MASS TRANSFER INTO THE LIQUID IN TURBULENT FLOW AT HIGH SCHMIDT NUMBERS. DISSOLUTION OF BENZOIC ACID INTO AQUEOUS SOLUTIONS OF GLYCEROL FROM INTERNAL SURFACE OF THE PIPE

František VAŠÁK, Václav KOLÁŘ and Zdeněk BROŽ

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02, Prague 6 - Suchdol

Theoretical relation derived in the last study for calculation of the mass transfer coefficient in the region of not fully developed concentration profile at high Schmidt numbers has been verified experimentally. This experimental study has been devoted to measurements of the rate of benzoic acid dissolution into aqueous solutions of glycerol from the internal surface of the pipe of circular cross section in the range $933 \leqq Sc \leqq 225000$ and $5000 \leqq Re \leqq 50000$. It has been possible to explain on basis of the theoretical model, the differences between the data of various authors and to obtain a unified description of the phenomena.

In theoretical part[1], the relation has been derived describing the mechanism of mass transfer in the region of not fully developed concentration profile (entrance region) at high Schmidt numbers $(Sc \geqq 10^3)$. This relation is here verified both by original experimental data and by data published in literature.

In experimental studies of the mass transfer mechanism across the interface at high values of the Schmidt number the electrochemical method or the dissolving wall method have been used. Both these methods have found a wide application[3-6]. Their advantages and disadvantages are widely discussed in literature, therefore it is possible to summarize here, that the electrochemical method gives the mass transfer coefficients which are mostly lower than with the dissolving wall method. This situation can be seen in Fig. 1 where the experimental data of various authors are compared. It is possible to see that the given data have a considerable scatter. From the theoretical model[1] results that this scatter can be caused not only by the experimental error, but as well by variation of ratio L/d, changing value of Reynolds number or due to measurement of the mass transfer coefficient averaged over different lengths of the experimental section.

Verification of the mass transfer mechanism in the region of high Schmidt numbers has been mostly considered in the pipe of circular cross section. Therefore this experimental verification is also performed for this geometry for which the model[1] is directly applicable.

Verification of the Model for Data Published in Literature

In the preceding study[1], theoretical relations have been derived enabling calculation of laminar layer concentration profiles and values of local or averaged mass transfer coefficients in the concentration entrance section. Verification of individual relations will be made successively.

Experimental determination of the concentration profile in the laminar layer is very difficult as any intrusion into the region of thickness of the order of magnitude of several hundredths of milimeters causes a considerable disturbance of hydrodynamics. Optical methods do not give information with sufficient accuracy. Thus the shape of concentration profile in the laminar layer has not been verified with regard to the lack of suitable data.

Data giving the local dimensionless mass transfer coefficients in the concentration entrance region are in the region of large Schmidt numbers very scarce. Vašák[6] has verified the model[1] with experimental data measured by the electrochemical method at Sc = 2400 and has obtained
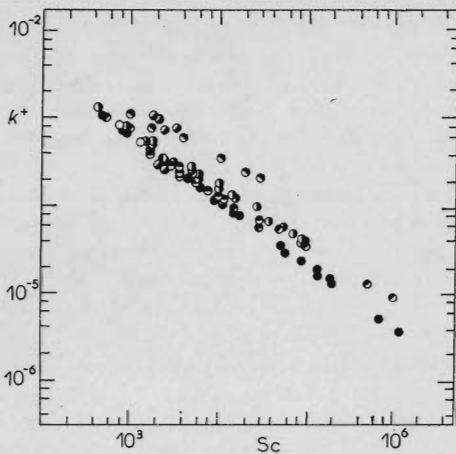

FIG. 1

Experimental data on mass transfer in the region of large Schmidt numbers. E Electrochemical method, R dissolving wall method ○ Lin and coworkers[7] E; ◑ Harriott and Hamilton[8] R; ◐ Son and Hanratty[9] E; ◓ Hubbard[10] E; ◔ Meyerink and Friedlander[11] R; ● Kishinevskii and coworkers[12] R; ◉ Gukhman and Kader[13] R; ◕ Kishinevskii and coworkers[14] R; ◒ Linton and Sherwood[15] R; ◖ Grassman and Tuma[16] E; ◗ Shaw and Hanratty[17] E)
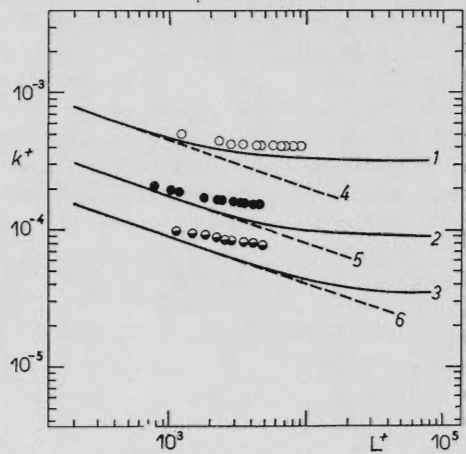

FIG. 2

Entrance section for turbulent mass transfer. *1* Sc = 2210, *2* Sc = 9310, *3* Sc = 26400 Vašák and coworkers[1], *4* Sc = 2210, *5* Sc = = 9310, *6* Sc = 26400 Krammers and Kreyger[18], ○ Sc = 2210, ● Sc = 9310, ◒ Sc = = 26400 Shaw and Hanratty[17]

an extremely good agreement. But this value of Schmidt number is from the point of the studied interval of Sc numbers too low. Data at higher Schmidt numbers have not been found in literature.

Dependence of the dimensionless mass transfer coefficient averaged over the length of experimental section k^+ in dependence on its length, measured by the electrochemical method, is given in the study by Shaw and Hanratty[17]. Their data together with theoretical values[1] are plotted in Fig. 2. The dashed line there represents the asymptote for small values of L^+. Its equation is equivalent to the relation which has been already in 1956 derived by Krammers and Kreyger[18] for mass transfer into the liquid in laminar flow of semiinfinite thickness, where for the friction factor is used the familiar Blasius relation for smooth pipe. It is understandable that experimental data are approaching the asymptote, as for short section with low value of L^+ the thickness of the concentration boundary layer is sufficiently small so that the thickness of the laminar layer in comparison with it could be considered to be a semiinfinite space. With this asymptote, in the region of small values of L^+, is identical our model[1] demonstrated by the solid line. From this figure results that in the region of small values of L^+, the agreement of theory with the experiment is very good. In the region of large values of L^+ the experimental data are larger than the theoretical values. This disagreement is perhaps due to the fact that the used experimental method did not enable measurement of k_∞^+ but some greater, successively developing value of the mass transfer coefficient.

Published experimental results[8,12,13,17] as well as the theoretical model[2] for Sc $\geqq$ 10 point to the fact that k_∞^+ is independent of the Reynolds number. But there exist experimental studies[10,19]; according to which k_∞^+ is dependent on Re number and explain it by the fact that Stanton number is not exactly proportional to the second root of friction factor. From the results of numerical calculations based on the presented model given in Table II of the preceding study[1] results, for usually used values of Re, Sc and ratio L/d: for low limits of the Reynolds numbers the measured mass transfer coefficient k^+ should be more than 5—10% higher than the steady value k_∞^+. For the upper limit of Re and at the same values of Sc and ratio L/d the systematic deviation is smaller by the order of magnitude due to the smaller thickness of the laminar layer. In correlation of the experimental data thus this results in the change of the slope of the dependence of St on Re or of St on f. So it is possible to explain *e.g.* the dependence of St on $f^{0.56}$ which has been obtained by Berger and Hau[19] in very accurate measurements by use of the electrochemical method in the experimental section with $L/d \sim 6$ in the range of Re $= 8 \cdot 10^3$ to $2 \cdot 10^5$ and Sc $= 1000$ up to 6000. In the measurements it is very difficult to obtain steady values of the mass transfer coefficient k_∞^+ in a wide range of experimental conditions. From Table II of the latest study[1] also results that for determination of k_∞^+ from the value of k^+ it is necessary to have several times longer experimental section than when k_∞^+ is determined from the local value by using the identity $k_\infty^+ = k_x^+$. Some authors who have not studied experimentally the effect of the ratio L/d on the obtained steady value k_∞^+ have measured usually at the high values of the Schmidt number and thus they were not able to determine k_∞^+. For example Kishinevskii[12], using the dissolving wall method proved the independence of k_∞^+ on Re only at low values of Schmidt numbers Sc $= 480$ and 930. As far as high values of Schmidt numbers Sc $= 10^4$ up to 10^6 concerns he assumed that the same conclusion holds. However, his experimental section with the ratio $L/d = 19.3$ corresponds according to Table II to measurements of k^+ and not k_∞^+. For low values of Sc the dependence of k^+ on Re is small, but is not negligible at high values of the Schmidt number Fig. 6 (ref.[1]). The independence of k_∞^+ on Re is also reported by Harriot and Hamilton[8] on basis of measurements at Sc $= 930$ up to 9810 and Gukhman and Kader[13] also in the range Sc $= 10^4$ up to 10^6. At the value Sc $= 10^6$ it is not possible to make general conclusions from the measurements in a narrow range of Reynolds number (Re $= 3490$—4190). The experimental data from studies[8,13] are moreover affected by the procedure

by which the experiments were performed at the use of the dissolving wall method as is described in the following part of this study.

On basis of the above made analysis results that the independence of k_∞^+ on Reynolds number cannot be considered as experimentally verified in the range of very large values of Sc because the measured mass transfer coefficients k^+ on the usually used lengths of experimental sections significantly differ from those k_∞^+ in steady state. But as the authors have tried to determine the values of k_∞^+ and have used — when possible — larger ratios L/d the obtained dependences of k^+ on Re are inexpressive and are frequently covered by the experimental error of the measurement.

Among the mostly studied dependences belongs also the dependence of k^+ on Sc. To be able to compare this dependence with theoretical calculation it has been assumed that the entrance section with not fully developed concentration profile has the length of the experimental section. It has been determined by calculation that for the majority of experimental data, the length of the entrance section necessary for reaching the steady concentration profile in the laminar layer is significantly larger than the usually used length of experimental sections as had been already stated earlier.

If our theoretical results are compared (empty points) with the experimental data according to Kishinevskii[12] (full points) see Fig. 3, for smaller values Sc $\sim 10^3$ the theory is in agreement
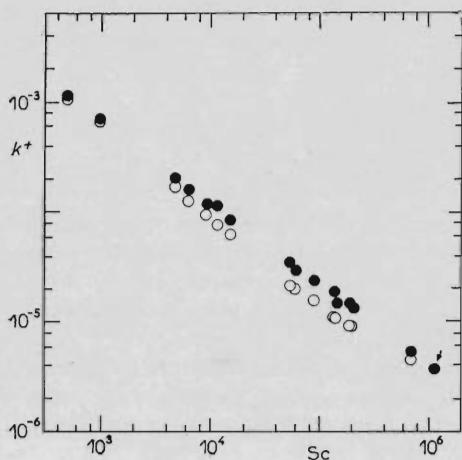

FIG. 3

Comparison of experimental data with theory. ○ Theory by Vašák and coworkers[1], ● experimental data by Kishinevskii and coworkers[12], arrow points ○ and ● became identical
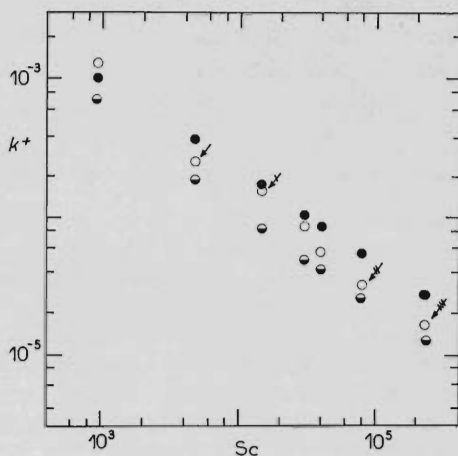
FIG. 4

Results of measurement of mass transfer coefficient for Re = 5000 and length of segment 30 mm. ○ Experimental values, ◐ theoretical values for not segmented experimental sections, ● theoretical values for segmented experimental sections, arrow Re = 4660, scratched arrow Re = 4620, double scratched arrow three measurements, triple scratched arrow two measurements

with the experiment. Similar results are obtained in the region of very large values Sc $\sim 10^6$. Toward the centre of the interval of measured values the deviation does not exceed 30%. But this deviation cannot be considered as proved in the whole region as in the middle of the given region the experimental data are not available and the validity of the verified model cannot be confirmed nor denied. The observed deviation can be possibly explained by the roughness formed in manufacture of the experimental section (the finish of internal surface of the experimental section has been made by the reamer before performance of the experiment) and at dissolution of the wall, and by dependence of the diffusion coefficient on concentration of benzoic acid *etc*. Moreover, in the figure a constant value of the Reynolds number was not kept and therefore the theoretical values are denoted as individual points. Similarly, the agreement is obtained by comparing the theory with experimental data published in the study by Grassman and Tuma[16].

It is also obvious from Fig. 1 that experimental data, with the exception of data from several studies[14,15] which are in comparison with the data of other authors affected by considerable experimental error, can be divided into two groups. Into the first group belong *e.g.* studies[16,17] which represent the electrochemical method and as the single representative of the dissolving wall method the study by Kishinevskii[12]. Into the second group belong the studies[8,13] which represent the dissolving wall method. The data of the second group are situated higher than the data of the first group and this difference increases with the increasing value of Sc number. The model[1] does not suit the second group of data. With regard to the mentioned discrepances of the data by different authors, the decision has been made to perform a set of experiments in a sufficiently wide range of Re and Sc numbers and compare them with the results of the theoretical description[1].

Verification of the Model for Original Experimental Data

The coefficient k^+ has been determined by measurements of the rate of dissolving of benzoic acid from the internal surface of circular pipe into aqueous solutions of glycerol of different concentrations. The system has been materialised by a soluble pipe (experimental section) made of benzoic acid of the length 300 mm and ID 20 mm. The pipe has been made of several segments of the lengths 30 and/or 10 mm, made of benzoic acid pressed in a special form[8,11,13]. The experimental section has been preceded by a hydrodynamic steadying section of the length 50 d and both have been as smoothly mutually interconnected as possible. On basis of the measured dissolving rate determined by taking the weight loss of the pipe the mass transfer coefficient has been evaluated from the relation

$$k^+ = \Delta m / [A \tau M (c^* - c_b) u^*] \qquad (1)$$

The physico-chemical data, have been taken from literature[8,11,13] and were experimentally verified except the diffusion coefficient. In production of the segments the effect of pressing pressure and particle size distribution of the used benzoic acid on quality of the internal surface of segments. It has been found out that the suitable pressing pressure for segments of the length 10 to 35 mm made of powdery benzoic acid is within the range from 100 to 150 MPa. So produced segments were smooth and glossy with sharp edges and in the considered range of Re numbers the decrease in mass which was due to errosion of turbulent flow has been negligible. Similarly the change in the diameter of segments during the performance of the experiment was smaller than 0·1 mm. At the beginning of the experiment the air has been removed from the apparatus

so that the change in viscosity of the solution could not take place due to formation of dispersion of air and solution of glycerol. The change in temperature of the solution at the inlet and outlet of the experimental section has been negligible and could not have affected the results of measurements. By measurement of pressure drop over the experimental section it has been determined that the experimental section appeared to be hydraulically smooth. More information on the measurement are given by Vašák[6].

The set of experimental data has been obtained expressing the dependence of k^+ on Reynolds and Schmidt numbers in the range of values $5000 \leqq Re \leqq 50000$ and $933 \leqq Sc \leqq 225000$ for the length of averaging about 300 mm. The experimental dimensionless mass transfer coefficients averaged over the length of experimental section k^+ are in dependence on Schmidt number given in Figs 4, 5, 7 and 8 for Reynolds number 5000, 10000, 20000, 50000 and the length of the segment 30 mm. On experimental section composed of segments with the length 10 mm the measurements have been performed only at $Re = 10000$, see Fig. 6. At largest Sc numbers (largest viscosities) the highest values of Re have not been reached due to limitations of the pumping capacity. Experimental data denoted as empty points are situated in all cases above theoretical values of k^+ calculated from Eq. *(12)* (ref.[1]) and denoted as half — empty points. To explain this difference our experimental data have been compared with the data plotted in Fig. 1. Our experimental data correspond to the dependence of the second group obtained
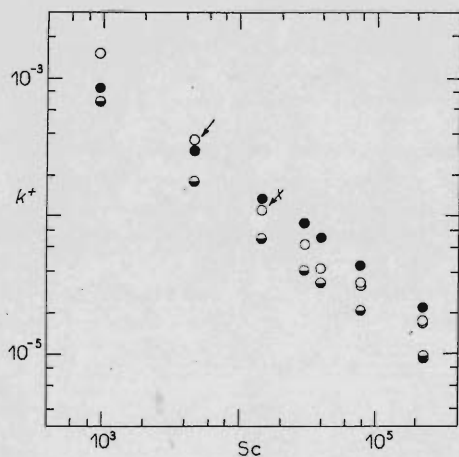

Fig. 5

Results of measurements of mass transfer coefficients for $Re = 10000$ and length of segment 30 mm. ○ Experimental values, ◐ theoretical values for not segmented experimental sections, ● theoretical values for segmented experimental sections; arrow $Re = 9300$, scratched arrow $Re = 9480$

Fig. 6

Results of measurement of mass transfer coefficient for $Re = 10000$ and length of segment 10 mm. ○ Experimental values, ◐ theoretical values for not segmented experimental sections, ● theoretical values for segmented experimental sections, arrow $Re = 9300$, scratched arrow $Re = 9480$
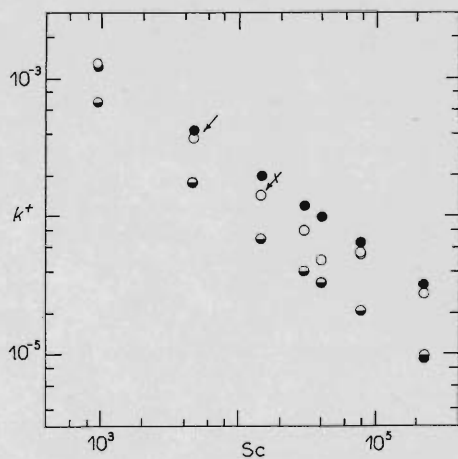
on segmented experimental sections. Because the first group of experimental data obtained on unsegmented sections agree quite accurately with predicted values[1] it is possible to consider some factor increasing k^+ in segmented sections. In the experiments performed with not segmented sections this factor has not appeared. By measurements both of external and internal surfaces of pressed segments it has been found out that they are perfectly cylindrical but that these surfaces are not co-axial. This is due to manufacturing tolerance of parts of the pressing form enabling various mutual assembly. In the assembly of the experimental section from segments and after levelling by their external surface, discontinuities of the internal surface can form comparable to the thickness of the laminar layer (orders of several hundredths of milimeter). These discontinuities cause a partial or total homogenisation of liquid in the laminar layer so that on the surface of the following segment a practically new concentration profile forms, as the thickness of the concentration boundary layer is much smaller than the thickness of the laminar layer. More profound changes in the flow do not take place, as from measurements of pressure drop the experimental section seems to be hydraulically smooth.

On basis of this explanation it is assumed that for description of the mass transfer mechanism in experimental sections composed of segments it is possible to use the same previous theory, except that for the length of averaging the length of segment is chosen instead of the length of experimental section. In Figs 4—8 are the experimental data (empty points) compared both with predicted values for the section not composed of segments (half-empty points) as well as with the
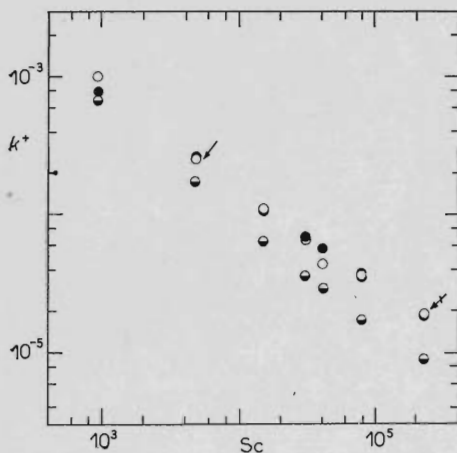

FIG. 7

Results of measurement of mass transfer coefficients for Re = 20000 and length of segment 30 mm. ○ Experimental values, ◐ theoretical values for not segmented experimental sections, ● theoretical values for segmented experimental sections, arrow Re = 18600, scratched arrow Re = 16500

FIG. 8

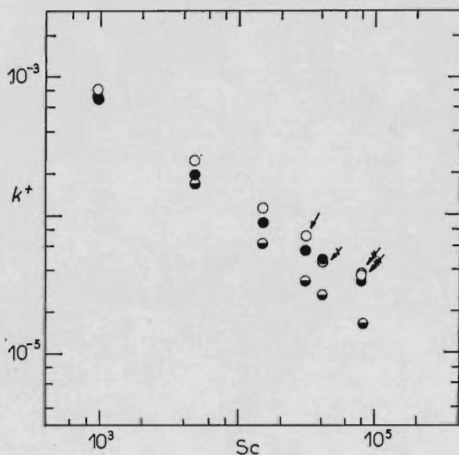Results of measurements of mass transfer coefficients for Re = 50000 and length of segment 30 mm. ○ Experimental values, ◐ theoretical values for not segmented experimental sections, ● theoretical values for segmented experimental sections, arrow Re = 45200, scratched arrow Re = 38500, double scratched arrow R = 28200, triple scratched arrow Re = 28000

values predicted on basis of the above given model for segmented sections (full points). The best agreement with the predicted values for sections composed of segments has been reached at large Reynolds numbers Re = 20 000 and 50 000 in Figs 7 and 8. On basis of these results it is possible to deduce that on contacts of segments a perfect mixing of the liquid takes place and thus that a new concentration entrance region of the length equal to that of the segment is formed. At smaller Reynolds numbers Re = 5 000 and 10 000 and larger values of Sc the predicted values for sections formed by number of segments are larger than the experimental ones (Figs 4—6). This is obviously due to larger thickness of laminar layer at smaller Re numbers and that discontinuity of a certain dimension on contacts of segments is not causing perfect mixing of liquid in laminar layer and thus the assumed mechanism of formation of the concentration boundary layer is fulfilled only partially. The proposed model for sections composed of segments has been applied also to experimental data obtained in other studies[8,13] which have been using segmented experimental sections, see Fig. 9. The agreement of theoretical values denoted by the solid line and the experimental values denoted as empty and full points is good. A better agreement can be obtained when the degree of homogenisation of liquid in the laminar layer is known for the given Reynolds number.

Our experimental data of k^+ in dependence on Re are plotted in Fig. 10. According to the theoretical part of this study, considerable decrease in k^+ values with increasing value of Re should be obvious first of all for large values of Sc. But from
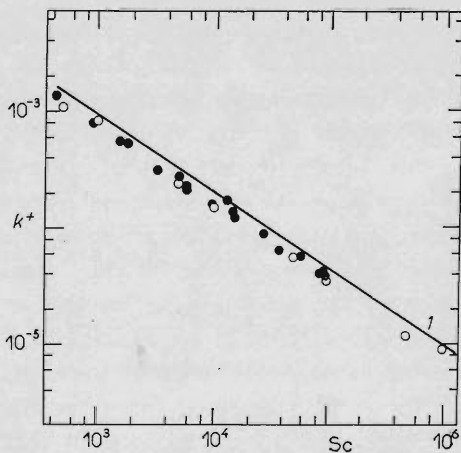

FIG. 9

Comparison of the model for segmented experimental sections with data published for Re = 10 000. ○ Gukhman and Kader[13], ● Harriott and Hamilton[8]; *1* model for segmented experimental sections
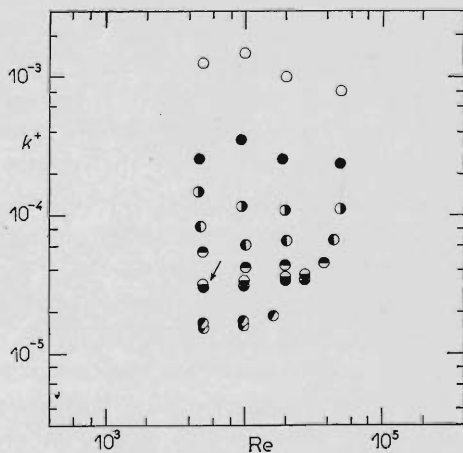
FIG. 10

Experimental values of k^+ in dependence on Reynolds number. ○ Sc = 933; ● Sc = = 4680; ◑ Sc = 14 700; ◐ Sc = 30 000; ◕ Sc = 39 300; ◔ Sc = 77 100; ◑ Sc = = 225 000; arrow three measurements

the mentioned figure results that in the studied range of Re numbers it is not possible to decide definitely if the k^+ for segmented experimental sections depends on Re or not. But it is possible to accept the opinion that k^+ for segmented experimental sections does not depend on Re. In agreement with this statement are also results of other studies[8,13] in which segmented experimental sections were used. For more general conclusions are lacking experimental data on k^+ at higher Re numbers. According to the theory for segmented experimental sections a slight dependence of k^+ on Re is obtained but this can be in the case of experimental data overlapped by the error resulting from measurements.

DISCUSSION AND CONCLUSIONS

Gukhman and Kader[13] have studied the dependence of k^+ on the number of contacts in the experimental section composed of segments with the length 25 or 50 mm and have obtained k^+ independent of the number of contacts of segments. This result has been verified on basis of a model derived for segmented experimental sections and it has been obtained that for conditions of the experiment[13] the dependence is very small so that it could be very easily covered by the experimental error. In our case the number of segments is three times larger and it is thus probable that this will result in the increase of the value of k^+ in spite of the effect of possible experimental error. This increase is well obvious by comparison of Figs 5 and 6.

The existence of discontinuities of the internal surface in the segmented experimental section is manifested like the steady state with a certain value k^+ be reached already in the second or third segment. But only steadying of the mechanism of formation of a new concentration profile has taken place on segments and measured values of the mass transfer coefficient are considerably larger than the values obtained on basis of not segmented experimental sections. In this respect it is of interest to discuss a model which had been proposed by Pinczewski and Sideman[20]. They described the mass transfer mechanism in the region of large values of Sc by the theoretical model based on idealized formation and decay of the laminar layer. This model has been developed for description of the mass transfer mechanism in a smooth pipe. But in fact the model is capable to describe in a reasonable way only the mass transfer mechanism in segmented experimental sections in which it had been verified. Data by Kishinevskii[12] (Sc $\sim 10^6$), measured for a smooth experimental section without joints are situated aside. Thus the model does not hold for experimental data measured in the region of large values of Sc on a smooth experimental section for which it has been derived[20], while on basis of the model[1] it is possible to describe the mass transfer mechanism both in segmented and not segmented sections.

From comparison of the model[1] with the experimental data available results that the model enables description of the mass transfer mechanism in the range

$10^3 \leqq \mathrm{Sc} \leqq 10^6$ and that on its basis it is possible to explain the difference between the experimental data measured on experimental section made of one piece (used mostly in the electrochemical method) and data measured on segmented experimental sections (used mostly in the dissolving wall method).

By verification of the model[1] has been proved that the assumptions[2] used are valid in the range $3 \cdot 10^{-3} \leqq \mathrm{Sc} \leqq 10^6$.

LIST OF SYMBOLS

A interfacial area (m^2)

c^* concentration of component at interface $(\mathrm{mol\,m}^{-3})$

c_b concentration of component in the core of liquid phase $(\mathrm{mol\,m}^{-3})$

d diameter of experimental section   (m)

D diffusivity of component $(\mathrm{m}^2\,\mathrm{s}^{-1})$

f friction factor

k mass transfer coefficient averaged over the length L $(\mathrm{m\,s}^{-1})$

$k^+ = k/u^*$

$k_\mathrm{x} = $ local mass transfer coefficient $(\mathrm{m\,s}^{-1})$

$k_\mathrm{x}^+ = k_\mathrm{x}/u^*$

k_∞ fully developed mass transfer coefficient $(\mathrm{m\,s}^{-1})$

$k_\infty^+ = k_\infty/u^*$

L length of experimental section   (m)

$L^+ = L\,u^*/v$

Δm decrease in mass during the experiment   (kg)

M molecular mass of dissolved compound $(\mathrm{kg\,mol}^{-1})$

$\mathrm{Re} = d\,u/v$ Reynolds number

$\mathrm{Sc} = v/D$ Schmidt number

$\mathrm{St} = k/u$ Stanton number

u component of velocity in the direction of flow in turbulent core $(\mathrm{m\,s}^{-1})$

$u^* = u\,\sqrt{(f/2)}$ friction velocity $(\mathrm{m\,s}^{-1})$

v kinematic viscosity $(\mathrm{m}^2\,\mathrm{s}^{-1})$

τ time of duration of the experiment   (s)

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