

APPLICATIONS OF THE ELECTROLYTIC METHOD—I. ADVANTAGES AND DISADVANTAGES, MASS TRANSFER BETWEEN A FALLING FILM AND THE WALL

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Abstract—The advantages and disadvantages of the electrochemical—or more exactly—electrolytic method for measuring mass-transfer coefficients are summarized. The most outstanding advantages are: high accuracy and high resolution in respect to time and location. Measurements for the mass transfer between a falling film and the wall with astonishing results are one example for its application to problems of chemical engineering.

NOMENCLATURE

- c , concentration of the electrolyte with low concentration [kmol m^{-3}];
- D , diffusion coefficient [$\text{m}^2 \text{s}^{-1}$];
- i_L , limiting current density [A m^{-2}];
- F , Faraday constant = 0.965×10^8 [$\text{As kg}^{-1} \text{Aeq}$];
- g , acceleration of gravity [ms^{-2}];
- I , electric current [A];
- Sh , $\equiv \beta\delta/D$ Sherwood-number;
- Re , $\equiv V^*/U$;
- U , circumference of the tube [m];
- V^* , flow of the liquid [$\text{m}^3 \text{s}^{-1}$];
- x , distance from the upper end of the tube [m];
- z , valence charge of an ion [kg Aeq kmol^{-1}].

Greek symbols

- β , mass-transfer coefficient [m s^{-1}];
- δ , thickness of the film [m];
- κ , specific electric conductivity [$\Omega^{-1} \text{m}^{-1}$];
- ν , kinematic viscosity [$\text{m}^2 \text{s}^{-1}$].

Superscripts

- ST , start;
- M , mean;
- L , local.

1. ADVANTAGES AND DISADVANTAGES OF THE ELECTROLYTIC METHOD

IT IS known for many years, that under certain circumstances the current going through an electrolytic cell is independent of the applied voltage, but is a function of mass transfer only [1–3]. Then it is possible to measure mass-transfer-coefficients by an ammeter. This was pointed out already 1955 by Ibl [4]. For this purpose a mixture of two electrolytes [1–3] is used: one—the active electrolyte—is present

in low concentration and has a low potential of discharge. The other—sometimes called the indifferent or supporting electrolyte—is present in high concentration and has a higher potential of discharge. When the voltage applied to the cell lies between the two potentials of discharge, the electric field in the bulk of the liquid is short circuited by the many ions of the supporting electrolyte. However, these ions can not be discharged at the electrodes, because the voltage is too low. Therefore, they do not contribute to the electric current. Instead they build up an electric double layer on the surfaces of the electrodes. Its thickness being in the order of magnitude of 1 nm, it is about 1000 times smaller than that of the sublayers, that determine heat and mass transfer. Since the electric field is absent in all the liquid except the electric double-layers the ions of the active electrolyte move only under the influence of convection and diffusion as it would be in the usual process of heat and mass transfer without any field at all. When the voltage is high enough all ions of this sort are discharged and the electric current becomes independent of voltage: a first plateau of the current-voltage-curve is reached. The corresponding “limiting current-density” i_L depends only on mass transfer according the well known, fundamental equation for this method

$$\beta = i_L / (zFc), \quad (1)$$

which follows from Faraday’s law and the equation of mass transfer. The concentration c of the active electrolyte is measured by titration. To obtain reliable results it should always be checked by experiments, that for a certain range of voltage the current through the electrolyte is independent of the voltage. This is only the case, when the voltage drop in the electrolyte is small compared to the difference between the discharge potentials of the ions of the active and the supporting electrolyte. For the electrolyte mentioned later this difference is about

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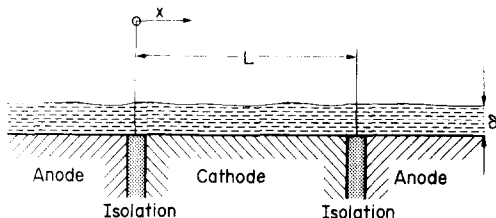


FIG. 1. Position of anodes near the cathode.

1 V ([5] p. 39). Thus difficulties arise only, if the limiting currents are extremely high ([6] p. 59, [7]) or the cross-section of the electrolyte small, as it is for thin films. Then the cathodes should be small and as near as possible to the anodes [8] (further possibilities in [7]). For the arrangement as in Fig. 1 (it is assumed to be independent of the coordinate orthogonal to the plane of the figure) the currents coming from the anodes on the left and on the right decrease linearly with the coordinate x according to the equation

$$I = bi_L(L/2 - x),$$

with b being the width of the electrodes in the direction perpendicular to the plane of Fig. 1. The potential-gradient is

$$dV/dx = -I/(\kappa b \delta) = -i_L(L/2 - x)/(\kappa \delta)$$

and the whole voltage drop is

$$V = - \int_0^{L/2} \frac{i_L(L/2 - x)}{\kappa \delta} dx = - \frac{i_L L^2}{8\kappa \delta}, \quad (2)$$

Ibl, Trueb and the author have developed this method since 1958. [9, 10] for measuring instantaneous and local transfer coefficients. The advantages and disadvantages of this electrolytic method are:

1. An accuracy of about 1%, generally not achieved in heat- and mass-transfer measurements, may be attained.

2. Local measurements are possible [11, 12, 18]. Trueb [10] used cathodes of width 0.45 mm, afterwards Reiss and Hanratty [14] employed circular cathodes with diameters between 0.13 and 1.6 mm. Such dimensions are possible since contrary to thermal isolation electric isolation needs only very small distances.

3. The possibility of instantaneous measurements allows investigation of the pattern of turbulence [9, 10, 13, 14] or the mass transfer of unsteady and fluctuating processes [5, 15]. However care has to be taken since the capacity of the electric double layer, which seems to be $10\text{--}70 \mu\text{F cm}^{-2}$ [15, 16], may cause some time delay. The time resolution may be reduced to about 1 ms [15].

4. Corresponding to the low diffusion coefficient of liquids the Sc -numbers of electrolytes lie between 1000 and 10000. Therefore it is always a risk to deduce equations for heat transfer, where we deal with Pr -numbers between 0.6 and 100, from electrolytic measurements.

5. It is nearly impossible to measure heat-transfer coefficients of liquids with high Pr -numbers at high Re -numbers. The heat generated by dissipation would be prohibitive. Here the electrolytic method fills a gap.

6. At present redox-systems are mostly used as electrolytes (e.g. [9, 10]). Then, in spite of mass transfer the concentration remains constant: the electron added at the cathode, where i_L is measured, is removed again at the anode. Therefore the driving force remains constant and does not decrease to very small values. These are difficult to measure, which is often a serious disadvantage for other methods.

7. It is possible to measure the local and the instantaneous shearstress at the wall (theory [17], application to the electrolytic method [18]).

8. The diffusion coefficient of the active electrolyte may be calculated from measurements, where the transfer coefficients are well known, e.g. for laminar flow.

9. The electrolyte mentioned later is sensitive to light and O_2 especially at temperatures above 60°C [15 p. 35].

2. MEASUREMENTS OF MASS TRANSFER FROM A FALLING FILM TO A PERPENDICULAR WALL

A difficulty for the measurement of heat-transfer from a falling film to the wall is, that after a length—say 0.5 m—thermal equilibrium would be nearly reached. Meyer [8] avoided this by using the redox-system; $0.025 \text{ kmol m}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6 + 0.025 \text{ kmol m}^{-3} \text{ K}_4(\text{CN})_6 + 2\text{N Na OH}$ with [5] $\rho = 1090 \text{ kg m}^{-3}$, $\nu = 1.457 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$, $D = 4.705 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $Sc = 3097$. The specific electric conductivity κ is $25\text{--}26$ for the 2N and $34\text{--}35 \Omega^{-1} \text{ m}^{-1}$ for the 5N Na OH solution.

The test section was a vertical tube, 2 m in length with an O.D. of 0.033 m. It was divided into 27 rings with lengths between 1 and 20 cm. These are indicated in Fig. 2 as EL-NR (= element numbers). Only 1/6 of the surface of each ring was used as cathode, the rest as anode.

The film of the electrolyte was regulated and distributed over the outer circumference of the tube by a conical slit at its upper end.

The theory of Nusselt [19] has been confirmed completely for the laminar film and for the wavy film with $Re_{crit} = 40$ up to $x \leq 0.5 \text{ m}$. Mass transfer, however, was increased for larger distances from the upper end of the tube by the influence of waves. The Sh -number $Sh = \beta \delta / D$ was calculated using

$$\delta = (3\nu^2/g)^{1/3} Re^{1/3} \quad \text{for } Re < 400 \quad (3)$$

and with $Re_{crit} = 400$ by

$$\delta = Re_{crit}^{-0.2} (3\nu^2/g)^{1/3} Re^{8/15} \quad \text{for } Re > 400. \quad (4)$$

The results are shown in Figs. 2 and 3. The curves beginning at the left margin of the figure correspond

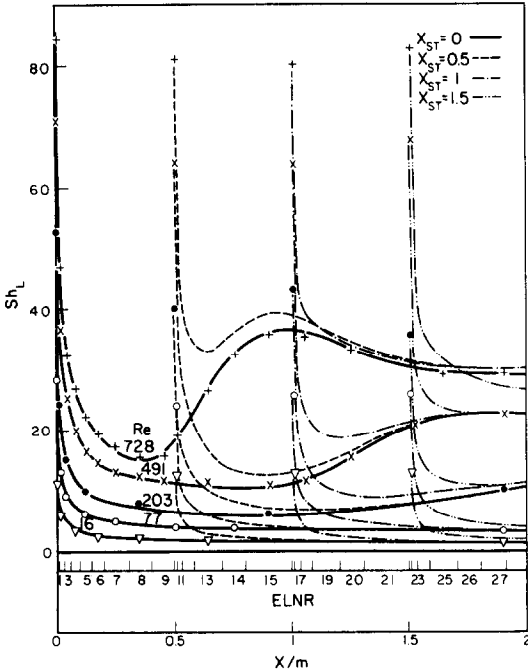


FIG. 2. Local Sh numbers as functions of the distance x from the upper end of the tube. Parameters are Re numbers and x_{ST} , that are the lengths, where mass transfer starts. $EL-NR$ = number of the element (= cathodes). The results of the measurement are indicated only for the curves $x_{ST} = 0$. For the others only the measurement at the first cathode appears in the figure. Further results see [8].

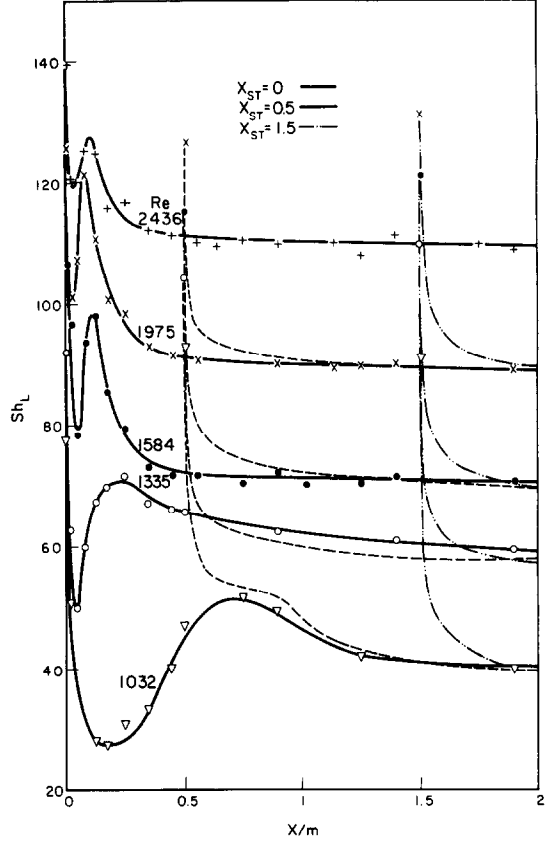


FIG. 3. Like Fig. 2, but for higher Re numbers [8].

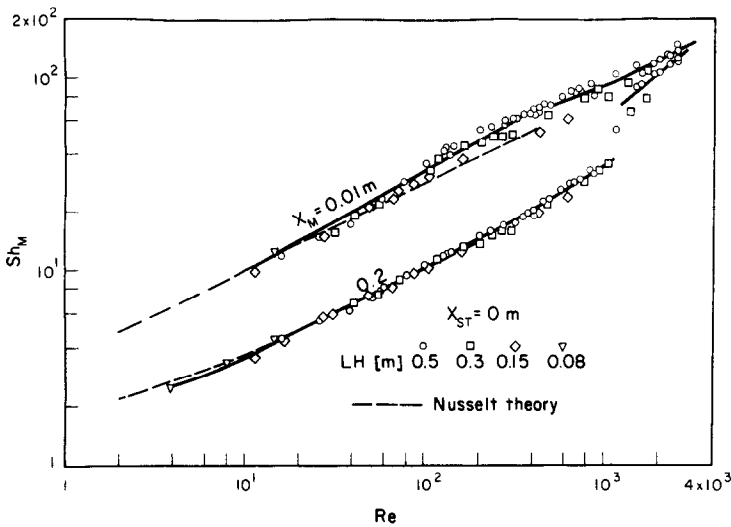


FIG. 4. MEAN Sh -number Sh_M as a function of Re for different lengths and liquid heads (= LH).

to an electric connection where mass transfer begins at the upper end of the tube. That means, that all anodes and cathodes are connected at the voltage source. However, only the cathode at the place, at which the local mass transfer had to be measured, was connected to the current recorder. If, on the contrary, mass transfer begins at—say— $x_{ST} = 0.5$ m, the curves with a pronounced maximum at this point

are obtained. They differ from the curves mentioned before, since for $x_{ST} = 0$ the hydraulic profile is not yet established, whereas it is better established at $x_{ST} = 0.5$ m. For further results see [8].

Figure 4 shows the mean Sh -numbers Sh_M as a function of Re for $x_M = 0.01$ and 0.2 . It can be seen, that the LH (= liquid head) above the slit at $x = 0$ has only small influence on the Sh -numbers.

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APPLICATIONS DE LA METHODE ELECTROLYTIQUE.

Ière PARTIE: AVANTAGES ET DESAVANTAGES, TRANSFERT MASSIQUE ENTRE UN FILM TOMBANT ET LA PAROI

Résumé—On résume les avantages et les désavantages de la méthode électrochimique—ou, plus exactement, électrolytique—pour mesurer des coefficients de transfert massique. Les avantages les plus marquants sont: la grande précision et la grande résolution par rapport au temps et à la localisation. Des mesures du transfert massique entre un film tombant et la paroi, avec des résultats étonnants, sont présentées en exemple d'application à des problèmes de génie chimique.

ANWENDUNGEN DER ELEKTROLYTISCHEN METHODE—I. VOR- UND NACHTEILE STOFFAUSTAUSCH ZWISCHEN EINEM RIESELFILM UND DER WAND

Zusammenfassung—Die Vor- und Nachteile der elektrochemischen oder—prägnanter ausgedrückt—der elektrolytischen Methode zur Messung von Stoffaustauschkoeffizienten werden zusammengestellt. Die wesentlichsten Vorteile sind: hohe Genauigkeit und hohe örtliche und zeitliche Auflösung. Als ein Beispiel ihrer Anwendung auf Probleme der Verfahrenstechnik dienen Messungen des Stoffaustauschs zwischen einem Rieselfilm und der Wand. Die Ergebnisse sind recht unerwartet.

ПРИМЕНЕНИЕ ЭЛЕКТРОЛИТИЧЕСКОГО МЕТОДА. ЧАСТЬ I. ПРЕИМУЩЕСТВА И НЕДОСТАТКИ МЕТОДА. ПЕРЕНОС МАССЫ МЕЖДУ СТЕКАЮЩЕЙ ПЛЕНКОЙ ЖИДКОСТИ И СТЕНКОЙ

Аннотация—Обсуждаются преимущества и недостатки электрохимического, а точнее, электролитического метода измерения коэффициентов массопереноса. Из наиболее существенных преимуществ можно отметить высокую точность и высокую временную и пространственную разрешающую способность метода. В качестве примера использования метода для решения задач химической технологии приведены результаты измерения переноса массы между стекающей пленкой жидкости и стенкой.