

## Packing structure and self-heating in capillary electrochromatography

Ligong Chen, Lei Chen, Xilong Yan, Qian-Hong Wan\*

*College of Pharmaceuticals and Biotechnology, Tianjin University, Tianjin 300072, China*

Received 12 August 2002; received in revised form 12 November 2002; accepted 14 November 2002

### Abstract

The origin of bubble formation during operation of capillary electrochromatography (CEC) has been an issue of debate. Ohmic heating resulted from current passed through a packed column was proposed as the primary cause. However, this explanation has been questioned on the ground that the current measured in CEC is much lower than that measured with open-tubular separation systems where no bubble formation occurs. To resolve this issue, we carried out a theoretical study correlating self-heating of the electrolyte with packing structure of the column. We used a bundle of capillary tubes, a bundle of two types of capillary tubes and two bundles of capillary tubes connected serially to model, respectively, the flow channels in the column of non-porous particles, in the column of porous particles and in the column of various packing densities. The results from this study indicate that, for columns of homogeneous packing density, the heat output is indeed smaller than that in open-tubular columns of the same dimensions. In this case, the self-heating cannot be a key factor responsible for the bubble formation in CEC. However, for columns of heterogeneous packing density, a large excess of heat release may be produced in column sections of high packing density and, in turn, over-heating in such sections may become the primary cause for the formation of bubbles. It follows from this study that preparation of columns of homogeneous packing structure is essential to obtain reproducible and bubble-free CEC systems.

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*Keywords:* Electrochromatography; Bubble formation; Self-heating; Packing structure

### 1. Introduction

Capillary electrochromatography (CEC) has emerged as a promising technique for the separation of neutral as well as charged compounds [1–8]. In this technique, a capillary column filled with conventional HPLC packing material is typically employed and a high voltage is applied across the column to

induce liquid flow. Since the electroosmotic flow generated in a porous packing structure is of plug flow profile, CEC promises a higher column efficiency than that offered by pressure-driven liquid chromatography. Another point of interest in CEC is the possibility to superimpose electrophoretic separation on chromatographic retention, thus providing greater selectivity than competitive techniques based on either mechanism alone.

Despite many advantages of CEC that have been demonstrated, several technical problems have delayed the widespread acceptance of this potentially

\*Corresponding author. Tel.: +86-22-2740-3650; fax: +86-22-2740-3759.

E-mail address: [qhwan@tju.edu.cn](mailto:qhwan@tju.edu.cn) (Q.-H. Wan).

powerful separation technique. One such problem is bubble formation during a chromatographic separation [9–11]. The bubbles formed in the frits or in column sections are particularly troublesome as they cause disruption of electroosmotic flow and in turn the CEC operation. Several factors are considered most likely to contribute to the formation of bubbles in the packing, which include self-heating due to electric conduction [2,3,12,13], insufficient degassing of the eluent [11], structural inhomogeneity of the frits [14,15], and non-uniformity of the surface zeta potentials between packed and open sections [16–18]. To date, however, the role of the self-heating in formation of bubbles has not been well understood. In their pioneering works on CEC, Knox and Grant [3] noted that drying out of the packed capillaries was particularly liable to occur with the wider capillaries, higher concentrations of electrolyte and higher electrical fields. They ascribed this to self-heating or excessive heat release due to current passed through the packed capillaries. Based on the observation that the formation of bubbles was not usually observed in open-tubular capillary separation systems such as capillary electrophoresis, others [9] argued the self-heating could not be the primary cause because the current measured in CEC was one or two magnitudes lower than that measured with open-tubular capillaries. Thus, for CEC with packed columns, the right questions are, “What is the relation between packing structure and self-heating?”, “What is the magnitude of the self-heating in packed capillaries?”, and “What is the consequence of the packing heterogeneity on self-heating?”

To answer these questions, the theoretical foundations of electrical and heat conduction through porous structure must be examined in terms of obstructive effects of packing materials. The specific geometric properties of the pore space within the packing materials can be estimated by one of several models developed to date, such as parallel-capillary models, pore-throat models and pore network models [18,19]. In parallel-capillary models, the porous structure of the particles is represented by a bundle of parallel cylindrical tubes of varying diameters but with the same length. This approach neglects the existence of the interconnections between the different pores in porous media. In pore-throat models, the porous structure is represented in the lattice network

by large voids defined as spheres and narrow throats interconnected the spherical voids defined as cylinders. In pore network models, the porous structure is represented by a lattice network of nodes interconnected by bonds representing the pores. The network is generated using a Monte Carlo simulation approach whereby cylindrical pores are randomly assigned to the bonds of the network. All of these models have been employed in studies of electrical conduction, convection and diffusion in porous media [20–26]. Our research has focused on elucidating a correlation between the characteristics of the porous structure and the self-heating of a capillary electrochromatographic column through the use of a well-established parallel-capillary model. The flow channels in a CEC column are represented by a bundle of capillary tubes, the diameter of which is determined by the porosity and tortuosity of the packing bed. In such a bundle of capillary tubes, the current is conducted and resulting Ohmic heating is dispersed.

## 2. Results and discussion

### 2.1. Heat release in an open-tubular column

In a cylindrical capillary tube filled with electrolyte, the electric current,  $I_o$ , generated under the influence of an electric field obeys Ohm's law:

$$I_o = AkcE \quad (1)$$

where  $A$  is the cross-sectional area of the capillary tube,  $k$  is the molar conductivity of electrolyte,  $c$  is the concentration of the electrolyte, and  $E$  is the applied electric field strength.

The heat release,  $Q_o$ , due to electric current is given by [27]:

$$Q_o = LAkcE^2 \quad (2)$$

where  $L$  is the capillary length.

### 2.2. Heat release in a column packed with non-porous particles

In a capillary column packed with non-conducting materials such as impermeable, spherical silica par-

ticles as used in CEC, the electric current is primarily conducted by electrolyte migrating along the flow channels formed between the particles. The flow channels in such a column can be viewed as a bundle of zigzag capillary tubes (see Fig. 1A). It is well known that effective electric conductivity in packed columns is reduced as compared to that in open-tubular capillary columns. Two geometrical obstructive effects are incurred to account for this reduction [20]. First, the tortuous flow channels in the porous media increase the path lengths and alter the directions, thus reducing the effective field strength. Second, the particles occupy some free space within the column, causing a reduction of the effective cross-sectional area available to the current. Allowing for these two effects, the electric current,  $I_p$ , in a packed capillary column is given by:

$$I_p = AkcE\epsilon_{\text{inter}}\gamma_{\text{inter}} \quad (3)$$

where  $\epsilon_{\text{inter}}$  is the interparticle porosity of the packed column,  $\gamma_{\text{inter}}$  is its tortuosity factor. Accordingly, the heat release in such a column is given by:

$$Q_p = LAkcE^2\epsilon_{\text{inter}}\gamma_{\text{inter}} \quad (4)$$

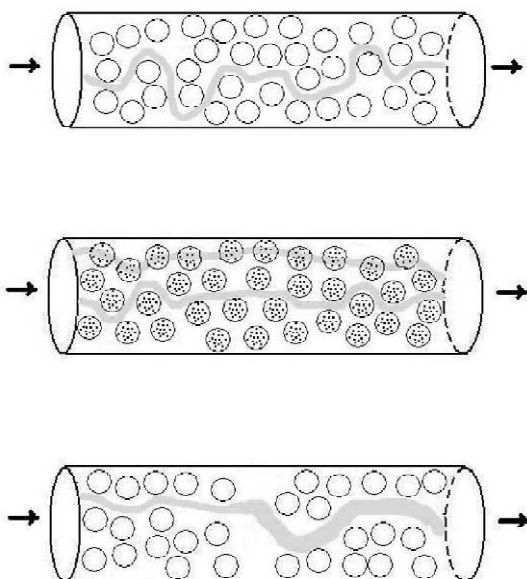


Fig. 1. Capillary bundles used to model the flow channels in packed columns. (A) Regular packing with non-porous particles; (B) regular packing with porous particles; (C) irregular packing with non-porous particles.

The magnitude of heat output in packed column relative to that in open-tubular column can be readily shown by the relative heat output defined as follows:

$$\frac{Q_p}{Q_o} = \epsilon_{\text{inter}}\gamma_{\text{inter}} \quad (5)$$

According to Slawinski [28], the tortuosity factor is related to the porosity of a packed bed by the following equation:

$$\gamma = \frac{1}{(1.3219 - 0.3219\epsilon)^2} \quad (6)$$

On substitution of  $\gamma$  in Eq. (5) with Eq. (6), we arrive at:

$$\frac{Q_p}{Q_o} = \frac{\epsilon_{\text{inter}}}{(1.3219 - 0.3219\epsilon_{\text{inter}})^2} \quad (7)$$

Fig. 2 shows that the relative heat output monotonically increases with the interparticle porosity, reaching a maximum when  $\epsilon_{\text{inter}} = 1$ .

Since the heat output in a column with homogeneous packing is always smaller than that in the column without packing, the self-heating is indeed unlikely to become a dominant factor responsible for the formation of bubbles in CEC operation. Other factors should be considered, such as inadequate degassing of the electrolyte and non-uniform electroosmotic mobilities along the column [16,17].

In the above treatment, we made two assumptions regarding electric current in a packed column. One is

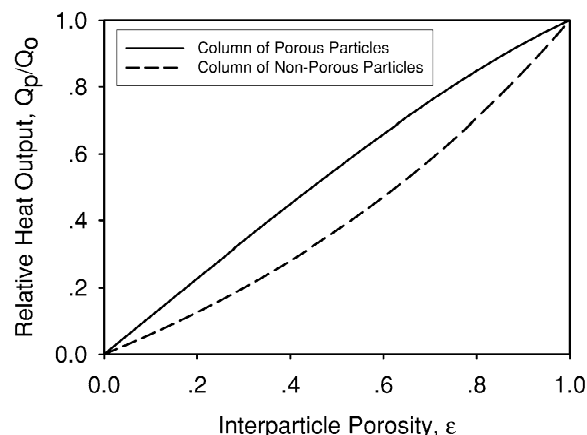


Fig. 2. Plots of relative heat output versus interparticle porosity.

that the electric conduction occurs entirely in the space between particles and the second is that the packing structure in a packed capillary column is homogeneous so that it can be characterized by the column porosity and tortuosity factor. These assumptions may deviate considerably from reality, particularly in the case where porous silica particles of uneven particle size distribution are used. The electric current may be transmitted through and around the porous particles. Considerable variation of packing density may occur across and along the column. As will be shown below, this could have some unexpected effect on heat output.

### 2.3. Heat release in a column packed with porous particles

The relative importance of the current transmission through and around the particles remains an arguable matter. To our knowledge, there are no direct measurements that allow distinction between interparticle and intraparticle conductions. For the sake of simplicity, we consider the column packed with porous particles as a bundle of two types of capillary tubes (see Fig. 1B), corresponding to the flow channels around and through the particles. Accordingly, the currents transmitted around and through the porous particles are, respectively, given by:

$$I_{\text{inter}} = kcAE\varepsilon_{\text{inter}}\gamma_{\text{inter}} \quad (8)$$

and

$$I_{\text{intra}} = kcA(1 - \varepsilon_{\text{inter}})E\varepsilon_{\text{intra}}\gamma_{\text{intra}} \quad (9)$$

where the subscripts inter and intra refer to flow channels formed between and within the particles, respectively.

In analogy to conductors connected in parallel, the electric current transmitted along the column is given by the sum of  $I_{\text{inter}}$  and  $I_{\text{intra}}$ :

$$I_p = AkcE[\varepsilon_{\text{inter}}\gamma_{\text{inter}} + (1 - \varepsilon_{\text{inter}})\varepsilon_{\text{intra}}\gamma_{\text{intra}}] \quad (10)$$

Accordingly, the heat output in such a column is given by:

$$Q_p = LAkcE^2[\varepsilon_{\text{inter}}\gamma_{\text{inter}} + (1 - \varepsilon_{\text{inter}})\varepsilon_{\text{intra}}\gamma_{\text{intra}}] \quad (11)$$

or

$$Q_p = LAkcE^2 \cdot \left[ \frac{\varepsilon_{\text{inter}}}{(1.3219 - 0.3219\varepsilon_{\text{inter}})^2} + \frac{(1 - \varepsilon_{\text{inter}})\varepsilon_{\text{intra}}}{(1.3219 - 0.3219\varepsilon_{\text{intra}})^2} \right] \quad (12)$$

The relative heat output is therefore determined by the interparticle and intraparticle porosities:

$$\frac{Q_p}{Q_o} = \frac{\varepsilon_{\text{inter}}}{(1.3219 - 0.3219\varepsilon_{\text{inter}})^2} + \frac{(1 - \varepsilon_{\text{inter}})\varepsilon_{\text{intra}}}{(1.3219 - 0.3219\varepsilon_{\text{intra}})^2} \quad (13)$$

With the assumption that  $\varepsilon_{\text{intra}} = \varepsilon_{\text{inter}}$ , the Eq. (13) simplifies:

$$\frac{Q_p}{Q_o} = \frac{2\varepsilon_{\text{inter}} - \varepsilon_{\text{inter}}^2}{(1.3219 - 0.3219\varepsilon_{\text{inter}})^2} \quad (14)$$

As shown in Fig. 2, the relative heat output increases with the interparticle porosity, but with a steeper change as compared with that observed for the column packed with non-porous particles. Since the heat output in this case is still less than that in the column without packing, we can conclude that the self-heating in this case is not the cause for the formation of bubbles during the CEC operation.

### 2.4. Heat release in a column of various packing densities

For a capillary column packed with particles of uneven size distribution, a variation in packing density along the column length is expected to set in for two reasons. Firstly, some smaller particles may be trapped in cavities formed between larger particles, causing a reduction in the local porosity of the packing. Secondly, under the influence of an electric field, the negatively charged particles such as silica particles tend to migrate to positive electrode, resulting in an uneven column packing with higher densities at the end near the positive electrode. Thus, the flow channels in the column of uneven packing densities may be modeled by two bundles of capil-

lary tubes connected serially (see Fig. 1C). The current in such a model is given by:

$$I_p = AkcE_{\text{high}}\varepsilon_{\text{high}}\gamma_{\text{high}} = AkcE_{\text{low}}\varepsilon_{\text{low}}\gamma_{\text{low}} \quad (15)$$

where the subscripts high and low refer to the flow channels formed in the sections of high and low packing density, respectively.

The electric field strengths in two sections vary with the dimensionless column length,  $\lambda = L_{\text{high}}/L$ , as shown by the following equation:

$$E = \frac{V_{\text{high}} + V_{\text{low}}}{L} = \lambda E_{\text{high}} + (1 - \lambda)E_{\text{low}} \quad (16)$$

Rearranging Eq. (15) yields

$$E_{\text{low}} = E_{\text{high}} \frac{\varepsilon_{\text{high}}\gamma_{\text{high}}}{\varepsilon_{\text{low}}\gamma_{\text{low}}} \quad (17)$$

By substituting Eq. (17) for  $E_{\text{low}}$  in Eq. (16), the equation is solved to give:

$$E_{\text{high}} = E \frac{\varepsilon_{\text{low}}\gamma_{\text{low}}}{(1 - \lambda)\varepsilon_{\text{high}}\gamma_{\text{high}} + \lambda\varepsilon_{\text{low}}\gamma_{\text{low}}} \quad (18)$$

and

$$E_{\text{low}} = E \frac{\varepsilon_{\text{high}}\gamma_{\text{high}}}{(1 - \lambda)\varepsilon_{\text{high}}\gamma_{\text{high}} + \lambda\varepsilon_{\text{low}}\gamma_{\text{low}}} \quad (19)$$

The total heat output in the column of two packing densities is given by:

$$Q_p = LAkcE^2 \frac{\varepsilon_{\text{high}}\gamma_{\text{high}}\varepsilon_{\text{low}}\gamma_{\text{low}}}{(1 - \lambda)\varepsilon_{\text{high}}\gamma_{\text{high}} + \lambda\varepsilon_{\text{low}}\gamma_{\text{low}}} \quad (20)$$

The relative heat output is then given by:

$$\frac{Q_p}{Q_o} = \frac{\varepsilon_{\text{high}}\gamma_{\text{high}}\varepsilon_{\text{low}}\gamma_{\text{low}}}{(1 - \lambda)\varepsilon_{\text{high}}\gamma_{\text{high}} + \lambda\varepsilon_{\text{low}}\gamma_{\text{low}}} \quad (21)$$

Let us consider two limiting cases: for  $\lambda = 0$ , we have  $Q_p/Q_o = \varepsilon_{\text{low}}\gamma_{\text{low}}$  and for  $\lambda = 1$ , we have  $Q_p/Q_o = \varepsilon_{\text{high}}\gamma_{\text{high}}$ . In either case, the heat output is reduced as compared with that in the open-tubular column under otherwise identical conditions. These correspond to the heat release in regular packing of non-porous particles where the heat is produced evenly along the column. However, in the case of uneven packing density, the heat is generated unevenly and therefore the heat output per unit volume is a more adequate measure for self-heating effects. To estimate the relative importance of the heat

releases in two sections of the column, we define a relative volumetric heat output as a ratio of the heat release per unit volume in the section of high density to that in the section of low density:

$$\frac{Q_{\text{high}}/L_{\text{high}}A}{Q_{\text{low}}/L_{\text{low}}A} = \frac{E_{\text{high}}^2\varepsilon_{\text{high}}\gamma_{\text{high}}}{E_{\text{low}}^2\varepsilon_{\text{low}}\gamma_{\text{low}}} = \frac{\varepsilon_{\text{low}}\gamma_{\text{low}}}{\varepsilon_{\text{high}}\gamma_{\text{high}}} \quad (22)$$

or

$$\frac{Q_{\text{high}}/L_{\text{high}}A}{Q_{\text{low}}/L_{\text{low}}A} = \frac{\varepsilon_{\text{low}}(1.3219 - 0.3219\varepsilon_{\text{high}})^2}{\varepsilon_{\text{high}}(1.3219 - 0.3219\varepsilon_{\text{low}})^2} \quad (23)$$

With assumptions that  $\varepsilon_{\text{low}} = 0.476$  for cubic packing of uniform spheres,  $\varepsilon_{\text{high}} = 0.125$  for cubic arrangement of spherical particles of two sizes [29], we obtain  $(Q_{\text{high}}/L_{\text{high}}A)/(Q_{\text{low}}/L_{\text{low}}A) = 4.58$ . Thus, the heat release in higher density sections is about 5-fold that in lower density sections. In relation to the practice of CEC, one may consider the possible fragmentation of the porous particles during column packing and the movement of these negatively charged particles towards the positive electrode under the influence of an applied electric field. These particle fragments will continue to negotiate through the channels formed between intact particles until they are entrapped firmly somewhere in the column. As a result, some sections of the column may attain packing densities considerably higher than that assumed for a regular packing bed. It is in these sections that excessive self-heating is liable to occur, giving rise to gassing of the running buffer and drying out of the column.

There are several indications that the heterogeneity of packing structure is closely related to the likelihood of bubble formation in CEC. Rebscher and Pyell [15] observed that if the frit at the inlet end of a prepared column has a low permeability, bubble formation during a chromatographic run is very likely to occur upon application of an electric field. Their observation suggests that not only difference in the surface zeta potential between frit and bulk packing but also an extremely high packing density of the frit can result in bubble formation. In an experimental study of the effects of particle size distribution on electrical conductivity of a packed capillary column used in CEC, we noted that the likelihood of bubble formation increases markedly for the column packed with ground silica particles

whose particle sizes range from less than 1 to 5  $\mu\text{m}$ . The results from this study will be reported in due course.

### 3. Conclusions

From the above analysis, it becomes clear that excessive heat release can result from transmitting current through column sections of high density. In order to satisfy the mass conservation law, same amount of electrolyte must pass through the column sections of various packing densities. Because the flow channels are narrower and more tortuous in the densely packed sections, a drastic increase in electric field is required to transmit the electrolyte through these sections. Consequently, a tremendous increase in heat output is produced in the sections of high packing density. In this sense, the self-heating can be a primary cause for the formation of bubbles observed in capillary electrochromatography. To eliminate the problems associated with uneven self-heating, one needs to consider preparation of packing structures in the column sections and frits as homogeneous as possible. The use of monodispersed particles [30], immobilization of the particles in the column [3,31,32], and avoidance of fragmentation of the particles during column packing appear to be beneficial for obtaining and maintaining a sustainable and bubble-free CEC system.

### Acknowledgements

This work was supported by Tianjin University's 21st Century Action Program.

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