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NATURE OF TEMPERATURE GRADIENTS IN CAPILLARY ZONE ELECTROPHORESIS

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SUMMARY

An expression for the radial temperature profile in capillary zone electrophoresis was derived, taking into account the temperature dependence of the buffer electrical conductivity and the polyimide coating of the quartz capillary. Calculations show that in typical capillary zone electrophoresis experiments; *i.e.*, capillaries with 50–100 μm I.D., 375 μm O.D., and up to 5 W power input, the temperature profile rigorously derived is nearly identical to a parabolic profile. At high input powers, the parabolic approximation underestimates the temperature at the capillary center.

INTRODUCTION

Capillary zone electrophoresis (CZE) is a separation technique the plate height efficiency of which can be very high. In practice, however, the theoretically calculated efficiencies are not observed. One possible reason for the lower than theoretical efficiencies can be traced to heating effect due to the passage of current through the capillary[1]. This heating effect causes a temperature difference between the center of the capillary and the wall, which, in turn, causes differences in the viscosity of the buffer electrolyte within the column. The resulting radial viscosity gradient produces a velocity difference between the center of the capillary and the wall. This velocity difference gives rise to mass transfer effects which lower the system efficiency. Grushka *et al.*[2] have studied the effect of temperature differences on the efficiency of CZE. In that study the assumed temperature profile produced a parabolic velocity profile across the capillary. In the present communication, this parabolic temperature profile assumption is justified.

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THEORY

Derivation of temperature profile

Modern CZE separations are carried out in quartz capillaries that are coated with a thin layer of polyimide. In this analysis, R_1 symbolizes the internal radius, R_2 the quartz radius and R_c the total radius of the capillary. The temperature dependence of the thermal and electrical conductivities should be taken into account in the heat balance equations in order to obtain the correct temperature profile. Using an approach similar to that of Coxon and Binder[3] and by Brown and Hinckle[4], the heat balance equation for CZE can be written as

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}T}{\mathrm{d}r}\right) = -\frac{G}{k_1} \tag{1}$$

where T is the temperature, r is the radial position, G is the heat generation per unit volume and k_1 is the termal conductivity of the buffer solution. The boundary condition is

$$-R_1k_1\frac{\mathrm{d}T}{\mathrm{d}r} = UR_1(T_1 - T_s) \qquad \text{at } r = R_1$$

where R_1 is the internal radius of the capillary, T_1 and T_s are the temperature at the glass wall and the capillary surroundings (*i.e.*, a thermostated bath) respectively, (at R_1), and k_1 is the thermal conductivity of the buffer. The quantity UR_1 is related to the heat dissipation through the capillary wall, and it is given by

$$\frac{1}{R_1U} = \frac{1}{k_2}\ln\left(\frac{R_2}{R_1}\right) + \frac{1}{k_c}\ln\left(\frac{R_c}{R_2}\right) + \frac{1}{R_ch} \tag{2}$$

where R and k indicate radius and thermal conductivity and subscripts 2 and c indicate quantities relating to the quartz glass and polyimide coating, respectively. Because of the electrical conductivity dependence on temperature, the rate of heat generation will be written as

$$G = G_0\left[1 + \alpha\left(\frac{T - T_s}{T_s}\right)\right] \tag{3}$$

where α is the temperature coefficient of electrical conductivity of the buffer, G_0 is the rate of heat generation in the absence of temperature dependence of the electrical conductivity and T_s is the temperature of the capillary surroundings. When this temperature dependence of the heat generation is taken into account, the equation describing the heat balance can be written as[3]

$$\frac{1}{y}\frac{\partial}{\partial y}\left(y\frac{\partial \theta}{\partial y}\right) = -S(1 + \alpha\theta) \tag{4}$$

where

$$y = \frac{r}{R_c}$$

$$S = \frac{G_0 R_c^2}{k_1 T_s}$$

$$\theta = \frac{T - T_s}{T_s}$$

The boundary condition is

$$-k_1 \frac{d\theta}{dy} = UR_c\theta_1 \qquad \text{at } y = y_1$$

The solution of eqn. 4 is

$$\theta = AJ_0(\beta y) - \frac{1}{\alpha} \tag{5}$$

where $\beta^2 = \alpha S$ and A is a constant of integration. Using the boundary conditions it can be shown that

$$A = \frac{1}{\alpha[J_0(\beta y_1) - (\beta/\gamma)\, J_1(\beta y_1)]} \tag{6}$$

where

$$\gamma = \frac{UR_c}{k_1}$$

The expression for the temperature profile is, therefore:

$$\theta = \frac{1}{\alpha}\left\{\frac{J_0(\beta y)}{[J_0(\beta y_1) - (\beta/\gamma)\, J_1(\beta y_1)]} - 1\right\} \tag{7}$$

or

$$T = \frac{T_s}{\alpha}\left\{\frac{J_0(\beta y)}{[J_0(\beta y_1) - (\beta/\gamma)\, J_1(\beta y_1)]} - 1\right\} + T_s \tag{8}$$

Evaluation of the temperature profile

The temperature expression in eqn. 8 is similar to the expression obtained by Coxon and Binder[3]. However, eqn. 8 accounts for the fact that the quartz capillary tubing used in CZE is coated with polyimide. To evaluate the temperature profile, it is essential to obtain G_0, which is needed to calculate β. Coxon and Binder[3] did not describe the manner by which G_0 is obtained. Since the correct evaluation of G_0 is crucial to the proper determination of the temperature, we will elaborate here on this point.

Since heat dissipation in the capillary is from the center to the wall, we will re-write the expression for G in terms of a differential equation in the radial direction

$$dG = 2\pi r L G_0(1 + \alpha\theta)dr$$

Or, in terms of reduced radius

$$dG = 2\pi L R_c^2 G_0(1 + \alpha\theta)y dy \tag{9}$$

Substituting for θ from eqn. 7 and rearranging, we get

$$dG = 2\pi L R_c^2 G_0[\alpha A J_0(\beta y)]y dy \tag{10}$$

Since the electrical conductivity of the buffer varies radially with the temperature, we integrate over y. Thus, a substitution for A and integration between 0 and y_1 yield

$$G = \frac{2\pi L R_c^2 G_0 y_1 J_1(\beta y_1)}{\beta[J_0(\beta y_1) - (\beta/\gamma)J_1(\beta y_1)]} \tag{11}$$

Eqn. 11 allows us to obtain the value of G_0 by iteration (note that β is also a function of G_0). However, due to the transcendental nature of eqn. 11, numerical procedures must be used.

Calculations

A computer program was written to compute G_0 iteratively for a given input power. The iteration of eqn. 11 should be done with caution since the equation can have many roots. The only physically significant solution is the smallest root. Therefore, the iteration should start with a low initial estimate of G_0 to insure the proper convergence.

Once the value of G_0 is determined, the temperature profile is calculated using eqn. 8, as well as the following parabolic profile

$$T = T_s + \frac{GR_c}{2U} + \frac{GR_1^2}{4k_1}\left(1 - \frac{r^2}{R_1^2}\right) \tag{12}$$

The values of the various parameters used in the calculation are given in the sub-titles of Tables I and II. The radii of the capillary used in the calculations are typical of the sizes used in practice; *i.e.*, inner diameter of 50 μm, quartz capillary outer diameter of 345 μm and polyimide coating thickness of 15 μm (giving a total outside diameter of 375 μm). Assuming that an 1-degree change will cause a 2% change in the conductivity, the value of α is then 7.75.

Table I gives the temperature at the capillary center, at the inner wall and ΔT as

TABLE I

BUFFER TEMPERATURES AT THE CENTER AND AT THE WALL OF THE CAPILLARY

Parameters used: $L = 1$ m; $R_2 = 1.725 \times 10^{-4}$ m; $R_c = 1.875 \times 10^{-4}$ m; $T_a = 298$ K; $h = 10000$ W/m^{2}K; $k_1 = 0.605$ W/mK; $k_2 = 1.5$ W/mK; $k_c = 0.155$ W/mK; $\alpha = 7.75$.

Power (W)	*Eqn. 8*			*Parabolic*		
	Center (K)	*Wall (K)*	*ΔT (K)*	*Center (K)*	*Wall (K)*	*ΔT (K)*
Internal diameter = 50 μm						
2	299.214	298.951	0.263	299.214	298.951	0.263
3	299.722	299.326	0.396	299.721	299.326	0.395
5	300.738	300.077	0.661	300.735	300.077	0.658
Internal diameter = 100 μm						
2	299.067	298.804	0.263	299.067	298.804	0.263
3	299.501	299.106	0.395	299.500	299.106	0.394
5	300.370	299.709	0.661	300.367	299.709	0.658

found from the two methods of calculation. Shown in Table I are results for several capillary internal radii and power inputs. The results in Table I have several important implications: (a) typical CZE systems exhibit small temperature drops between the center and the wall —under the usual operating conditions, temperature effects are minimal[2]; (b) within the limits of the power input shown in the table, the temperature difference between the center and the inner wall of the capillary is independent of the inner radius. However, the actual temperatures are a function of the internal radius, showing a decrease with an increase in the diameter; (c) the temperatures calculated using eqn. 8 are identical, for all practical purposes, to those calculated from eqn. 12 over the whole cross section of the capillary. Fig. 1 shows the temperature profile within the capillary. The line depicting the temperature behavior is actually the superposition of two lines, one calculated using eqn. 8 and the other calculated using the parabolic profile, eqn. 12.

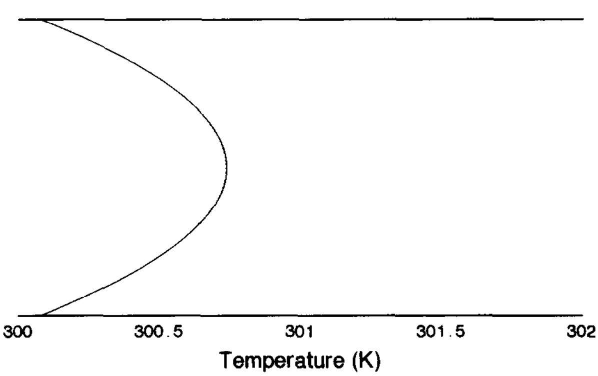

Fig. 1. Temperature profile as calculated from eqn. 8. Parabolic equation yields identical profile. Parameters used in the calculations are identical to those in Table I. Input power, 5 W; radius of capillary, 25 μm.

TABLE II

BUFFER TEMPERATURE AT THE CENTER AND AT THE WALL AT HIGH INPUT POWERS

Parameters used: $L = 1$ m; $R_2 = 1.725 \times 10^{-4}$ m; $R_c = 1.875 \times 10^{-4}$ m; $T_a = 298$ K; $h = 10000$ W/m^{2}K; $k_1 = 0.605$ W/mK; $k_2 = 1.5$ W/mK; $k_c = 0.155$ W/mK; $\alpha = 7.75$; internal diameter = 50 μm.

Power (W)	*Eqn. 8*			*Parabolic*		
	Center (K)	*Wall (K)*	*ΔT (K)*	*Center (K)*	*Wall (K)*	*ΔT (K)*
10	303.280	301.954	1.326	303.270	301.954	1.315
15	305.826	303.832	1.995	305.805	303.832	1.973
25	310.930	307.586	3.344	310.874	307.586	3.288

Table I describes the results for a capillary whose overall outer diameter is 375 μm. The conclusions drawn from the table are valid even if the capillary radius is changed, provided that the power input is the same. Eqn. 8 and the parabolic profile will yield similar results as long as the power input is relatively small. When the power is increased, the discrepancy between the two temperature profiles increases. Table II shows the results of the calculation for power inputs of 10, 15 and 25 W. If the CZE system is thermostated, such power inputs can be tolerated, as evidenced from the relatively low predicted temperatures. We see from Table II that as the power increases, eqn. 8 predicts a greater temperature difference between the center and the inner wall of the capillary. Both, eqns. 8 and 12 give a similar wall temperature. However, eqn. 8 calculates a higher center temperature than the parabolic equation. Fig. 2 shows the temperature profile as determined by both approaches. From Fig. 2 we can see that the greatest difference between eqn. 8 and the parabolic equation occurs in the center of the capillary. The difference between the two profiles is small even at very high power input values, which are not used in the conventional practice of CZE (*e.g.*, 0.06 degree difference at a power input of 25 W). At such high input powers, the temperature difference between center and wall is rather high (above 3 degrees) so that the contribution to the plate height is prohibitively high[2].

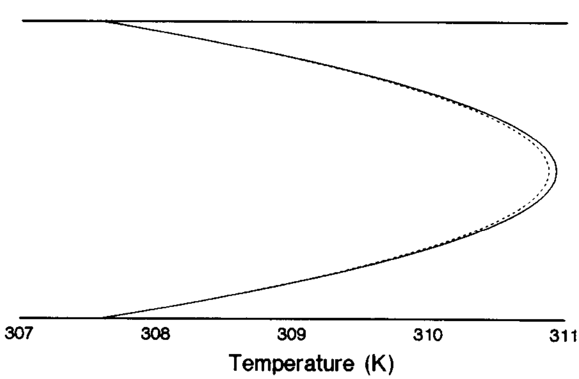

Fig. 2. Temperature profiles as calculated from eqn. 8 (——) and from the parabolic equation (– – –). Parameters used in the calculations are identical to those in Table II. Input power, 25 W; radius of capillary, 25 μm.

With relatively wide tubes (several mm in diameter), the resulting current is quite high at voltages which yield reasonable analysis times. In such cases, the power dissipated in the tube is very high, and eqn. 8 will be more accurate than eqn. 12 in predicting the temperature profile. However, the use of very wide tubes for CZE is not recommended since the temperature difference between center-to-wall will be much too large to obtain efficient separations.

CONCLUSIONS

Under the normal operating conditions, the nearly identical behaviors of eqns. 8 and 12, justify the use of parabolic temperature profiles in determining the effect of temperature on the efficiencies of CZE separations[2].

SYMBOLS

A Integration constant
G heat generation rate (W/m^3)
G_0 heat generation in the absence of temperature dependence of the buffer (W/m^3)
h heat transfer coefficient (W/m^2K)
J_0 Bessel function of zero order and first kind
J_1 Bessel function of first order and first kind
k_1 thermal conductivity of the buffer (W/mK)
k_2 thermal conductivity of the capillary wall (W/mK)
k_c thermal conductivity of the polyimide coating (W/mK)
L capillary length (m)
R_1 inner radius of the capillary (m)
R_2 outer radius of the quartz wall (m)
R_c outer radius of the capillary; glass and polyimide (m)
S reduced coefficient of heat generation (see eqn. 4)
T_1 temperature at the inside wall of the capillary (K)
T_s temperature of the capillary surrounding (K)
U overall heat transfer coefficient (W/m^2K)
y_1 dimensionless radial position r/R_1
α coefficient of electrical conductivity of the buffer (dimensionless)
β $(\alpha S)^{1/2}$
γ reduced heat transfer coefficient (see eqn. 6)
θ reduced temperature (see eqn. 4)

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