Thermal effect in magnetic capillary columns

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Abstract. The linearized Poisson-Boltzmann equation is used to estimate the radial distribution of potentials in a coaxial capillary and confirmed by experimental data. \( \xi \)-potentials are estimated for a capillary column with a sorbent containing magnetic nanoparticles. The thermal power in the column is calculated on the basis of the strength of an electric field with a certain electric conductivity. The column heating is calculated taking into account a thermal effect of the electric field for two estimates of the thermal diffusivity coefficient in the radial cross-section of a column comprising two layers of compounds with different physical properties.

Introduction

Presently the application of magnetic nanoparticles (MNP) in the capillary electrochromatography (CEC) is focused on pseudo-stationary phases (PSP-CEC) [1], open-tubular (OTCEC) [2-7] and monolithic capillary columns [8-10]. In OT CEC and monolithic columns MNP are either used to modify the sorbent surface or incorporated into its polymeric matrix. This approach provides the adjustment of polarity, charge, ionization degree, adsorption activity, hydrophilic-hydrophobic properties and other performances of sorbents in capillary columns depending on the reaction mixture composition, polymerization conditions and physicochemical properties of MNP. Unfortunately, studies reported so far on this issue do not consider the effect of the magnetic field generated by MNPs in/on the polymer matrix upon the electrochromatographic separation since MNPs are either not magnetized or taken into account only indirectly on the basis of empirical data, hence the corresponding conclusions are without the consideration of magnetic field effects. The interpretation of magnetic field effect upon the analytical performances of the columns is complicated primarily by an insufficient reproducibility of the sorbent structure and MNP distribution uniformity at the sorbent synthesis in capillary columns. Presently no available publications present data on the application of capillary columns with MNPs in capillary electrochromatography providing the estimation of MNP magnetic field effects upon the analyte separation, transport, etc. Nevertheless, MNP incorporation into sorbents and magnetic field generated by MNPs in the sorbent polymer matrix determines a new fundamental factor in the electrokinetic separation method. MNP-generated magnetic field in the sorbent polymer matrix affects such basic parameters of electromigration separation as the analyte and electrosomotic flow profiles, dielectric permittivity, spatial distribution of the potential, \( \xi \)-potential, etc. The presence of MNPs in the sorbent at simultaneous effects of electric and magnetic fields can be also supposed to affect the separation process due to the temperature change in the capillary column.

This study is aimed at the development of mathematical modeling and assessment of MNP effects in the polymer sorbent layer upon the thermal diffusivity in an electromagnetic field.
The main objectives of this research are the study of the radial heat transfer and estimation of MNP presence effect upon this process schematically is illustrated in Figure 1.

![Figure 1. Scheme of heat-transfer in the capillary](image)

**The model description**

Electric field acts as a heat source in capillary column. A possible heat care is calculated taking into account the thermal diffusivity coefficient at certain (ambient) temperature at the outer boundary of the capillary. The thermal power of the capillary column is determined according to the strength of longitudinal electric field (E) with a certain electric conductivity [11].

The mathematical model based on a linearized Poisson-Boltzmann equations (1) and (2). It has an analytical solution in the form of a linear combination of modified Bessel functions, market as $I_0$ and $K_0$. This approach allowed us to estimate a radial distribution of potentials $\phi(x)$ (3) and electro-osmotic flow (EOF) rate (4) based on the following defining parameters: $R$ – outer radius of the coaxial capillary, $c_0$ – concentration of charged particles in the buffer (defining the solution pH value), $T$ – temperature, $\varepsilon$ - dielectric permittivity of the medium, as well as Faraday (F), Boltzmann ($k_b$), universal electric ($\varepsilon_0$) constants and electron charge ($e$). Argument $x$ is the $R$-normalized radial coordinate, $\Delta_r$ – radial component of Laplace operator, $\xi$ - value of the corresponding $\xi$-potential.

\[
\Delta_r \phi = \alpha^2 \phi \quad (1)
\]

with conventional boundary conditions: first - $\phi$-function is limited for $x$ tending to zero; second – at $x=1$ $\phi=1$ (i.e. the potential at boundary is equal to $\xi$-potential).

\[
\alpha^2 = \frac{2Fe\varepsilon_0 R^2}{\varepsilon \varepsilon_0 k_b T} \quad (2)
\]

\[
\phi(x) = \frac{(K_0(\alpha)-K_0(\alpha \rho))I_0(\alpha x)+(I_0(\alpha \rho)-I_0(\alpha))K_0(\alpha x)}{I_0(\alpha \rho)K_0(\alpha)-I_0(\alpha)K_0(\alpha \rho)} \xi 
\]

\[
V(x) = E \frac{\varepsilon \varepsilon_0}{\eta} (\xi - \phi(x)) \quad (4)
\]

The heat balance calculation (particularly the estimation of the effect of capillary heating promoted by the electric field) requires the determination of thermal diffusivity coefficient for the material comprising areas with different physical properties (polymer matrix and MNPs). The studied performances were averaged similar to the Lichtenecker procedure (power relationship with $k=1$) for the characterization of dielectric properties of composites [12].

The equation (5) affords averaging of the thermal diffusivity coefficient ($\alpha$) taking into account
the contributions of water-like buffer, polymer coating and MNPs in the capillary, while the equation (6) gives average thermal conductivity coefficient \( (k) \), medium density \( (\rho) \) and specific heat capacity \( (C) \), followed by the calculation of the thermal diffusivity coefficient according to the determined average values.

\[
\alpha^{(1)} = \alpha_1 (1 - \delta) + \alpha_2 \delta \\
\alpha^{(2)} = \frac{k_1(1-\delta)+k_2\delta}{(\rho_1(1-\delta)+\rho_2\delta)(C_1(1-\delta)+C_2\delta)}
\]

where \( \delta \) is a relative thickness of the near-wall layer; indices “1” and “2” correspond to the water-like buffer and near-wall layer with nanoparticles, respectively.

Results

The validity of linearized Poisson-Boltzmann equation application for the estimation of potentials distribution along the channel (capillary column) cross-section and EOF determination was tested using the equations (1) - (4) and results of mathematical processing for earlier obtained [13] experimental data on the estimation of EOF mobility value in capillary columns with different charges of the sorbent surface and various pH values of the buffer.

The equations (1) - (4) are applicable to the considered problem in the case EOF mobility changes for buffers with pH 4, 7 and 9 (7) is only determined by the difference in \( \xi \)-potentials (charges on the sorbent surface). The distribution of potentials along the column cross-section remained constant at a given pH value. Consequently, the ratio (7) should be complied

\[
\frac{\mu(7)-\mu(4)}{\mu(9)-\mu(4)} = \text{const}
\]

where \( \mu(7), \mu(9), \mu(4) \) are EOF marker mobility in the buffers with pH 4, 7 and 9 [13].

The adequacy of the mathematical model confirmed by performance of the condition (7) for two types of columns with the error is not more than 2%.

The expressions (3) and (4) in combination with \( \mu(7) \) value [1] were used to estimate \( \xi \)-potential on the sorbent surface. Upon \( x \) value, based averaging of \( \phi(x) \) according to (3) the average ratio \( \phi(x)/\xi \) is 0.4994. Given the dynamic viscosity coefficient of the water-like buffer is equal to 0.87 \( \times 10^{-3} \) m\(^2\)/s [14] and temperature is 26°C, the estimated \( \xi \)-potential is 115 mV.

A priori MNP role in the electroosmotic effect can be described as follows. Due to their presence in the wall layer on the capillary surface, relative permittivity (\( \varepsilon \)) significantly decreases in urn resulting in the increase of the potential gradient and consequently in EOP rate gradient. The transferred substance is further concentrated near the channel axis promoting the increase in average convective rate and decrease of the peak width relating to the sample components. Actually magnetic forces at the used rates and magnetic field strengths are negligible even in comparison with the diffusion of large molecules.

The transversal electric field strength was approximately estimated as \( \xi \)-potential divided by the half of the coaxial gap (65 \( \mu \)m). The overestimated transversal electric field strength of 18 V/cm is about 11 times less compared with the axial longitudinal strength 220 V/cm. Thus the radial component can be neglected and the thermal power can be assessed only according to the axial component of vector \( \text{E} \).

The results of thermal diffusivity coefficient estimation according to models (5) and (6) at different relative (R-normalized) thickness of near-wall layer with MNPs (comprising 25% vol. of the polymer matrix) are shown in the Figure 2.
Figure 2. Dynamics of thermal diffusivity coefficient as a function of MNP-containing near-wall layer thickness: – full averaging of the of thermal diffusivity $\alpha^{(1)}$; ▼ - averaging by separate components $\alpha^{(2)}$.

The figure indicates that thermal diffusivity coefficient grows with the polymer sorbent matrix thickness (with linear increase for $\alpha^{(1)}$ and non-linear growth of $\alpha^{(2)}$). Upon the addition of MNPs to the polymer matrix in OTCEC or modifying coating on the internal surface of the capillary in the migration analysis procedures the near-wall sorbent layer with 25 vol.% MNP content results in almost double increase in the thermal diffusivity coefficient thus providing a more intensive cooling of the capillary. The changes in electric field thermal power can be only determined by the transversal (radial) field component which contribution is only about 1%.

Conclusion
The performed calculations indicated that the presence of MNPs in the sorbent provides an increase of the transversal electric field strength consequently resulting in the enhancement of its thermal power in the capillary column. The increase of MNP in the near-wall layer of the sorbent further strengthens this effect, however the transversal electric field contribution into the thermal effect is only about 1% of the total thermal power of the electromagnetic field. Heating by longitudinal (axial) electric field in the capillary column does not exceed several hundredths of a degree per second. Nevertheless, during the sample separation within 100 s in the absence of external cooling, the eluent and analyte heating achieves up to 5-6°C and can linearly grow with the analysis time that is critical in respect of biological samples separation. Their identification can be complicated due to significant changes in viscosity and diffusion coefficient upon temperature changes even by several degrees resulting in the change of release time for the corresponding component of the sample.

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