+ versus Sc. ○ Section manufactured by casting, ● section assembled from segments manufactured by pressing, ◑ seamless section manufactured by pressing, ◐ nickel experimental section
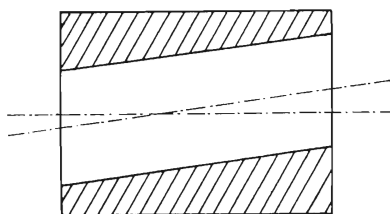
FIG. 2

Disalignment of the external and internal surface of segments after pressing (exaggerated)

manner (●) markedly deviate, especially at high values of Sc, from the third group of data[19] (⊙) where the effect of transitions between individual segments on the mass transfer coefficient has been eliminated and which are the lowest. In this case the experimental section was again manufactured by pressing but without contact surfaces. Nevertheless, even in this case partial damage of the internal section may occur either due to the dissolution proper or due to the erosion by the turbulent flow.

Principally different is the model experiment based on the electrochemical reaction taking place on the internal surface of a tubular electrode passed by an electrolyte (electrochemical method). A more detailed description of the method may be found elsewhere[20-22]. Among the most often used systems belongs the ferrocyanide–ferricyanide system in an aqueous solution of NaOH, when the $Fe^{II} \rightleftharpoons Fe^{III}$ redox reaction takes place on a nickel or platinum electrode. The change of Sc is effected by a change of concentration of NaOH, a change of temperature or by addition of a viscous substance (e.g. ethylenglycol). A disadvantage of the electrochemical method is the difficulty of achieving high values of Sc. Thus far realized experiments in the turbulent region covered[23] range up to $Sc = 37\,000$ in comparison with $Sc \approx 10^6$ for the method of wall dissolution. Difficulties arising from insufficient polarization of a longer experimental section were removed by Grassman and Tuma[25]. The development of the electrochemical experimental method of measurement of the mass transfer coefficient has lead, similarly as in the case of soluble wall, to gradual decrease of k^+. Recent data (○) are also shown in Fig. 1. It is seen that their agreement with the results obtained by dissolution of an unsegmented experimental section (⊙) is very good.

It may be therefore concluded that there exist two methods for the determination of the mass transfer coefficient in region of very high values of the Schmidt number: the electrochemical method and the method of soluble wall. Progress in both techniques has lead to the situation that k^+ values obtained by these two independent methods agree in the investigated range of Sc values. From the analysis of experimental data it is seen that only data from the papers of Kishinevskii and coworkers[19] (soluble wall method) and Grassmann and Tuma[25] (electrochemical method) may be regarded as correct. At the same time, however, the data of Kishinevskii and coworkers represent k^+ values while those of Grassmann and Tuma are supposedly k_∞^+ values. This may be explained by the fact that in region of low Sc values, the value of k_x^+ almost instantaneously equalizes with k_∞^+ and hence $k^+ \approx k_\infty^+$. On the contrary, in region of high Sc values it may be expected that the data of Kishinevskii and coworkers are influenced by the averaging across the length of the experimental section and cannot be regarded as k_∞^+ but instead k^+. In this region the electrochemical method data are missing, and hence a comparison is impossible.

Certain scatter of the experimental data may be accounted for as effects of factors as vibrations, the L/d ratio, dependence of the friction coefficient on Re, eventual

hydrodynamic disturbances in the entrance and the exit region, or the concentration dependence of diffusivity. These factors have been mostly neglected. It is believed that both methods have been worked out to the extent that the principal effects of the roughness of the internal surface of the tube and the contact surfaces between the segments have been eliminated. Nevertheless, no experiments have been carried out in region of high Sc, which would permit one to distinguish whether the measured values of k^+ or k_x^+ may be regarded with sufficient accuracy as k_∞^+. Thorough analysis of this problem and its consequences is given below. We shall there make use of the above classification of experimental data and the problem shall be illustrated on some theoretical models.

THEORETICAL MODELS

The usual approach in the literature is that the experimental data obtained at high Schmidt numbers are declared to be k_∞^+ and correlated on the basis of turbulent diffusivity[26]. It is also expected that the correlation should yield either the relation

$$k_\infty^+ \sim Sc^{-2/3} \tag{1}$$

or the relation

$$k_\infty^+ \sim Sc^{-3/4} . \tag{2}$$

The last two expressions were derived from the asymptotic relationships for the turbulent diffusivity in the close proximity of the wall. Eq. (1) was used by Harriott and Hamilton[14] or Gukhman and Kader[18] to correlate their experimental data. Similarly Kishinevskii and coworkers[19,24] used Eq. (2). It is apparent that with increasing value of Sc the difference between Eq. (1) and (2) becomes more marked. The fact that both Gukhman and Kader[18] and Kishinevskii and coworkers[19] carried out their measurements up to $Sc \approx 10^6$, when the difference between Eqs (1) and (2) is significant, casts some doubt on the validity of the model of turbulent diffusivity or the correctness of the experimental data. For this conclusion testifies also the fact that Shaw and Hanratty[23] correlated their data, measured by the electro-chemical method, by the following equation

$$k_\infty^+ \approx Sc^{-0.704} \tag{3}$$

in the range $700 < Sc < 37\,000$ in which the exponent of Sc falls between $-2/3$ and $-3/4$; this value is unadmissible from the standpoint of the theory of the limiting expressions for the turbulent diffusivity.

In the light of this discrepancy it appears as more advantageous the model of Kolář[27]. Even though the theoretical concept of the model represents a certain simplifica-

tion of the process at the interface, the model is capable of describing the mechanism of mass transfer in the region $3 \cdot 10^{-3} \leqq Sc \leqq 10^6$, as has been found in previous works[27-29]. For the steady state value of the dimensionless mass transfer coeficient, k_∞^+, the model[27] yields for $Sc \geqq 10$ a simple expression as

$$k_\infty^+ = 1/(\delta^+ Sc + Sc^{1/2}\lambda^+ \sqrt{(\pi)}/2), \qquad (4)$$

where δ^+ and λ^+ are dimensionless thicknesses of the laminar sublayer and the transition layer. In the original paper[27], the values of the dimensionless thickness of the laminar sublayer $\delta^+ = 1$ and the transition layer $\lambda^+ = 20$ were computed from the experimental mass transfer coefficients for $Sc = 1$ and $Sc = 100$ for $Re = 10\ 000$, i.e. in region where the experimental data may be regarded as correct and reproducible. With this low values of Sc, however, the thickness of the laminar sublayer has a small effect on the mass transfer coefficient. It would have been therefore more advantageous to determine the value of δ^+ from Eq. (4) for $Sc \gg 1$ as the term with λ^+ for such conditions vanishes and Eq. (4) changes to a simple film theory, i.e.

$$k_\infty^+ = 1/(\delta^+ Sc). \qquad (5)$$

As has been already noted, the value k_∞^+ may be in principle obtained from the local value k_x^+ for sufficiently high x under the conditions of a steady concentration profile within the laminar sublayer or from the averaged value of k^+ measured on a substantially greater length of the experimental section, L. This problem has been examined in the earlier papers[28,29] and it has been shown that in the region of high Sc numbers the dimensionless length of the entrance section, L^+, required to develop, in our case linear, concentration profile in the laminar sublayer strongly depends on Sc. This work shows for clarity in the graphical form in Fig. 3 the dependence of the L/d or x/d ratio on the Schmidt number for both above given methods of determination of the mass transfer coeficient, namely for $Re = 10\ 000$. The solid line in Fig. 3 shows the ratio of the length and the diameter of the experimental section required to get the local value of the mass transfer coefficient, measured at the end of the experimental section, by 5% (arbitrarily selected) higher than the steady state value, i.e. $k_x^+ = 1{\cdot}05k_\infty^+$. It is apparent that lower percentual deviations from steady state values can be reached at higher values of the ratio considered, as may be calculated from Table II published by Vašák and coworkers[28]. Similarly one can use the broken line for the averaged value of the mass transfer coefficient. For the latter value we can write $k^+ = 1{\cdot}05k_\infty^+$. From comparison of both dependences it follows that the length of the experimental section in the latter case is about eight times greater. The chosen value of 5% deviation corresponds approximately to the accuracy with which one can determine the mass transfer coefficient. Shorter

length of the entrance region can be achieved by measurement at higher Reynolds numbers but the feasibility of the experiments at correspondingly high volume flow rates is impaired, not to speak about other problems associated with high rates of energy dissipaton.

The aim of the experiments is mostly to verify the model concepts of the mechanism of heat or mass transfer under the turbulent flow regime. On an example it will be shown the manifestations of the effect of the length of the entrance region in the interpretation of measurement by the model of turbulent diffusivity and the model due to Kolář[27]. Let us assume that we have obtained values of the mass transfer coefficient on an experimental section of a given L/d ratio for two values of the Schmidt number differing by a factor of ten. The value measured at the higher of the two values of Sc was higher than the steady state value of the mass transfer coefficient, while for the lower Sc a correct value was obtained. In the case of the turbulent diffusivity model the absolute value of the exponent of the Schmidt number drops by a certain value, independent of Sc. A simple calculation shows that for the deviation of 10% the decrease of the exponent amounts to 0·041 and for 20% to 0·079. This may cause a change from the dependence given by Eq. (2) to that in Eq. (3) and further to Eq. (1) with the exponent $-2/3$, which, at the same time, corresponds to the mass transfer in region of undeveloped concentration entrance region[30,31]. This may also explain why the majority of experimental data for $Sc < 10^4$ may be correlated by Eq. (2) and the majority of data for $Sc < 10^4$ by Eq. (1). The majority of data measured for $Sc < 10^4$ are thus not k_∞^+, but k^+, affected by averaging over the length of the experimental section. For an eventual correction of δ^+ and λ^+ value, reliable experimental data covering sufficiently wide region of Sc are thus far missing.
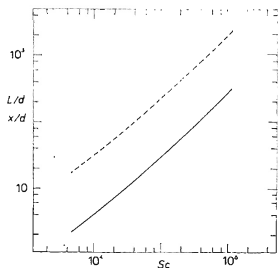

FIG. 3

Dependence of the length of the entrance region on Sc ($Re = 10\,000$); $----$ L/d, $\underline{\qquad}$ x/d

CONCLUSION

Measurements at high values of the Schmidt number, and correct and reproducible measurements with sufficiently accurate values of their physico-chemical parameters in particular are needed for correct assessment of adequacy of individual models of mass transfer in high Sc number region. More attention must be paid to both experimental work and interpretation of experimental results. Physico-chemical data should be determined by independent experiment in a sufficiently wide range of experimental conditions (the effect of temperature, concentration). Utmost attention should be given to the hydrodynamics of the flow (smooth surface, thermal regime of the experiment). As shown in Fig. 3, design of an experiment yielding k_∞^+ from either k^+ or k_x^+ data is not easy. Efforts should be aimed at working out new independent methods of determination of the mass transfer coefficient, for the authors believe that especially the method of soluble wall has been worked out to precision when further modifications cannot bring qualitative gains. It is apparent that without sufficiently accurate and reliable measurements on sufficiently long experimental sections at high values of Sc the problem of turbulent mass and heat transfer can hardly be further elucidated.

LIST OF SYMBOLS

d	diameter of experimental section (m)
k^+	dimensionless mass transfer coefficient averaged over the length L
k_x^+	dimensionless local mass transfer coefficient
k_∞^+	steady state value of dimensionless mass transfer coefficient
L	length of experimental section (L^+ dimensionless length) (m)
Pr	Prandtl number
Re	Reynolds number
Sc	Schmidt number
u^*	friction velocity (m/s)
x	axial coordinate measured from the section inlet in the direction of flow (m)
δ^+	dimensionless thickness of the laminar sublayer
δ_c	thickness of the concentration boundary layer (m)
λ^+	dimensionless thickness of the transition layer

REFERENCES

1. Sherwood T. K.: Chem. Eng. Progr., Symp. Ser. *55*, 71 (1959).
2. Harriott P.: Can. J. Chem. Eng. *40*, 60 (1962).
3. Rozen A. M.: Khim. Prom. (Moscow) *41*, 85 (1965).
4. Rozen A. M., Krylov V. S.: Int. Chem. Eng. *6*, 429 (1966).
5. Scriven L. E.: Chem. Eng. Educ. *2*, 10 (1968).
6. Scriven L. E.: Chem. Eng. Educ. *2*, 150 (1968).
7. Scriven L. E.: Chem. Eng. Educ. *3*, 26 (1969).
8. Scriven L. E.: Chem. Eng. Educ. *3*, 94 (1969).
9. Sherwood T. K., Pigford L. R., Wilke C. R.: *Mass Transfer.* McGraw Hill, New York 1975.

10. Sideman S., Pinczewski W. V.: *Topics in Transport Phenomena*, p. 47. Wiley, New York 1975.
11. Ruckenstein E.: Int. Chem. Eng. 7, 490 (1967).
12. Kader B. A., Aronov A. R.: Teor. Osn. Khim. Tekhnol. 4, 637 (1970).
13. Vašák F.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1979.
14. Harriott P., Hamilton R. M.: Chem. Eng. Sci. 20, 1073 (1965).
15. Vieth W. R., Porter J. H., Sherwood T. K.: Ind. Eng. Chem. Fundam. 2, 1 (1963).
16. Linton W. H., Jr., Sherwood T. K.: Chem. Eng. Progr. 46, 258 (1950).
17. Kishinevskii M. Kh., Denisova T. B., Parmenov V. A.: Int. J. Heat Mass Transfer 9, 1449 (1966).
18. Gukhman A. A., Kader B. A., Teor. Osn. Khim. Tekhnol. 3, 216 (1969).
19. Kishinevskii M. Kh., Kornienko T. S., Parmenov A. V.: Teor. Osn. Khim. Tekhnol. 4, 489 (1970).
20. Mizuchina T.: Advan. Heat Transfer 7, 87—162 (1971).
21. Selman J. R., Tobias Ch. W.: Advan. Chem. Eng. 10, 211 (1978).
22. Fahidy T. Z., Mohanta S.: Advan. Transp. Processes 1, 83 (1980).
23. Shaw D. A., Hanratty T. J.: AIChE J. 23, 28 (1977).
24. Kishinevskii M. Kh., Kornienko T. S., Loginov A. V.: Heat Transfer-Soviet Research 9, 26 (1977).
25. Grassmann P., Tuma M.: Ger. Chem. Eng. 1, 276 (1978).
26. Sideman S., Pinczewski W. V.: Advan. Therm. Eng. (Top. Transp. Phenom.) 6, 47 (1975).
27. Kolář V.: This Journal 42, 1311 (1977).
28. Vašák F., Kolář V., Brož Z.: This Journal 46, 1445 (1981).
29. Vašák F., Kolář V., Brož Z.: This Journal 46, 1566 (1981).
30. Krammers H., Kreyger P. J.: Chem. Eng. Sci. 6, 42 (1956).
31. Son J. S., Hanratty T. J.: AIChE J. 13, 689 (1967).

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