

Effect of Electroosmotic Flow on the Electrical Conductivity of Packed Capillary Columns

Qian-Hong Wan[†]

Laboratory for Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received: November 6, 1996; In Final Form: April 4, 1997[®]

The electrical conductivity of a packed capillary column is primarily a function of column porosity and tortuosity; therefore it can be used for column characterization in capillary electrochromatography (CEC). However, a deviation from this functionality may occur due to electroosmotic flow, which contributes to the observed conductivity by transporting excess charges in double layers. On the basis of Rice and Whitehead's theory combined with a capillary tube model, we have shown that the electroosmotic conductivity increases with the ζ potential but decreases with the particle diameter and electrolyte concentration. Under typical conditions employed in current CEC, the electroosmotic conductivity accounts for less than 5% of the bulk conductivity of the same electrolyte and indeed can be neglected for practical purposes.

Introduction

Efforts to develop capillary electrochromatography (CEC) into a viable analytical tool are currently confronted with several technical difficulties, some of which are associated with the heterogeneity of the packing structure.^{1–4} To circumvent these difficulties, it is desirable to have an appropriate method for characterizing the packed capillary columns prepared and for monitoring a change of packing structure during CEC operations. In a recent paper³ we have described such a method, which involves the measurement of the electrical conductivity for an open tube and packed capillary columns. The ratio of the conductivity to that without packing is used to indicate the quality of the packed columns. The conductivity ratio has a typical value around 0.33 for a good column, which is apparently independent of the particle size, column dimension, and electric field strength applied. On geometrical grounds, the conductivity ratio is shown to be primarily a function of bed porosity and tortuosity factor of the packing.

However, the above treatment has assumed that the electrical conductivity due to electroosmotic movement can be neglected. The electroosmotic flow causes an additional conductivity by transporting the excess charges in the double layer. This contribution to the observed electrical conductivity, referred to as electroosmotic conductivity hereafter, is not amenable to a direct experimental determination and therefore must be estimated in line with appropriate theoretical models. The aim of this work is to provide an estimation of the electroosmotic conductivity under various experimental conditions such as ζ potential, particle diameter, and electrolyte concentration and to examine its contribution relative to the bulk conductivity in order to justify, in principle, the validity of this assumption in cases where typical CEC conditions are employed.

Results and Discussion

The axial current, I_t , due to transport of charge by electroosmotic flow is given by

$$I_t = \int_A u \rho \, dA \quad (1)$$

where u is the electroosmotic velocity, ρ the net charge density, and A the cross sectional area. Using the Debye–Hückel approximation for a 1–1 electrolyte, Rice and Whitehead⁵ have performed the integral of eq 1 for a cylindrical capillary, giving

$$I_t = I_b \frac{(\epsilon_0 \epsilon_r \zeta \kappa)^2}{\eta c \Lambda_b} \left[-1 + \frac{2I_1(\kappa a)}{\kappa a I_0(\kappa a)} + \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \quad (2)$$

where I_b , ϵ_0 , ϵ_r , ζ , κ , η , c , Λ_b , and a represent, respectively, the conduction current of the bulk solution, the permittivity of a vacuum, the relative permittivity of the medium, the ζ potential of the flow channel, the reciprocal of the electrical double-layer thickness, the viscosity of the medium, the electrolyte concentration, the molar conductivity of the bulk solution, and the radius of the flow channel. I_0 , I_1 are, respectively, the zero-order and first-order modified Bessel functions of the first kind. It should be noted that due to the use of the Debye–Hückel approximation, the above equation is strictly valid only at low values of ζ potential. Fortunately, the recent theoretical studies concerning the electrokinetic flow at high ζ potentials show that the results obtained by Rice and Whitehead's approach represent a good approximation to those given by a more exact numerical solution of eq 1 for ζ potentials up to 100 mV.⁶

For purposes of comparison, a relative conductivity λ is introduced, which is defined as the ratio of the electroosmotic conductivity to the bulk conductivity of the same electrolyte. Since $\Lambda = I/cEA$ and $\kappa = (2cF^2/\epsilon_0 \epsilon_r RT)^{0.5}$ (where E is the electric field strength, F the Faraday constant, R the universal gas constant, and T the absolute temperature), the relative conductivity λ is found by rearranging eq 2 as

$$\lambda = \beta \zeta^2 \left[-1 + \frac{2I_1(\kappa a)}{\kappa a I_0(\kappa a)} + \frac{I_1^2(\kappa a)}{I_0^2(\kappa a)} \right] \quad (3)$$

where $\beta = 2\epsilon_0 \epsilon_r F^2 / \eta \Lambda_b RT$, which has a typical value of 391 V⁻² for aqueous solutions of a 1–1 electrolyte at 25 °C, where $\epsilon_r = 80$, $\eta = 0.001$ N s m⁻², and $\Lambda_b = 0.015$ m² Ω⁻¹ mol⁻¹ are assumed.

Equation 3 can be used to calculate the dependence of the relative conductivity on the ζ potential, which governs the net charge distribution in the electrical double layer. In Figure 1,

[†] Present address: Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3. Tel: (902) 494 7079. Fax: (902) 494 1310. Email: wanq@is.dal.ca

[®] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

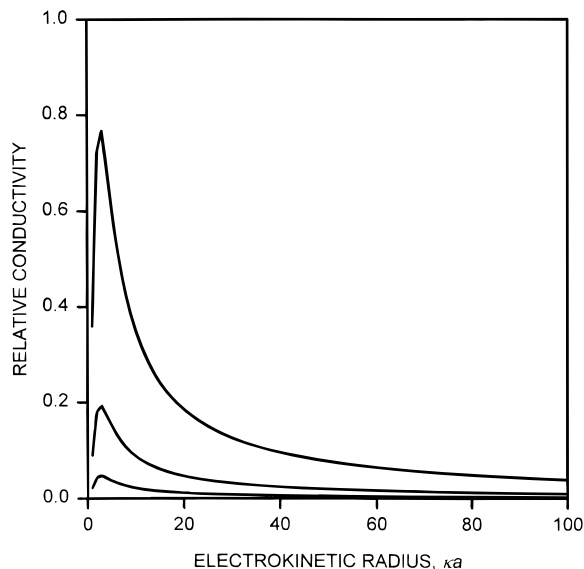


Figure 1. Variation of relative conductivity with electrokinetic radius for ζ potentials 25, 50, and 100 mV (from the lower to the upper curve).

the relative conductivity is plotted against the electrokinetic radius κa for three values of ζ , between 25 and 100 mV. Over the range that κa varies from 0 to 100, the relative conductivity rises rather steeply to a maximum at $\kappa a = 3$ and then declines to nearly zero afterward for all values of ζ . The trend that the relative conductivity falls off with κa is anticipated on the grounds that the net charge density approaches zero with increasing κa when the electroosmotic velocity u is held constant. The opposite trend at low values of κa points to the double-layer overlap effect, by which the electroosmotic conductivity is suppressed as a result of diminished electroosmotic flow. While the electroosmotic conductivity at its maximum value is only about 5% of the bulk conductivity for $\zeta = 25$ mV, its importance increases rapidly with the ζ potential, with a maximum value being nearly 80% for $\zeta = 100$ mV.

As can be seen from Figure 1, the electroosmotic conductivity is of some significance only at relatively small values of κa , e.g., $\kappa a < 100$. Under the typical conditions mentioned above for a 1-1 electrolyte of concentration 1 mM with a capillary radius $a = 1 \mu\text{m}$, $\kappa a = 100$. This magnitude of capillary radius is obviously too small to be practically useful in current open tubular electrochromatography. However, the radii of flow channels smaller than $1 \mu\text{m}$ are commonplace in packed column electrochromatography. Since the exact values of the mean channel radius are not available due to the complex geometry of the flow channels formed between particles, the channel size is usually estimated with the aid of a theoretical model. There are several models developed attempting to take into account effects of variations in channel diameter and flow direction, but none of them provide a satisfactory description.⁷ In this work we resort to a simplified capillary tube model for estimating the mean channel diameter. In this model the porous medium such as a packed capillary column is treated as a bundle of straight capillary tubes, all of the same diameter, d , embedded in a solid. The permeability, k , for such a conceptual model is

$$k = \frac{nd^2}{32} \quad (4)$$

where n is the interparticle porosity. By setting it equal to the permeability given by the well-known Kozeny-Carman equa-

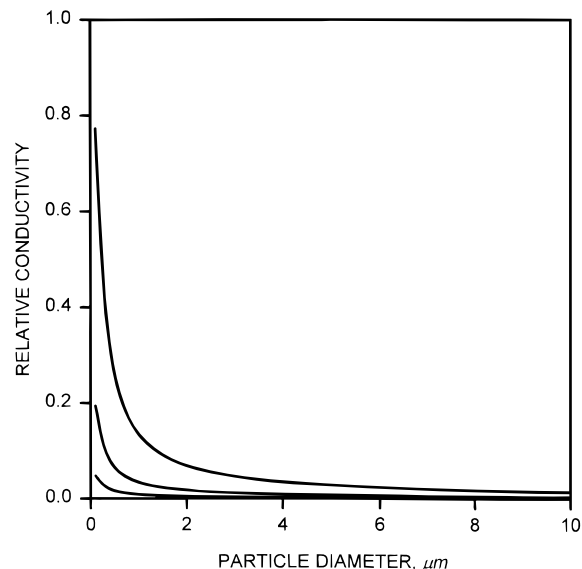


Figure 2. Variation of relative conductivity with particle diameter for ζ potentials 25, 50, and 100 mV (from the lower to the upper curve), where $\kappa = 0.10 \text{ nm}^{-1}$ is assumed.

tion for a packed column,⁸

$$k = \frac{dp^2n^3}{180(1-n)^2} \quad (5)$$

one can readily arrive at a relationship between the mean channel diameter d and the mean particle diameter d_p :

$$d = \frac{0.42d_p n}{1-n} \quad (6)$$

For slurry packed columns having a typical value of interparticle porosity $n = 0.40$,⁸ we have

$$d = 0.28d_p \quad (7)$$

It is noted that a similar relationship has been derived by Knox and Grant⁹ from the ratio of the column resistance parameter for a packed column to that for an open tube.

The effect of particle diameter on electroosmotic conductivity can be shown by substituting $0.5d$ from the above equation for a in eq 3. In the case where $\kappa = 0.10 \text{ nm}^{-1}$, the relative conductivity is plotted as a function of d_p in Figure 2 for three values of ζ between 25 and 100 mV. As can be seen, the electroosmotic conductivity is diminished rapidly with an increase in particle diameter for all values of ζ , and with a decrease in ζ potential for all values of d_p .

The electrolyte concentration affects the electroosmotic conductivity through the ζ potential and the electrical double-layer thickness. As noted by several workers,⁹⁻¹² the ζ potential of a glass tube or silica particles varies linearly with the logarithm of molar concentration over a reasonable range:

$$\zeta = B + C \log c \text{ (V)} \quad (8)$$

where B and C are empirical constants determined for a given system.

The reciprocal of the double-layer thickness is related to the molar concentration by eq 9 for aqueous solution of a 1-1 electrolyte at 25 °C:¹³

$$\kappa = 3.29c^{0.5} \text{ (nm}^{-1}\text{)} \quad (9)$$

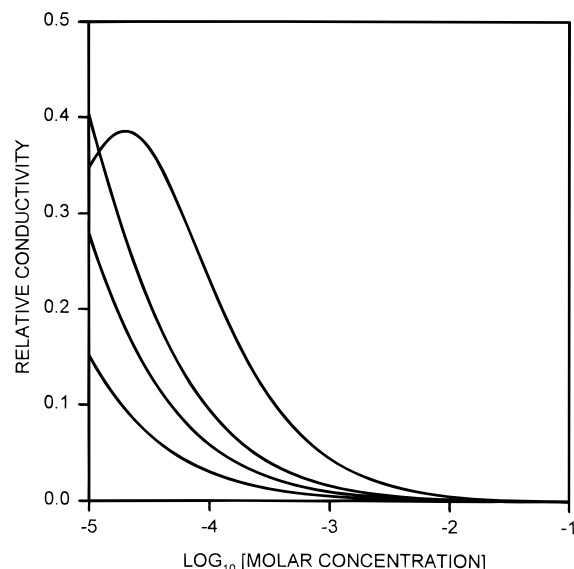


Figure 3. Variation of relative conductivity with electrolyte concentration for particle diameters 1, 3, 5, and 10 μm (from the upper to the lower curve), where $B = -0.012$ and $C = -0.018$ are assumed.

The electroosmotic conductivity as a function of $\log c$ was calculated by substituting eqs 8 and 9 for ζ and κ in eq 3, and the results are shown in Figure 3 for four values of particle diameter between 1 and 10 μm . The calculations assumed $B = -0.012$ and $C = -0.018$ for the silica particles at pH around 7.⁹ In general, the contribution to the conductivity from the electroosmotic flow is decreased with increasing electrolyte concentration over the range 0.01–10 mM.

If we take typical conditions in electrochromatography as $d_p = 3 \mu\text{m}$, $c = 1.0 \text{ mM}$, and $\zeta = 44 \text{ mV}$,⁹ the electroosmotic conductivity accounts for less than 5% of the bulk conductivity. This contribution of electroosmotic flow is indeed negligible from a practical point of view. This conclusion is expected to hold for porous particles on the argument that electroosmotic flow within the pores of the particles is virtually absent due to the double-layer overlap effect.⁵

From the results presented above, it may be concluded that our theoretical analysis of electroosmotic conductivity based on electrokinetic theory and the capillary tube model indicates

that the effect of electroosmotic flow on electrical conductivity of a packed capillary column increases with ζ potential but decreases with increasing particle size and electrolyte concentration. Under the typical conditions employed in current CEC this contribution to the observed electrical conductivity is insignificant. A reduction of electrical conductivity in packed columns relative to the bulk conductivity is therefore largely accounted for in terms of the obstructive effect of the packing. However, a marked increase in the electrical conductivity may be observed corresponding to an increase in ζ potential at high pH's or a decrease in particle size. In these cases, allowance for the electroosmotic effect is required in order to correlate the electrical conductivity with the packing structure for purposes of column characterization in CEC.

Acknowledgment. I thank Professor H. Poppe (University of Amsterdam) for his encouragement and support during the research. The work was supported by a postdoctoral fellowship from the University of Amsterdam. Part of the work was presented at the 5th International Symposium on High Performance Capillary Electrophoresis, Orlando, January 25–28, 1993.

References and Notes

- (1) Stevens, T. S.; Cortes, H. J. *Anal. Chem.* **1983**, *55*, 1365–1370.
- (2) Knox, J. H.; Grant, I. H. *Chromatographia* **1991**, *32*, 317–328.
- (3) Wan, Q. H. *Anal. Chem.*, submitted.
- (4) Wan, Q. H. *Anal. Chem.* **1997**, *69*, 361–363.
- (5) Rice, C. L.; Whitehead, R. J. *Phys. Chem.* **1965**, *69*, 4017–4024.
- (6) Levine, S.; Marriott, J. R.; Neale, G.; Epstein, N. J. *Colloid Interface Sci.* **1975**, *52*, 136–149.
- (7) Bear, J. *Dynamics of Fluids in Porous Media*; American Elsevier: New York, 1972; Chapter 4.
- (8) Giddings, J. C. *Dynamics of Chromatography*; Marcel Dekker: New York, 1965; Chapter 5.
- (9) Knox, J. H.; Grant, I. H. *Chromatographia* **1987**, *24*, 135–143.
- (10) Rutgers, A. J.; De Smet, M. *Trans. Faraday Soc.* **1945**, *41*, 758–771.
- (11) Hunter, R. J.; Wright, H. J. L. *J. Colloid Interface Sci.* **1971**, *37*, 564–580.
- (12) Miller, N. P.; Berg, J. C. *J. Colloid Interface Sci.* **1993**, *159*, 253–254.
- (13) Hunter, R. J. *Zeta Potential in Colloid Science: Principles and Applications*; Academic Press: London, 1981; Chapter 2.