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Thermo-compensation of electrodiffusional wall velocity gradient measurements

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Abstract

Thermo-dependence of electrodiffusional measurements of wall velocity gradient has been studied in a fully developed turbulent channel flow. In isothermal conditions, the direct thermo-compensation can be provided using the measurements of thermo-dependence of molecular diffusivity and viscosity. The simultaneous transient and steady-state limiting diffusion current measurements open the possibility for in situ compensation of thermal effects in electrodiffusional flow diagnostics at non-isothermal conditions where the local temperature gradients are presented. The feasibility of the proposed method of thermo-compensation has been confirmed experimentally for the case of local heating of the solution by means of pulse hot-wire technique.

Keywords: Flow measurements; Electrodiffusion diagnostics; Wall velocity gradient; Thermo-compensation

1. Introduction

The electrodiffusional method has been proved to be well appropriate for near wall liquid flow measurements (Hanratty and Reiss, 1962; Cognet, 1971; Martemianov and Danaila, 2003; Deslouis et al., 1990; Grafov et al., 1990; Sobolik et al., 1998; Legrand et al., 2000; Grigoriev et al., 2003; Adolphe et al., 2005, 2007). The main idea is based on the measurements of the limiting diffusion current I_L delivered by electrodes flush mounted with the wall in contact with the liquid electrolyte flow. These measurements give directly access to the mass transfer coefficient at the solid–liquid interface

$$k = \frac{I_L}{nFAC_0}. \quad (1)$$

For the case of circular microelectrodes, the limiting diffusion current measurements lead to determine the wall velocity gradient S via the well known Lévêque equation (Lévêque, 1928)

$$I_L = \varsigma S^{1/3}; \quad \varsigma = 0.83nFC_0D^{2/3}A^{5/6}. \quad (2)$$

Here I_L is the limiting diffusion current, A is the microelectrode active surface, D is the diffusion coefficient, C_0 is the bulk concentration of electroactive species, n is the number of electrons involved in electrochemical process and F is the Faraday's constant.

We stress that electrodiffusional technique does not perturb the flow and does not require the using of visualization particles, as in case of LDA (laser Doppler anemometry) and PIV (particles image velocimetry). Thus, electrodiffusional flow diagnostics can be used as well in the opaque as in transparent mediums.

In principal, the numerical constant ς in Eq. (2) is known, however the influence of undesirables effects such as thermo-dependence of the diffusion coefficient, the

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Nomenclature

A	microelectrode active surface (m^2)
C_0	bulk concentration of electroactive species ($mol\ m^{-3}$)
D	diffusion coefficient ($m^2\ s^{-1}$)
D_h	hydraulic diameter of channel (m)
F	Faraday number, $F = 96{,}500$ ($C\ mol^{-1}$)
k	mass transfer coefficient ($m\ s^{-1}$)
I_L	limiting diffusion current (A)
I_{el}	current intensity (A)
n	number of electrons transferred in the electrochemical reaction
S	wall velocity gradient (s^{-1})
T	temperature (K)
t	time (s)
U	flow velocity ($m\ s^{-1}$)
Re_h	Reynolds number($=UD_h/v$)

Greek symbols

α	Levich coefficient ($A\ rad^{-1/2}\ s^{1/2}$)
β	Cottrell coefficient ($A\ s^{1/2}$)
μ	dynamic viscosity ($kg\ m^{-1}\ s^{-1}$)
Ψ	thermo-compensation constant
χ	thermo-compensation constant
λ	skin friction coefficient
ρ	density ($kg\ m^{-3}$)
v	cinematic viscosity ($m^2\ s^{-1}$)
ς	Lévêque constant ($A\ s^{1/3}$)
ΔL	distance in the pressure drop (m)
ΔP	pressure drop (Pa)

Superscripts

Lev	Levich
Cot	Cottrell
Geo	geometric

variation in time of the electroactive species concentration and microelectrode active surface limit practical applications of this method. In this article, we will analyze the cited above phenomena in order to avoid or to decrease the influence of these undesirable effects. The final goal is developing of the calibration protocol for electrodiffusional measurements.

2. Experimental setup and procedure

A hydraulic flow loop used in this study presents recirculation circuit which supplies a horizontal testing duct. The latter is a two-dimensional Plexiglas rectangular channel (Fig. 1) of 460 mm length with a cross-section of 15.3 mm × 4 mm; the hydraulic diameter is equal to $D_h = 6.3$ mm. The channel is formed by a superposition of three rectangular parts screwed by bolts between which plastic joints are added to ensure the sealing. The lower part (1) of the channel contains two points for pressure drop measurements distant of 150 mm and centred on the channel axis. The higher part (2) of the channel contains a hole of 20 mm in diameter instrumented by a support (3) which is used as system for introduction of the microelectrodes (electrochemical sensors). The higher and the lower parts are separated by rectangular plate (4) giving place to a cross-section of the channel.

An aqueous solution of potassium sulfate (K_2SO_4; 300 $mol\ m^{-3}$) containing a fast reversible redox system of ferri- ferrocyanide ($K_3Fe(CN)_6/K_4Fe(CN)_6$; 25 $mol\ m^{-3}$) is used for electrochemical flow measurements. The viscosity of the solution have been measured with an Ubbelholde capillary viscosimeter and the following linear equation is obtained:

$$v(T) = v(T_0) + \xi_1\left[\frac{T - T_0}{T_0}\right], \tag{3}$$

where $\xi_1 \approx 5 \times 10^{-6}\ m^2\ s^{-1}$ at the range of temperature investigated ($280\ K < T < 320\ K$); the viscosity $v\ (T_0)$ is equal to $10^{-6}\ m^2\ s^{-1}$ at $T_0 = 298$ K.

Table 1 presents the nomenclature of circular microelectrodes made of platinum wires 0.8 and 0.2 mm in diameter. The geometrical surface is calculated by a numerical image treatment of photographs obtained from an optical microscope connected to a camera CDD. The microelectrodes are flush mounted with the wall of the channel. The electrochemical reduction of the ferricyanide takes place on the platinum working electrode

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}, \tag{4}$$

with the reverse reaction at the stainless counter electrode of a grand surface ($4 \times 10^{-4}\ m^2$).

The electrolyte circulation has been provided by a non-corrosive centrifuge pump, the using of the thermostat in hydraulic circuit made it possible the temperature regulation and control. The flow rate is measured with a flow meter and the pressure drop by means of a differential manometer. The points for pressure drop measurements and the support containing the electrochemical sensors are located respectively at $L_1 = 155$ mm and $L_2 = 415$ mm from the channel entrance $\left(\frac{L_1}{D_h} \approx 25\right)$, in order to ensure fully developed turbulent flow conditions in the measuring section at the range of the Reynolds numbers investigated ($6000 < Re_h < 23000$).

Hydraulic calibration of the rectangular channel is checked by measuring of the dependence of the friction coefficient λ on the hydraulic Reynolds number Re_h. The

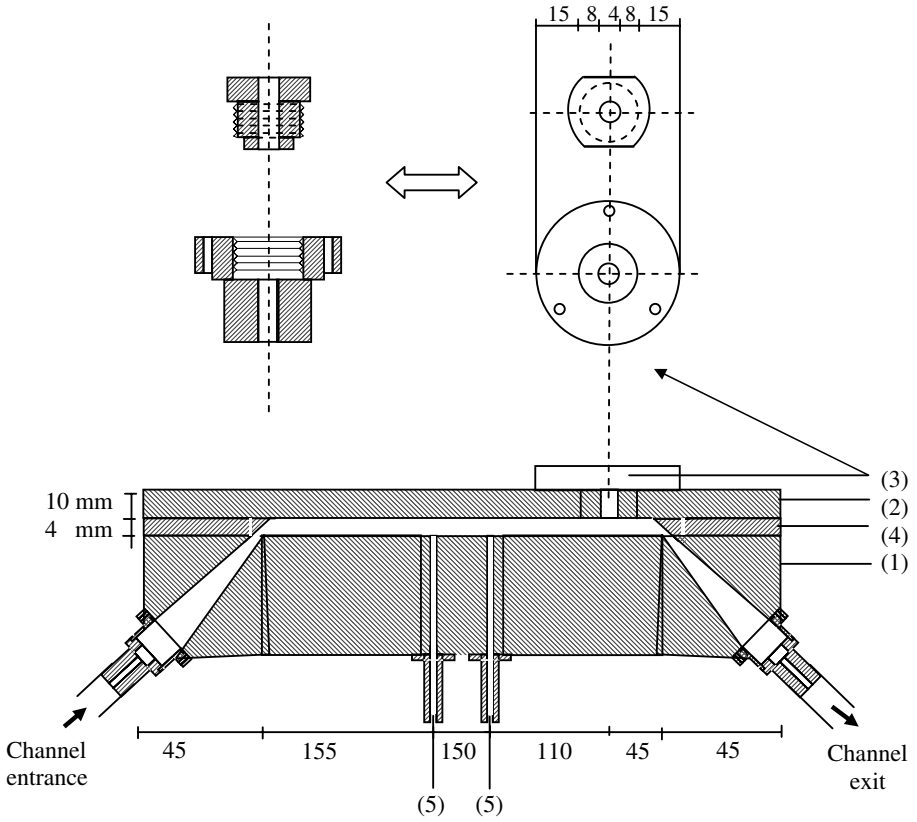

Fig. 1. Schematic diagram of the experimental set-up: (1) lower part; (2) higher part; (3) support of electrochemical sensor; (4) intermediary plate and (5) points for measure drop (measures are in mm).

Table 1
Evaluation of the active surface for circulars microelectrodes using the Cottrell and Lévêque methods, $C_0 = 25$ mol m^{-3}

C_i	T (K)	$A_{Geom} \times 10^{-6}$ (m^2) by an optic technique	$\beta \times 10^6$ (As$^{1/2}$)	$\varsigma \times 10^6$ (As$^{1/3}$)	$A_{Cot} \times 10^{-6}$ (m^2) calculated from β	$A_{Lev} \times 10^{-6}$ (m^2) calculated from ς
C_1	288		23.9	7.61	0.68	0.43
	293		24.5	8.44	0.66	0.45
	298		26.5	9.25	0.67	0.46
	303	0.527	26.8	9.69	0.65	0.49
	308		26.5	10.18	0.61	0.43
	313		28.0	10.80	0.61	0.43
	318		28.0	11.29	0.58	0.42
C_2	25	0.037	2.2	0.89	0.056	0.033

friction coefficients λ have been calculated from the pressure drop ΔP measurements (Tanner, 1985)

$$\lambda = 2\frac{\Delta P}{\Delta L}\frac{D_h}{\rho U^2}, \tag{5}$$

where U is the mean flow velocity, ΔL is the length between the two pressure taps and ρ is the fluid density. The results of the hydraulic calibration are presented in Fig. 2.

We note that in turbulent regime ($Re_h \geqslant 5000$) the friction coefficient follows the Blasius law (Schlichting, 1987; Cousteix, 1989):

$$\lambda = 0.32 Re_h^{-1/4} \tag{6}$$

and in the laminar regime ($Re_h \leqslant 2000$) the experimental points fit well the following law:

$$\lambda = \frac{a}{Re_h}, \tag{7}$$

where the constant a is equal to 76.8 in a good agreement with the Idel'cik value (Idel'cik, 1999) for channels corresponding to our geometry.

Thus, our installation allows determining the wall velocity gradient by measuring the pressure drop ΔP

$$S = D_h \frac{\Delta P}{4\rho\nu\Delta L}. \tag{8}$$

Consequently it is possible to verify the Lévêque law, Eq. (2), by measuring the dependence of the limiting diffusion current on the wall velocity gradient, see Fig. 3.

In principal, Fig. 3 can be interpreted as the calibration curve for electrochemical sensors. However, the thermo-dependence of electrodiffusion measurements put on the question of compensation of temperature effects, in particular for the measurements in non-isothermal conditions. Moreover, possible time variations of the active surface A and the bulk concentration C_0 should be taken into account.

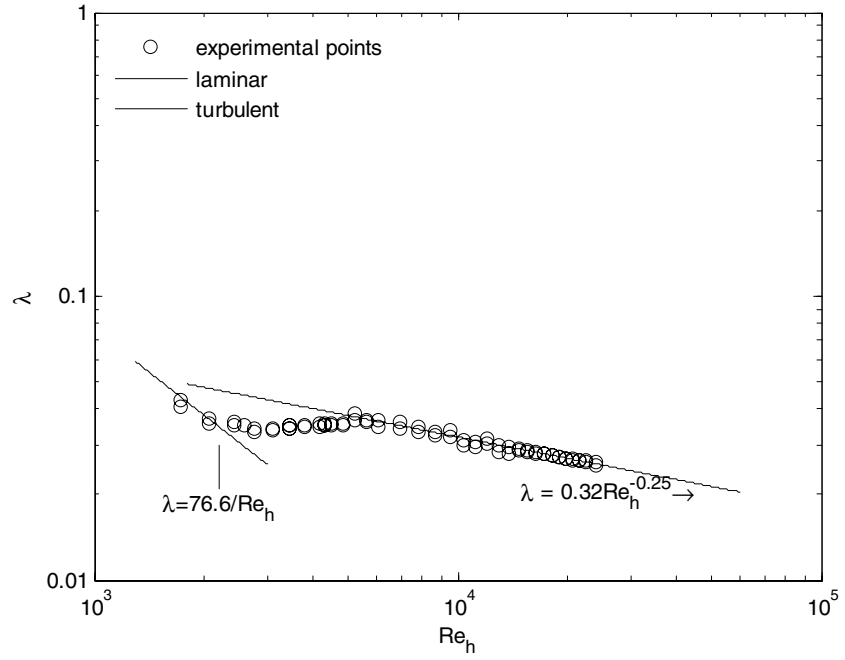

Fig. 2. Hydraulic calibration curve.

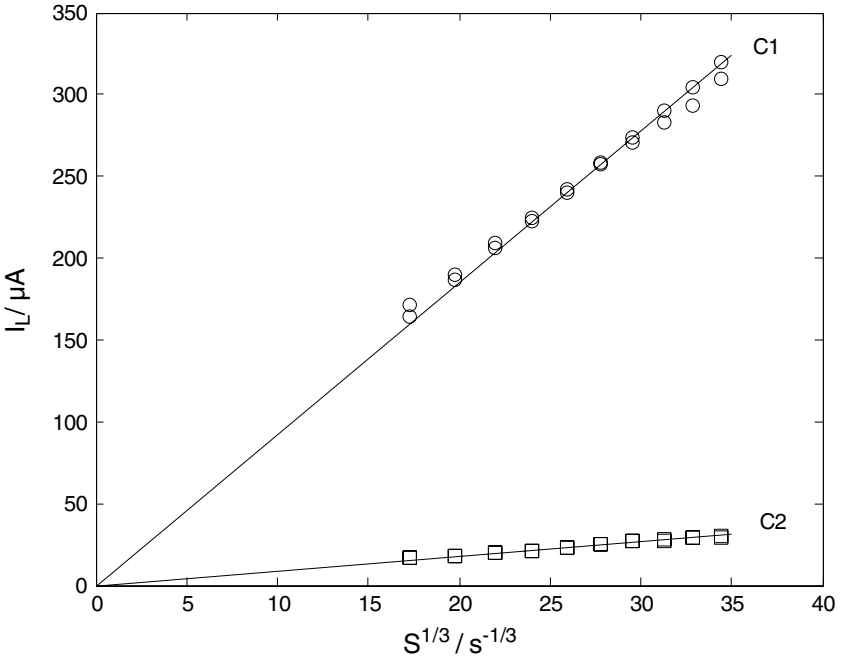

Fig. 3. Lévêque curve at $T = 298$ K, $C_0 = 25$ mol m^{-3}: dependence of the limiting diffusion current on the wall velocity gradient for circulars electrodes: C_1 (○), C_2 (□).

3. Thermal compensation of electrodiffusion measurements in isothermal conditions

Electrodiffusion measurements necessitate special attention to the temperature control because this parameter has a considerable effect on the limiting current and consequently on the determination of the wall velocity gradient from these measurements. Fig. 4 illustrates clearly these phenomena. Thus for a correct use of electrodiffusional method expensive thermostated installation should be used. Another possibility which we retain with interest consists in compensation of thermal effects.

The thermal effects in electrochemical flow diagnostics are related with thermo-dependence of the molecular viscosity and diffusivity. The temperature dependence of the molecular diffusion coefficient can be obtained using

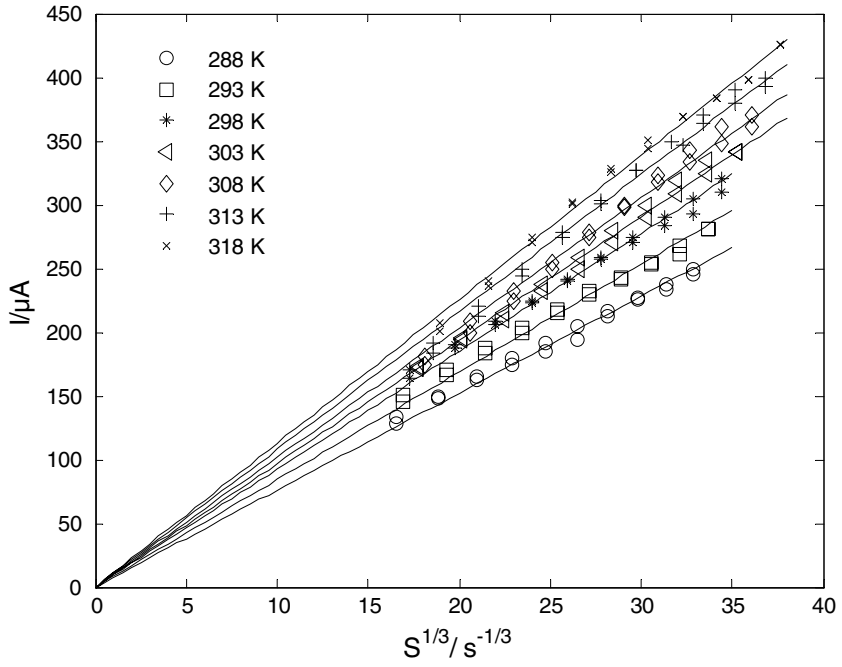

Fig. 4. Lévêque curves for circular electrode C_1 at different temperatures, $C_0 = 25\ \text{mol m}^{-3}$.

the classical rotation disc electrode system (Frumkin et al., 1960; Levich, 1962). The advantage of this installation deals with the possibility to use the working electrode with well defined surface (in our experiments $A = 3.14 \times 10^{-6}\ \text{m}^2$) and to work with small electrolyte volume in well controlled electrochemical conditions (Pleskov and Filinovski, 1972; Coeuret and Storck, 1984). The diffusion coefficient D is obtained from the experimental dependences $I_L = \alpha\Omega^{1/2}$ of the limiting diffusion current I_L versus angular rotation speed of the disc Ω (Levich, 1962)

$$D_{\text{Lev}} = \left[\frac{\alpha}{0.62nFC_0Av^{-1/6}}\right]^{3/2}. \tag{9}$$

Using the rotating disc electrode we have determined the molecular diffusion coefficient as the function of the temperature (Fig. 5), the data fit the following equation for temperature ranges investigated (280 K < T < 320 K):

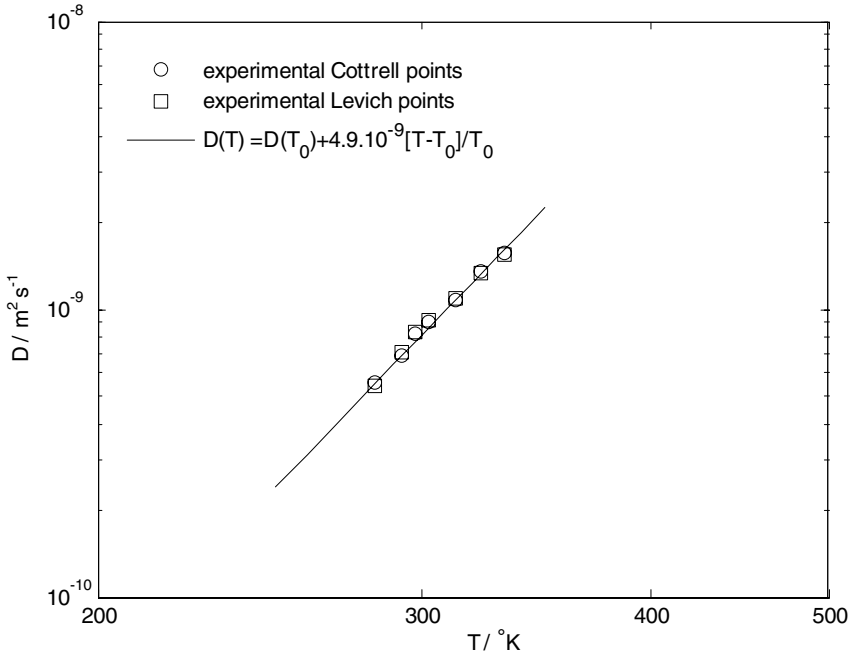

Fig. 5. Thermo-dependence of diffusion coefficient obtained with Levich and Cottrell methods, rotating disc electrode ($A = 3.14 \times 10^{-6}\ \text{m}^2$), $C_0 = 25\ \text{mol m}^{-3}$.

$$D_{\mathrm{Lev}}(T) = D_{\mathrm{Lev}}(T_0) + \xi_2\left[\frac{T - T_0}{T_0}\right], \tag{10}$$

where $\xi_2 \approx 4.9 \times 10^{-9}$ m^2 s^{-1}; $T_0 = 298$ K, and the diffusion coefficient $D(T_0)$ is equal to 8.33×10^{-10} m^2 s^{-1}.

The limiting diffusion current at arbitrary temperature $I_{\mathrm{L}}(T)$ can be obtained from the limiting diffusion current at the reference temperature $I_{\mathrm{L}}(T_0)$:

$$I_{\mathrm{L}}(T) = \chi(T) I_{\mathrm{L}}(T_0), \tag{11}$$

where the compensation constant is equal to

$$\chi = \frac{I_{\mathrm{L}}(T)}{I_{\mathrm{L}}(T_0)} = \left[\frac{D_{\mathrm{Lev}}(T)}{D_{\mathrm{Lev}}(T_0)}\right]^{2/3}. \tag{12}$$

In our experimental conditions (280 K $< T <$ 320 K) the thermo-compensation constant have been evaluated by using Eq. (9)

$$\chi = 1 + \xi_3\left[\frac{T - T_0}{T_0}\right]; \quad \xi_3 \approx 4.3. \tag{13}$$

The proposed thermo-compensation method have been verified using the limiting diffusion current measurements provided in channel flow at different temperatures, see Fig. 4. The results are presented on Fig. 6, where the measurements at different temperatures are reduced to a reference temperature $T_0 = 298$ K. All data gather near the solid reference line, which corresponds to the calibration curve of the electrodiffusion sensor at $T_0 = 298$ K, with an average deviation of about 10%.

The wall velocity gradient S calculated from the electrodiffusional measurements at different temperatures have been also confronted with hydraulic measurements. The results are presented on Fig. 7, in terms of the dependence of the friction coefficient λ from the Reynolds number Re_{h}. On this figure the solid line correspond to the Blasius law, open symbol to the results of electrodiffusion measurements with thermo-compensation and the solid symbol to the pressure drop measurements. The accuracy of the proposed method of thermo-compensation is about 12%.

4. Thermal compensation of wall velocity gradient measurements in non-isothermal conditions

Compensation of thermal effects in non-isothermal experiments is more complicated problem. The proposed in the previous paragraph method is based on the supposition that the temperature is uniform in the experimental set-up and cannot be used for compensation of thermal effect in situations when local temperature gradients are involved. For these reasons we discuss below another possibility of "in situ" compensation of thermal effects using the Cottrell method (Cottrell, 1902).

The principal of this technique is based on the short-time measurement (less than 1 s) of a transient diffusion limiting current $I_{\mathrm{L}}(t)$ after voltage-step polarization of the working electrode (Cottrell, 1902; Sobolik et al., 1998). The temporal evolution of the limiting diffusion current is obtained by solving of unsteady diffusion equation (Macero and Ruffs, 1959)

$$I_{\mathrm{L}}(t) = nFAC_0\sqrt{\frac{D_{\mathrm{Cot}}}{\pi t}}, \tag{14}$$

then the diffusion coefficient can be determined from the experimental curve $I_{\mathrm{L}}(t) = \beta t^{-1/2}$. Fig. 8 presents the results of transient limiting current measurements obtained with

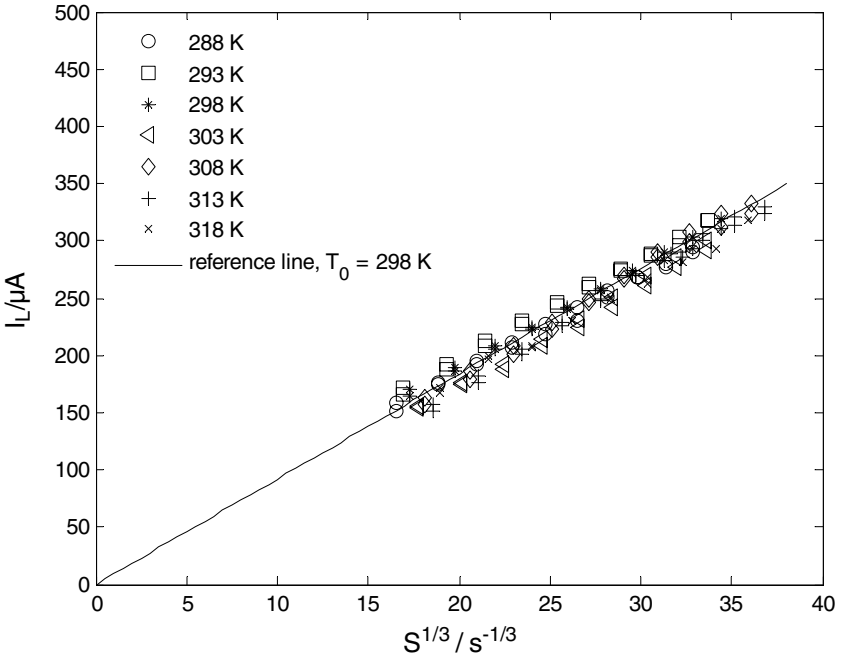

Fig. 6. Effect of thermal compensation on the channel hydrodynamic measurements, circular electrode C_1, $C_0 = 25$ mol m^{-3}.

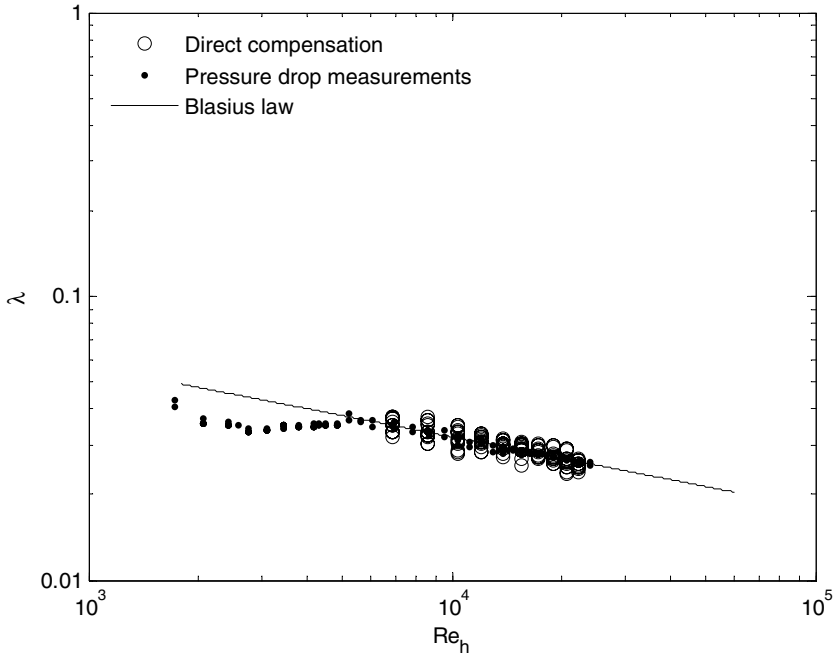

Fig. 7. Comparison between the direct compensation and the pressure drop measurements of the skin friction, circular electrode C_1, $T = 298$ K, $C_0 = 25$ mol m^{-3}.

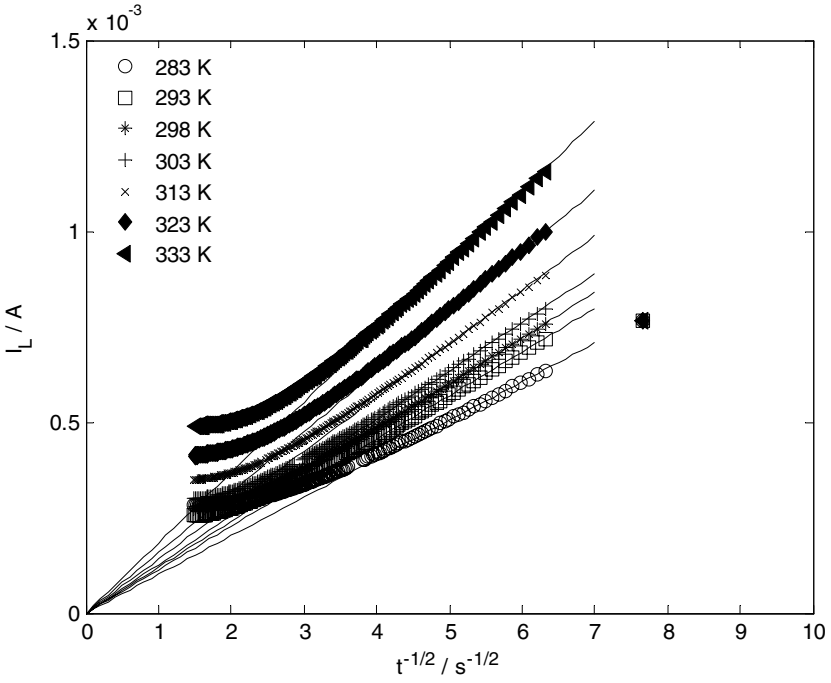

Fig. 8. Time-evolution of transient limiting current at different temperature, rotating disc electrode, $E = -0.6$ V, $C_0 = 25$ mol m^{-3}, $\Omega = 500$ tr mn^{-1}.

the 2 mm diameter rotating disc electrode ($A = 3.14 \times 10^{-6}$ m^2) at different temperatures.

The Table 2 presents the values of the slopes α, β and the magnitudes of the diffusion coefficient $D_{\mathrm{Lev}}(T)$, $D_{\mathrm{Cot}}(T)$ deduced from Levich and Cottrell curves. We note the well concordance between these two experimental methods as well as the agreement between our experimental data and Stokes–Einstein equation obtained for low viscosity electrolytes (Cussler, 1984; Arvia et al., 1968, 1967; Legrand et al., 2000)

$$D\mu/T \approx 2.6 \times 10^{-15}\ \mathrm{m^2\ Pa\ K^{-1}}. \quad (15)$$

Cottrell method allows to compensate the temperature effects in electrochemical diagnostics of flows with local temperature gradients. Indeed, the calibration constant ς

Table 2
Physical properties of the electrolytic solution, rotating disc electrode, $C_0 = 25$ mol m^{-3}

T (K)	$\nu \times 10^6$ (m^2 s^{-1})	$\alpha \times 10^6$ (A rad$^{-1/2}$ s$^{1/2}$)	$\beta \times 10^6$ (A s$^{1/2}$)	$D_{Lev} \times 10^{10}$ (m^2 s^{-1})	$D_{Cot} \times 10^{10}$ (m^2 s^{-1})	$\frac{D_{Cot}\mu}{T} 10^{15}$ (m^2 Pa k^{-1})	$\frac{D_{Lev}\mu}{T} 10^{15}$ (m^2 Pa k^{-1})
283	1.39	29.46	100.55	5.41	5.53	2.73	2.67
293	1.11	36.62	112.40	7.07	6.91	2.61	2.67
298	1.00	41.55	122.64	8.33	8.23	2.77	2.80
303	0.89	45.21	128.38	9.18	9.02	2.65	2.70
313	0.74	52.23	139.98	10.90	10.72	2.55	2.59
323	0.63	61.55	156.98	13.38	13.49	2.64	2.61
333	0.56	69.35	168.98	15.55	15.63	2.64	2.63

in Lévêque Eq. (2) can be expressed in terms of the Cottrell constant β

$$\varsigma = 0.83(nFC_0)^{-1/3}\pi^{2/3}A_{Lev}^{-1/2}\beta^{4/3}, \quad (16)$$

thus, combination of the transient and steady-state limiting diffusion current measurements gives one the possibility of "in situ" determination of the calibration constant ς. The interest of the proposed method deals with the possibility to avoid the direct thermal compensation of the diffusion coefficient in Eq. (2) which is based on the knowing of the near wall electrolyte temperature.

Space resolution of the proposed method of thermo-compensation is determined by the electrode length (in longitudinal and transversal directions) and by the diffusion layer thickness in the normal direction. Microelectrodes which are used for electrodiffusion measurements can be about 100 μm of diameter or less, the corresponding diffusion layer thickness is usually less than some micrometers. The time resolution is determined by the time scale of the Cottrell measurement (<1 s).

Sure the proposed method of thermo-compensation is based on the supposition that the bulk concentration of the electrolyte C_0 and the microelectrode active surface A_{Lev} are known or at least constant in time. Nevertheless, we note relatively small dependence of the constant ς in Eq. (16) regarding the bulk concentration (power – 1/3) and the active surface area (power −1/2). It means that relatively small variations of the surface area and the bulk concentration can be neglected.

The determination of the electroactive surface area is a delicate problem. In principal, it can be obtained either from the Lévêque or Cottrell measurements provided in isothermal conditions at known temperature (see Table 1). Some difference between A_{Lev} and A_{Cot} should be noted. This difference can be related with the existence of roughness on the microelectrodes surface. The thickness of the developing with time diffusion layer is very small that is why using Cottrell method we measure "three-dimensional" surface. Electrochemical measurements of wall velocity gradient are based of steady-state current measurements which are sensitive to the Lévêque surface.

It means that correct utilisation of electrochemical flow diagnostics requires direct calibration of electrodiffusional sensors in known hydraulic conditions at some given temperature in order to estimate the Lévêque surface A_{Lev}. After, the calibration constant ς can be determined using Cottrell calibration measurements with the help of Eq. (16).

5. Thermal compensation of mass transfer coefficient measurements

The proposed above method (Section 4) can be applied also for mass transfer coefficient measurements when the temperature in the vicinity of the electrode surface is unknown. This situation arises, for example, during local heating of the electrolyte solution by means of a hot-wire (Gründler et al., 1995; Gründler and Degenring, 2001).

Let us consider (Fig. 9) a small thermostated cell equipped with fine platinum wire (15 mm long, 25 μm in diameter and 99% purity) welded at ends to tantalum prongs according to procedure described previously (Allouch et al., 1982). The platinum wire is submerged in the electrolyte described in Section 2 and integrated in two independent electrical circuits as shown on Fig. 9. The first is composed of an electrical source (Keithley K2400) and nanovoltmeter (Keithley K2182) controlled by "Labview" software. This electrical circuit is used for the local pulse heating of the solution by supplied a current intensity I_{el}. The second electrical circuit allows voltage-step Cottrell measurements, for this purpose a platinum counter electrode of a grand surface (4×10^{-4} m^2) is immerged in the solution as well. This circuit is composed of a potentiostat (Solartron 1480 MultiStat) controlled by "CorrWare" software. The electronic devices are interconnected by GPIB Boards with PC; this allows local pulse heating of the solution with simultaneous measurements of transient limiting diffusion current.

Under these conditions, the mass transfer coefficient in Eq. (1) at unknown temperature $k(T)$ can be expressed in terms of the Cottrell constant β

$$k(T) = \psi(T)k(T_0); \quad \psi(T) = \frac{\beta}{\beta_0}, \quad (17)$$

where β is the Cottrell constant at unknown temperature; $k(T_0)$ and β_0 are respectively the mass transfer coefficient and Cottrell constant at some reference temperature T_0.

The Cottrell constant can be determined using the short time measurements ($t < 0.5$ s), we will assume that over this time scale the temperature of the solution is constant.

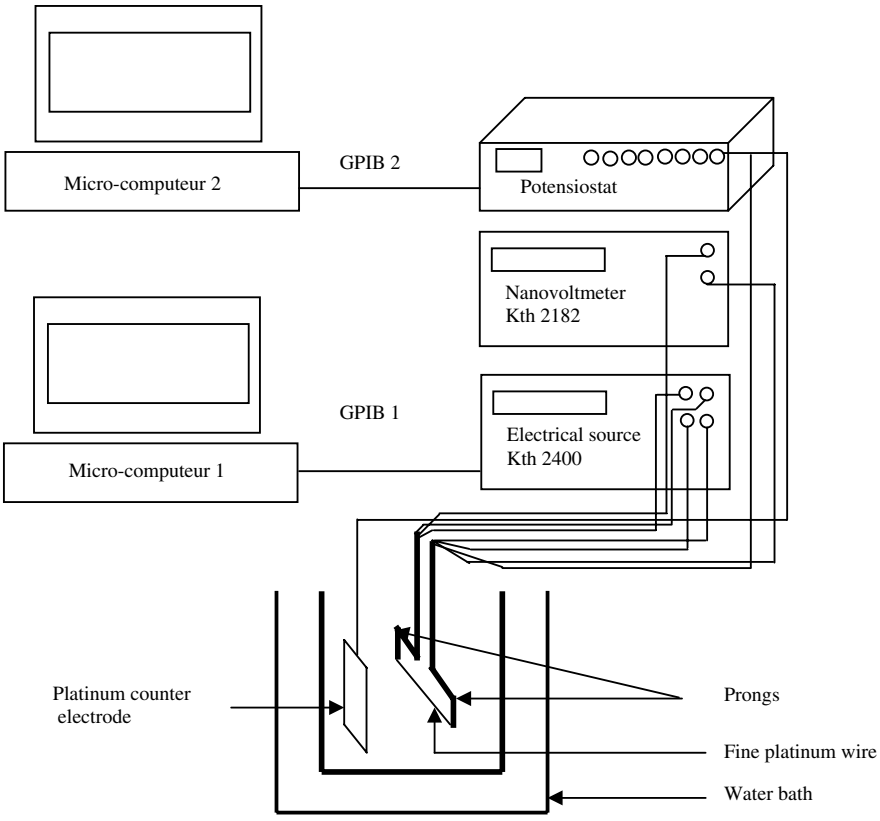

Fig. 9. Schematic representation of the hot-wire cell.

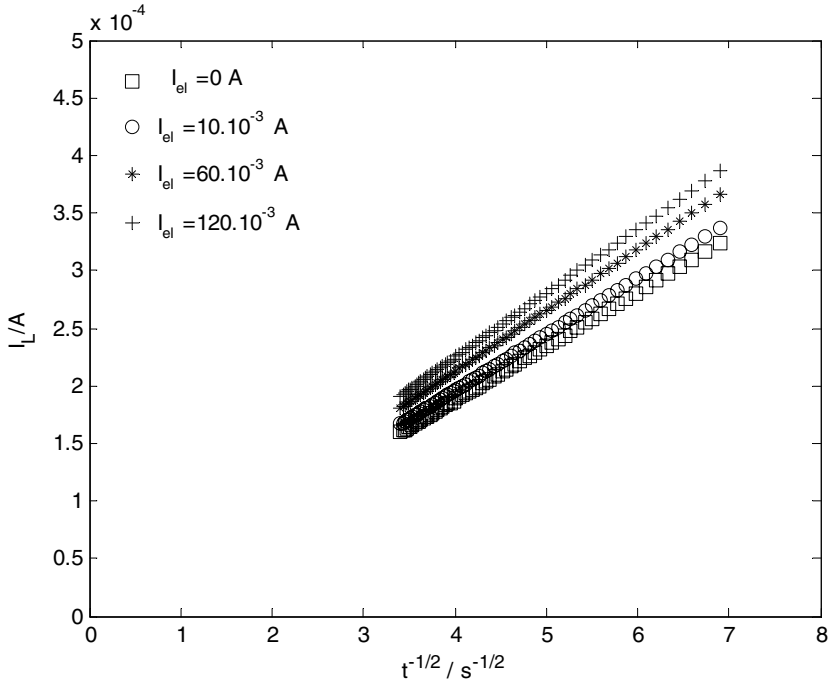

Fig. 10. Time-evolution of transient limiting current for different current intensity, platinum wire, $T_0 = 294.8$ K, $C_0 = 25$ mol m^{-3}.

Fig. 10 presents the results of the Cottrell measurements provided for different electrical powers supplied to the hot platinum wire. The electrodiffusional measurements provided in isothermal conditions give the value $k(T_0) = 6.03 \times 10^{-5}$ ms^{-1} for the mass transfer coefficient at the reference temperature of the solution (before heating) $T_0 = 294.8$ K. The presented on Fig. 9 results allow to determine the Cottrell constant β and, thus the

Table 3
Mass transfer coefficient for different current intensity, platinum wire, $C_0 = 25\ \text{mol m}^{-3}$

$I_{el} \times 10^3$ (A)	0	10	60	120
$\Psi(T)$	1.00	1.05	1.14	1.20
$k(T) \times 10^5$ (m s^{-1})	6.03	6.33	6.87	7.56

thermo-compensation coefficient $\psi(T)$ according to Eq. (17), see Table 3. In this way the mass transfer coefficient can be obtained in non-isothermal experimental conditions.

6. Conclusion

Thermal effects related with electrodiffusional measurements of wall velocity gradient have been studied in turbulent channel flow. In isothermal conditions, the direct thermo-compensation can be provided using the measurements of thermo-dependence of molecular diffusivity and viscosity. The direct thermo-compensation has been successfully applied to skin friction factor measurements: it has been found that electrodiffusional measurements realized at different temperatures are in a good agreement with hydraulic measurements, the maximal deviation does not exceed 12%.

Using the rotating disc electrode system we have proved that temperature dependence of the molecular diffusivity can be successfully obtained also using the Cottrell method (voltage-step transient method). The deviation in comparison with Levich method is about 3%. The simultaneous transient and steady-state limiting diffusion current measurements open the possibility for in situ compensation of thermal effects in electrodiffusional measurement at non-isothermal conditions, where the local temperature gradients are presented.

Moreover, the influence of the electrode active surface A and bulk concentration of electroactive species C_0 on electrodiffusion measurements can be avoid partially under this way. Indeed, these factors are presented in Eq. (16) for the calibration constant ς with power factors 1/2 and 1/3, respectively. Nevertheless, it is preferable to determine preliminary the electrode active surface A using direct Lévêque calibration in known hydrodynamic conditions in order to use correctly electrodiffusional flow diagnostics.

The feasibility of the proposed method of thermo-compensation in non-isothermal conditions have been confirmed experimentally for the case of local heating of the solution by means of pulse hot-wire technique.

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