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EFFECTS OF JOULE HEAT ON THE STEADY-STATE TEMPERATURE PROFILES AND THE MEAN VALUES OF TEMPERATURE IN ISOTACHOPHORESIS

Z. RYŠLAVÝ, P. BOČEK, M. DEML and J. JANÁK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 662 28 Brno (Czechoslovakia)

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SUMMARY

The dependence of the steady-state temperature in isotachophoretic columns on dissipated electric power has been investigated. The requirements of the heat regime in isotachophoretic columns from the standpoint of separation are discussed. A quotient $\bar{Q}$ has been defined in order to permit a comparison of the efficiency of cooling for symmetrically cooled columns with different cross-sectional areas and shapes. Quotients $\bar{Q}$ were measured for three types of cooling on the basis of conductivity measurements on an electrolyte, the conductivity of which was dependent on temperature. The measurements were performed at various electric powers and cooling temperatures. A method for obtaining cross-sectional temperature profiles from the experimental data is proposed for symmetrically cooled columns with circular cross-sections.

INTRODUCTION

One of the factors that can influence the isotachophoretic separation of ionic compounds is temperature. Both the density of the medium where the migration takes place and the effective mobilities of separated ionic constituents and counter ions (owing to the temperature dependence of ionic mobilities and dissociation constants) are sensitive to temperature. Ideally, the temperature in the column should be constant. However, as a consequence of the generation of Joule heat and to the finite rate of the heat transfer, radial and axial temperature gradients are formed. Consequently, an individual constituent may have various effective mobilities according to its position in the column. In addition to these effects, the density gradients cause convection, violating the boundaries between zones.

Knowledge of radial temperature profiles is of great importance in the evaluation of separation efficiency, as the zone boundaries are distorted owing to the radial temperature profiles. It is important to know the mean temperatures in zones. The mean temperatures control the mean effective mobilities in the zones of compounds to be separated and thus also their concentrations. The radial distribution of temperature in columns with a circular cross-section for the radial-independent energy dissipation has been the subject of calculations by several workers[1–6]. This model corre-

sponds to the neglect of the effect of temperature on the conductivity of an electrolyte. The resulting steady-state temperature profiles calculated on the basis of this model are of parabolic shape.

Calculations of the stady-state radial temperature distribution for heat generation in an electrolyte, the conductivity of which is linearly dependent on temperature, were carried out by Brown and Hinckley for capillary tubes with circular[7] and rectangular[8] cross-sections. Coxon and Binder[9,10] made similar calculations. They incorporated the properties of column walls into their solutions, which they extended to unsteady states. The profiles calculated are, in comparison with the parabolic profiles, somewhat steeper, i.e., there are greater differences between the temperature in the centre of the capillary tube and that of marginal layers at the column walls.

The measurements of temperature profiles were not performed in isotachophoretic columns, but steady-state temperature distributions were measured in wide packed electrophoretic columns by using thermocouples[4,11,12]. These profiles generally conformed with the theoretical parabolic profiles.

In order to calculate the temperature profiles and the analytically important mean temperature, it is necessary to be familiar with several constants that characterize the materials (thermal conductivity coefficient, heat transfer coefficient and temperature coefficient of conductivity of the electrolyte). The heat transfer coefficient, however, is usually unknown, but can be determined from the dependence of the mean temperature on dissipated length power and from other data. The complete profiles can then be calculated. From the standpoint of analytical isotachophoresis, the influence of dissipated electric power and column geometry on the mean value of temperature in a zone are fundamentally important.

The aim of this work was to investigate the dependence of the steady-state mean temperature in isotachophoretic columns on dissipated power and column geometry for various ambient temperatures and, on the basis of theory and accesible data, to draw conclusions which permit radial temperature profiles for capillary tubes with circular cross-sections to be calculated.

THEORETICAL[*]

It is advantageous to express the steady-state radial temperature profiles in the form of the increase in temperature at unit power dissipated over unit length of a column:

$$Q = \frac{T - T_0}{P} \tag{1}$$

If T represents $\bar{T}$ then the resulting quotient, $\bar{Q}$, indicates the increase in the mean value of the steady-state temperature if unit heat power is generated in unit length of an isotachophoretic column. Quotient $\bar{Q}$ is a measure of the imperfection of thermostating. If the system is thermostated ideally, then $\bar{Q} = 0$. The product $\bar{Q}\,S$ corresponds to the increase in the mean temperature at unit mean volume power dissipated in a column. This product is suitable for the comparison of the efficiency of cooling for columns with different cross-sectional areas and shapes.

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[*] For list of symbols, see p. 24.

The mean temperature for columns with a circular cross-section is given by

$$\bar{T} = \frac{1}{S} \int_0^S T \mathrm{d}S = \frac{2}{R_1^2} \int_0^{R_1} r T(r) \mathrm{d}r \tag{2}$$

For linearly variable heat generation the following relationships apply to the steady-state[7,9]:

$$Q(r) = \frac{1}{2\pi k_1} \cdot \frac{J_0(\beta r) - J_0(\beta R_1)}{\beta R_1 J_1(\beta R_1)} + Q(R_1) \tag{3}$$

$$\bar{Q} = \frac{1}{2\pi k_1} \cdot \frac{\dfrac{2}{\beta R_1} \cdot J_1(\beta R_1) - J_0(\beta R_1)}{\beta R_1 J_1(\beta R_1)} + Q(R_1) \tag{4}$$

and

$$Q(R_1) = \frac{1}{2\pi k_2} \left(\ln \frac{R_2}{R_1} + \frac{k_2}{H R_2} \right) \tag{5}$$

The solution, which applies to an infinitely long zone without a counter flow, neglects convection, variations in thermal conductivity with temperature (this assumption has been checked elsewhere[9]) and electrokinetic phenomena. When calculating the profiles numerically, we choose P_v as a parameter for a set of material constants and it is then easy to calculate the corresponding values of $\bar{T}$, $T(r)$ and P. Provided that we have thus determined corresponding pairs of values P and P_v, it is possible to find, for a measured P, the appropriate P_v and thus to determine the radial temperature distribution in the system.

In addition to the aforementioned temperatures inside the column, the temperature at the outer capillary surface is also an important quantity, and monitoring of this temperature is the substance of thermometric detection of zones[6]. For the quotient of the increase in temperature with P at the wall periphery, it holds that

$$Q(R_2) = \frac{1}{2\pi H R_2} \tag{6}$$

In order to determine the value of $\bar{Q}$ for an isotachophoretic column, a model system is used that employs an electrolyte, the electrolytic conductivity of which can be approximated by the relationship

$$G_T = G_{T_0} [1 + \alpha (T - T_0)] \tag{7}$$

Then we can write for the dependence of conductivity on dissipated power at constant thermostat temperature:

$$G_P = G_{P=0} (1 + \gamma P) \tag{8}$$

From eqns. 1, 7, and 8, it follows that

$$\bar{Q} = \frac{\gamma}{\alpha} \qquad\qquad (9)$$

EXPERIMENTAL

The measurements of the dependence $G = f(P)$ at various thermostating temperatures were carried out by using the circuit in Fig. 1 at the mains frequency (50 Hz). Two columns with circular cross-sections and a flat column with a rectangular cross-section[13] were investigated. One column with a circular cross-section was thermostated by using a water-cooled aluminium cylinder round which a PTFE capillary tube was coiled helically[14], the column plus the cylinder being placed in an air-bath. The column of the second type was directly surrounded by the cooling liquid (LKB 2127 Tachophor; LKB, Bromma, Sweden). Four-electrode conductimetry[15] was used for the flat column filled with 1 M potassium chloride solution (the voltage was measured at the points 1, 1 in Fig. 1). The choice of electrolyte and the experimental method were influenced by the construction of the apparatus, requirements of the range of voltage and electric current and requirements of polarization resistance. In spite of different conditions of measurements, the results are comparable, as is explained later.
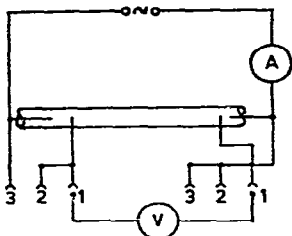

Fig. 1. Schematic diagram of experimental arrangement for the measurements of the increase in conductivity with generated Joule heat.

The design of the helical column did not allow the use of four electrodes without serious damage to the original column. Therefore, one measuring electrode was connected with the appropriate electrode supplying the column with electric current directly (*i.e.*, points 2, 2 in Fig. 1). In order to suppress polarization, 0.01 M potassium chloride solution was used for the LKB 2127 Tachophor. The voltage was measured at points 3, 3 in Fig. 1, as two-electrode conductimetry could be used. The dependence $G = f(P)$ was measured at various thermostatting temperatures in the range 10–50 °C, except for the LKB 2127 Tachophor, where the temperatures were set between 0° and 29 °C on the dial. The voltage and electric current were increased until an evolved gas bubble broke the circuit.

RESULTS AND DISCUSSION

An example of the measured dependences $G = f(P)$ for the flat column at a parametrically chosen T_0 is shown in Fig. 2. The dependences form a system of

parallel lines, *i.e.*, for a given P the increase in temperature, $\bar{T} - T_0$, is independent of the thermostating temperature. Hence, the quotient $\bar{Q}$ is a characteristic constant for a column within the temperature and electric power ranges investigated and it can be used advantageously as a measure of the cooling efficiency.
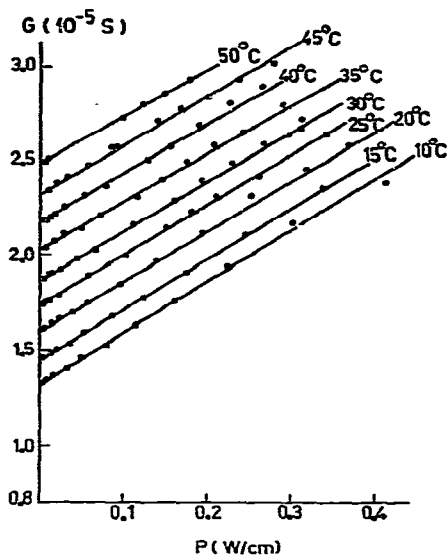

Fig. 2. Dependence of the conductivity of 1 M potassium chloride solution in the column with a rectangular cross-section ($L = 17.5$ cm). Thermostating temperature ranged parametrically from 10 °C to 50 °C.

The values of $\bar{Q}$ can be obtained from the dependences $G = f(P)$ in two ways. From the slopes of the lines, γ, and the values of α, $\bar{Q}$ can be determined directly by using eqn. 9. By means of a comparison of the calibration plot $G = f(P = 0, \bar{T})$ and the dependences $G = f(P, T_0)$, the value of $\bar{Q}$ can be checked. It was found that the results are comparable under the experimental conditions used.

A general need to cool isotachophoretic columns can be represented by the requirement that the values of $\bar{Q}$ should be minimal. Such a requirement is obvious from the situation in a column during separation. Temperatures in the zones increase progressively towards a terminator and thus the differences between the effective mobilities of successive zones are influenced the more, the higher is $\bar{Q}$. The difference may decrease or increase according to the values of the temperature coefficients of conductivity of ionic constituents and changes in chemical equilibria in the zones. Therefore, the results for the same analyses performed in several isotachophoretic columns may differ, in spite of the same conditions of separation being used. High heat powers result from rapid analyses employing high current densities. To prevent the formation of gas bubbles and other disturbing effects, columns with minimal values of $\bar{Q}$ should be used.

From the values given in Table I, it follows that, in spite of an imperfect contact with the coolant (from one side only), the flat column shows fairly favourable properties. This is in agreement with the classical work of Tiselius[18], who enunciated

that the minimal temperature shift occurs in columns with rectangular cross-sections. The cooling type where the capillary column is coiled helically around a metal cylinder is nearly left at present time, but the value of $\bar{Q}$ for such a column could be useful for a comparison of the results published previously with the present results.

TABLE I

VALUES OF $\bar{Q}$ AND $\bar{Q} S$

Column	$\bar{Q}$ $(K \cdot cm \cdot W^{-1})$	$\bar{Q} S$ $(K \cdot cm^3 \cdot W^{-1})$	Reference
Flat	93	0.388	13
Helical	509	0.917	14
LKB 2127 Tachophor	13t	0.324	

LKB 2127 Tachophor has very good contact of the capillary with the cooling medium except for the connection to the reservoirs and the detection cell. The measurements were made at the locations where the capillary tube was in direct contact with the coolant. The LKB 2127 Tachophor has the best cooling as regards the temperature shift in the measured area, as follows from Table I. Overheating occurs in the connections to the reservoirs at lower powers and thus the operating range is reduced. Overheating and possible breakage of the column of electrolyte commonly occurs at about 60 °C in aqueous solutions owing to elimination of dissolved gases from the water.

If there are different materials and/or wall thicknesses in the proper column and the detection cell, the heat regime inside the column is unstable and $\bar{Q}$ is not constant along the separation path. Another reason for instability of the heat regime may be that the analysis (*i.e.*, passage of zones through the detection cell) is finished before the temperature is stabilized, so that the radial and longitudinal temperature profiles vary during the separation. The analysis of such unsteady-state heat conduction problems has been carried out with regard to the maximal allowable temperature in columns and with the aim of achieving the flattest radial profiles[9,10]. These authors proposed working at the maximal heating rate for which the maximal temperature in the column centre did not exceed the maximal allowable temperature. By using such a heat regime, the mean temperatures of the zones increase towards the end of the analysis. The result is a time-unstable system in which the ratios of the mobilities of the constituents being separated vary continuously.

As mentioned above, the measured values of $\bar{Q}$ gives a measure of the efficiency of thermostating. Moreover, in some instances, a knowledge of $\bar{Q}$ allows one to determine the steady-state temperature profiles for arbitrary experimental conditions (characterized by the values of T_0 and P). For example, on assuming a homogeneously cooled column with a circular cross-section, for the evaluation of $T(r)$ it is necessary to know the value of H or $Q(R_1)$. However, these values are usually unknown and it is therefore necessary to measure $\bar{Q}$ by means of the method described above. Evaluation of eqns. 3–5 in terms of the data from Table II yields

$$\bar{Q} = 6.5 + Q(R_1) \tag{10}$$

TABLE II

DATA USED IN CALCULATIONS OF $Q(r)$

Parameter	Value	Reference
k_1	$6.029 \cdot 10^{-3} \, K^{-1} \cdot W \cdot cm^{-1}$	16
k_2	$2.328 \cdot 10^{-3} \, K^{-1} \cdot W \cdot cm^{-1}$	16
α	$2.32 \cdot 10^{-2} \, K^{-1}$	17
R_1	$2 \cdot 10^{-2} \, cm$	—
R_2	$3 \cdot 10^{-2} \, cm$	—

$Q(R_1)$ can be found from eqn. 10 and the experimental value of $\bar{Q}$. The value of H can be determined with help of Fig. 3, where the dependence of $Q(R_1)$ on k_2/HR_2 is plotted (curve a). The dependence was calculated by using the data given in Table II. The dependence of $Q(R_2)$ on k_2/HR_2, which is also plotted in Fig. 3 (curve b), makes it possible to determine the temperature at the column surface. Here it should be mentioned that the values of $\bar{Q}$ and/or $Q(r)$ are not strictly constant as P_v increases. Their changes, however, are negligible and it is not worth taking them into account. Having measured $\bar{Q}$, we can determine $Q_m = Q(0)$ from Fig. 4. As the value of H increases, both Q_m and $\bar{Q}$ decrease; their ratio, however, increases, i.e., the radial profiles grow steeper[9].
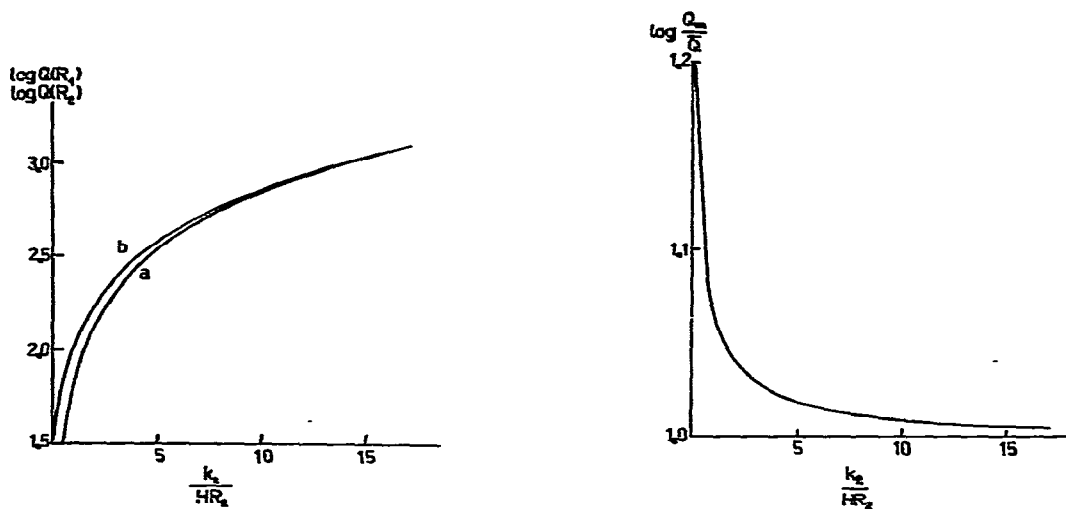

Fig. 3. Dependences of log $Q(R_1)$ (curve a) and log $Q(R_2)$ (curve b) on k_2/HR_2.

Fig. 4. Dependence of log $Q_m/\bar{Q}$ on k_2/HR_2.

CONCLUSIONS

Temperature is one of the factors that can influence the isotachophoretic separation of ionic compounds and the analytical interpretation of the signal from a detector. The temperature in isotachophoretic columns is the result of the superposition of Joule heat and the temperature of the thermostat. A suitable quantity for the

description of the heat regime in isotachophoretic columns is the quotient $\bar{Q}$ defined by eqn. 1. This quantity is measurable and it renders a comparison of different columns possible. The outstanding factors that influence the values of $\bar{Q}$ are the geometry of the cross-section of the column and the contact of the column with the cooling medium. Moreover, the experimental value of $\bar{Q}$ yields a good approximation for the determination of the heat transfer coefficient through the outer column surface. On the basis of this coefficient and some other data, it is possible to calculate the $Q(r)$ function, *i.e.*, the complete steady-state radial temperature distribution.

ACKNOWLEDGEMENT

LIST OF SYMBOLS

G_T electric conductivity of the column of an electrolyte at temperature T (S);

G_P electric conductivity of the column of an electrolyte at power P dissipated in the column (S);

H heat transfer coefficient (W·cm^{-2}·K^{-1});

J_0 Bessel function of zero order and first kind;

J_1 Bessel function of first order and first kind;

k_1 coefficient of thermal conductivity of electrolyte (W·cm^{-1}·K^{-1});

k_2 coefficient of thermal conductivity of tube walls (W·cm^{-1}·K^{-1});

P electric power dissipated in unit length of a column (W·cm^{-1});

P_v theoretical electric power dissipated in unit volume at temperature T_0 (W·cm^{-3});

$Q(r)$ temperature increase in a distance r from the capillary centre at unit length power dissipated (K·cm·W^{-1});

$\bar{Q}$ mean value of $Q(r)$ function (K·cm·W^{-1});

Q_m $Q(r)$ function at point $r = 0$ (K·cm·W^{-1});

r distance from capillary centre (cm);

R_1 inner radius of tube (cm);

R_2 outer radius of tube (cm);

S cross-sectional area (cm^2);

T temperature (K);

$\bar{T}$ mean temperature (K);

T_0 temperature of thermostat (K);

α temperature coefficient of conductivity at temperature T_0 (K^{-1});

$$\beta = \sqrt{\frac{\alpha P_v}{k_1}}$$

γ coefficient of the dependence of conductivity on dissipated length electric power at temperature T_0 (cm·W^{-1})

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