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Numerical study of radial temperature gradient effect on separation efficiency in capillary electrophoresis ☆

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Abstract

Joule heating effect is one of the factors that can decrease the separation efficiency in capillary electrophoresis. A mathematical model, including the Poisson–Boltzmann equation, the modified Navier–Stokes equation and the energy equation, is used to calculate temperature and velocity distributions in the capillary under different capillary inner radii, heat transfer coefficients and solution concentrations. By substituting the velocity distributions under these conditions into two different expressions for the thermal plate height, various effects on the thermal plate height and separation efficiency in capillary electrophoresis are analyzed. It is found that at the same electrical field strength, larger capillary radius, lower heat transfer coefficient and higher solution concentration can lead to a larger thermal plate height and therefore lowering the separation efficiency. The results of the separation efficiency based on the two different expressions agree well with each other.

Keywords: Capillary electrophoresis; Joule heating; Thermal plate height; Separation efficiency

1. Introduction

Capillary electrophoresis is an important chemical separation technique that has been widely used for chemical, biological analysis and medical diagnosis. Under an externally imposed electric field, different solute bands in the capillary (which is a microchannel) can be separated because of their different migration velocities. The separation efficiency of capillary electrophoresis is often expressed in terms of the theoretical plate height, where the higher is the theoretical plate height, the lower is the separation efficiency. The increase of the total plate height can be caused by many factors, such as the injection plug length, the width of the detector, longitudinal diffusion, Joule heating, and sample adsorption to the capillary wall [1]. The Joule heating effect, as one of the factors that can lower the capillary separation efficiency, has been studied recently [2–5].

Xuan and Li [6] analyzed band-broadening in capillary zone electrophoresis with axial temperature gradient in terms of the theoretical thermal plate height. Porras et al. [7] studied the role of the solvent on thermal peak broadening,

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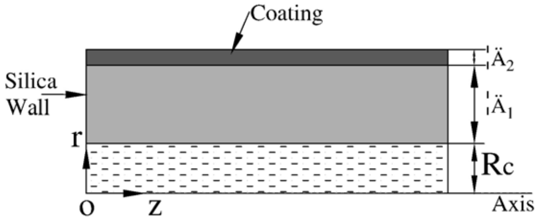

Fig. 1. Schematic diagram of the circular capillary.

and found that the thermal plate height is significantly larger in organic solvents. Similar work was done by Palonen et al. [8], who used ethanol as the electrolyte solvent. Peterson et al. [9] found that the main influence of Joule heating on separation efficiency is owing to the establishment of a radial temperature profile across the lumen of the capillary or channel while an overall temperature increase of the buffer solution has little influence on the efficiency. But they did not study other factors that may affect the thermal plate height.

In this study, we first obtain temperature and velocity distributions in the capillary under different capillary inner radii, heat transfer coefficients and solution concentrations by solving the mathematical model used previously by Tang et al. [10]. A numerical solution is obtained for velocity and temperature distributions of the electrolyte solution in the capillary far from the inlet and outlet, where the changes in these quantities in the axial direction are small. The velocity and temperature distributions thus obtained are then substituted in two expressions of thermal plate height, which were developed by Grushka et al. [11] and Knox and Grant [12], respectively, to study various factors that affect the thermal plate height.

2. Numerical model

Fig. 1 shows a capillary with an inner radius of R_c, in which the motion of an electrolyte solution is driven by an imposed electric field. The thickness of silica wall and the polyimide coating is assumed to be δ_1 and δ_2, respectively.

2.1. Poisson–Boltzmann equation

When a solid surface is in contact with a polar liquid, an electrical double layer (EDL) will be formed on the charged surface. According to the theory of electrostatics, the potential distribution of electric double layer (EDL), ψ, is governed by the Poisson equation [10]:

$$\frac{1}{r}\frac{\partial}{\partial r}\left[r\varepsilon_r(T)\frac{\partial\psi}{\partial r}\right]+\frac{\partial}{\partial z}\left[\varepsilon_r(T)\frac{\partial\psi}{\partial z}\right]=-\frac{\rho_e}{\varepsilon_0} \tag{1}$$

where $\varepsilon_r(T)$ is the relative dielectric constant of the electrolyte given by $\varepsilon_r(T)=305.7\exp\left(-\frac{T}{219}\right)$; ε_0 is the permittivity of vacuum, and ρ_e is the net charge density. Assuming that the equilibrium Boltzmann distribution equation is applicable, which implies uniform dielectric constant and no fluctuation, for a symmetric electrolyte, (i.e., the valence, $|\sigma_+|=|\sigma_-|=\sigma$), the net charge density in a unit volume of the fluid is given by:

$$\rho_e=\sigma e(n_+-n_-)=-2n_0\sigma e\sinh\left(\frac{\sigma e\psi}{k_\mathrm{b}T}\right) \tag{2}$$

where e is the fundamental charge, n_0, the ionic number in the bulk phase (i.e. far from the charged surfaces), k_b, the Boltzmann constant, T, the absolute temperature. Substituting Eq. (2) into Eq. (1) gives the well-known Poisson–Boltzmann equation:

$$\frac{1}{r}\frac{\partial}{\partial r}\left[r\varepsilon_r(T)\frac{\partial\psi}{\partial r}\right]+\frac{\partial}{\partial z}\left[\varepsilon_r(T)\frac{\partial\psi}{\partial z}\right]=\frac{2n_0\sigma e}{\varepsilon_0}\cdot\sinh\left(\frac{\sigma e\psi}{k_\mathrm{b}T}\right) \tag{3}$$