Electrical Conductivity as a Tool for Characterizing Packing Structure in Capillary Electrochromatography

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Electroosmotic flow in packed capillary electrochromatography (CEC) may deviate considerably from the assumed flat velocity profile due to thermal and electrical double-layer overlap effects occurring in sections of poor permeability. It is thus highly desirable to devise a method for proper characterization of the flow permeability of packed columns used in CEC. Here we describe such a method which is based on the well-known relationships between the electrical properties and structural factors of a porous medium. The approach involves the measurement of electrical conductivity for columns with and without chromatographic packing and the calculation of relative conductivity λ. The λ value is then used to indicate the flow permeability of the packed column. Experiments with three well-packed capillary columns found the λ values ranging from 0.31 to 0.34. These results appear to confirm the theoretical prediction that relative conductivity is essentially a structural constant and thus independent of column dimensions, particle size, and field strength.

1. Introduction

The presence of solid particles in a chromatographic column generally causes a dispersion of the flow and diffusion of solute in the mobile phase.[1] This effect, known as "eddy diffusion", is an important factor limiting the column efficiency in conventional chromatography.[1] In capillary electrochromatography (CEC) with electroosmotic flow as the driving force, the dispersion effect of the packing can be reduced substantially if the favorable flat profile of electroosmotic flow is retained.[2−7] Thus, CEC promises a considerable increase in the performance of liquid chromatographic separations. However, in many cases,[6,7] the CEC column efficiencies are shown to be little different from those obtainable with pressure-induced flow, indicating that the assumed flat electroosmotic velocity profile may not actually exist in these experiments. Recently, it has been shown that thermal and electric double-layer overlap effects are among the factors that cause variations in the electroosmotic velocity profile.[4−6,8−10] In packed columns, these effects may become more pronounced due to packing irregularities. Given the heterogeneous nature of a chromatographic packing, it is reasonable to expect that flow channels within the packed column vary widely in size, depending upon the particle size distribution and local packing density. While no significant perturbation to the electroosmotic flow is to be expected in loose packed regions, severe thermal and double-layer overlap effects may occur in dense packed regions where the flow channels are considerably narrower than those assumed for the average. It appears that the transcolumn electroosmotic velocity profile in a packed column is a strong function of the local properties of the packing structure, contrary to the common belief that a uniform flow rate should exist anywhere in a packed column regardless of the complexity of the packing structure.[2,3]

Clearly, a precise characterization of the flow permeability of the packing structure is highly desirable not only for understanding the nature of electroosmotic flow in porous materials but also for optimizing the kinetic performance of CEC in routine analysis. In conventional chromatography, a dimensionless flow resistance parameter ϕ is used for this purpose, which is expressed in terms of the pressure drop across a particle relative to the linear velocity of eluent over a particle.[1,11] For a well-packed chromatographic column, the value of ϕ is expected to fall in the range 500−1000. If the observed value of ϕ is much larger than 1000, this probably indicates a collapse of the regular packing structure or a partial blockage of the system. Thus, the magnitude of the flow resistance can give diagnostic information about the column as well as the flow system as a whole. In CEC where eluent flow is induced by an electric field rather than a pressure gradient, the flow permeability of a column can be evaluated in terms of the relative conductivity λ, which is defined as a ratio of the electrical conductivity of the column packing regarded as homogeneous, saturated with an electrolyte solution, to the bulk conductivity of the same electrolyte solution.[12] Although largely ignored in the chromatographic literature, the electrical properties of electrolyte-filled porous media are often used in studies of flow through porous media. In cases where a nonconducting porous material such as silica-based chromatographic packing is considered, the current is entirely conducted by movement of ions in electrolyte solution. The conductivity of such a material then depends on the geometry of the voids and the conductivity of the fluid with which these voids are filled. Both theoretical and experimental studies have shown that there exist correlations of electrical conductivity of a porous material with other physical properties such as porosity, tortuosity, and fluid permeability.[13−16] However, these relationships have not been addressed in connection with the CEC conditions. In this work, we wish to investigate the correlation between the electrical conductivity and the flow permeability of a chromatographic packing and to explore the applications of electrical conductivity measurements to the characterization of electrochromatographic columns.

2. Theory

Permeability is a measure of the capacity of a porous medium to transmit eluent flow. Under electrically driven conditions,

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the permeability of a porous system can be correlated with the electrical conductivity as illustrated by the following development.

Since the packing structure is too complicated to be represented precisely by any mathematical models, it is permissible to treat the packing structure as composed of a bundle of capillary tubes. As a starting point, let us consider electroosmotic flow and electrical current in an open tube where the absence of electrical double-layer overlap is assumed. The volumetric flow rate v_0 of eluent is given by Smoluchowski's equation[17]

$$v_0 = (\epsilon_0\epsilon_r\zeta/\eta)AE \qquad (1)$$

where ϵ_0, ϵ_r, η, ζ, A, and E represent respectively the permittivity of a vacuum, the relative permittivity of the fluid, the fluid viscosity, the zeta-potential of the tube, the cross-sectional area of the tube, and the applied electric field strength.

The electrical current I_0 in the same system is governed by Ohm's law

$$I_0 = \kappa AE \qquad (2)$$

where κ is the specific conductivity of the electrolyte.

In a column packed with impermeable particles, both the electroosmotic flow and electrical current will be lower than those in the open tube of the same diameter and the same material. As has been shown previously,[5,6] the reduction can be largely accounted for by two geometrical considerations. First, the tortuous paths in the packing structure increase the path lengths and alter the directions, thus reducing the effective field strength E. Second, the particles occupy a certain portion of the free space within the tube and hence reduce the effective cross-sectional area A available to flow. Accordingly, allowing for both effects, the volumetric flow rate v_p and electrical current I_p in packed columns will be reduced by the same factor relative to those in open tubes:

$$v_p = v_0\epsilon\gamma \qquad (3)$$

and

$$I_p = I_0\epsilon\gamma \qquad (4)$$

where ϵ and γ are column porosity and tortuosity factor, respectively.

In analogy to the specific permeability defined for a porous system under pressure-driven conditions,[1] we can readily show that the specific permeability k under electric-driven conditions is a function of the column porosity and tortuosity factor:

$$k = A\epsilon\gamma \qquad (5)$$

The product of ϵ and γ can be determined readily from the relative conductivity λ, which is expressed as a ratio of electrical conductivity of a column with packing to that without packing materials:

$$\lambda = I_p/I_0 = \epsilon\gamma \qquad (6)$$

A variety of expressions have been proposed to show the dependence of relative conductivity on porosity.[13-16] The best known of these is perhaps the Slawinski equation:[14]

$$\lambda = \frac{\epsilon}{(1.3219 - 0.3219\epsilon)^2} \qquad (7)$$

From the Slawinski equation, it follows that the relative
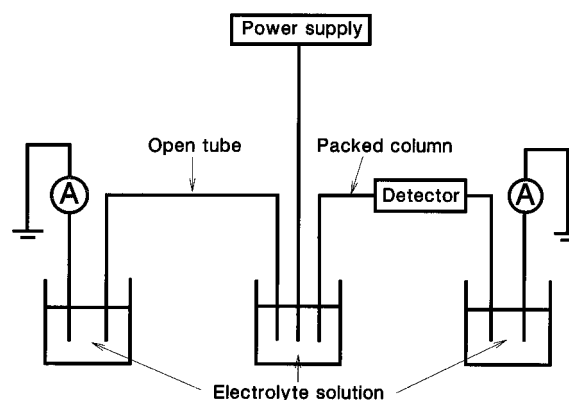
Figure 1. Outline of experimental setup for capillary electrochromatography and electrical conductivity measurements.

conductivity of a porous packing is independent of particle size, column length, and field strength.

When applied to electrochromatographic columns packed with porous particles, the above simple analysis needs to be extended to allow for the differential effects of packing structure on electroosmotic flow and electrical current. While the electrical current may be transmitted through and around the porous particles, the electroosmotic flow will occur only outside the particles since the pores within the particles are normally so small that the electroosmotic flow is completely suppressed by double-layer overlap effects.[6,9] For this reason, the specific permeability to electrical current is likely to be greater than that to electroosmotic flow. Since problems concerning electroosmotic flow and current within porous particles have not been well understood, it is impossible to analyze these structural effects in precise mathematical terms. Therefore, reliance has to be placed primarily on experimental correlations based on laboratory measurements. Although the observed electrical conductivity of a packed column is essentially a measure of the column permeability to electrical current, they should also give indications of the column permeability to electroosmotic flow.

3. Experimental Section

As shown in Figure 1, the equipment used for electrochromatography and current measurements was housed in a polycarbonate box equipped with an interlock to prevent electric shock. Electrical contact between the columns with capillary tubings obtained from Polymicro Technology and the high-voltage power supply (Model HCN 35-35000, FUG, Rosenheim, Germany) was established using platinum-wire electrodes dipped into electrolyte solution vials. Electric currents flowing through the columns were measured directly on Metex M4630 digital multimeters (Klassing Electronics, Oosthout, The Netherlands) provided with BD40 chart recorders (Kipp & Zonen, Delft, The Netherlands). On-column detection was carried out with a Model 356 XM helium−cadmium laser (Omnichrome) induced fluorescence detector as described by Tock et al.[18] The output from the fluorescence detector was fed into a Model 1394 integrator from Hewlett-Packard.

The columns and the electrolyte solution vials were thermostated at 25 ± 1 °C in the polycarbonate box in which an air fan was operated to speed up the dissipation of the Joule heat from the columns. The inlet ends of the open tubular and packed columns were placed in the same vial to ensure the same conductivity of the electrolyte in these two columns.

The slurry packed capillary columns were produced by a method similar to that described by Knox and Grant.[6] Porous frits were made at both ends of the column to hold the particles

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TABLE 1: Physical Properties of Capillary Columns

column	packing material	particle size, μm	column dimensions	κ, 10^{-3} ohm^{-1} m^{-1}	λ
1	Zorbax BP C8	7	44 cm × 75 μm i.d.	4.16 ± 0.13	0.34
2	Zorbax BP C8	7	44 cm × 100 μm i.d.	4.05 ± 0.24	0.33
3	ODS-Hypersil	5	53 cm × 75 μm i.d.	3.78 ± 0.25	0.31
4	none		60 cm × 100 μm i.d.	12.3 ± 0.2	1.00

within the column. The type of packing material, particle size, and column dimensions used are listed in Table 1, together with relevant parameters for the open tube used.

The electrolyte solution containing 75% (v/v) acetonitrile: 25% (v/v) aqueous sodium phosphate solution (4 mM, pH 7.0) was used as eluent throughout the work. The sample solutions were obtained by dissolving appropriate amounts of the aromatic hydrocarbons in the above solution.

The general procedure for carrying out electrochromatography and current measurements was as follows. First the columns were filled with the chosen electrolyte solution under pressure gradient. For this purpose, a negative pressure was applied to the electrolyte solution vial in which the outlet end of the open tube was immersed whereas a high pressure up to 400 bar was required to force the electrolyte solution through the packed column, which was generated by a Spectroflow 400 high-pressure pump (ABI Analytical Kratos Division, Rotterdam, The Netherlands). The pumping was continued until no bubbles emerged from the outlet end of the packed column for at least 30 min. The packed column filled with the eluent was then installed in the electrochromatographic system while maintaining the two ends immersed in the electrolyte solutions. The column was preconditioned by applying a positive electric field between 10 and 30 kV, and the process was followed by observing the change of current trace on the recorder. Electrochromatographic separations and current measurements were made only when the current trace became stable, and typically this took about 1 h.

4. Results and Discussion

Given a strong dependence of electrical conductivity on the packing structure, it is certainly true that a large variation in relative conductivity could be obtained on comparing a loosely filled column with a densely packed one. To obtain a characteristic value for a given packing material, a comparison needs to be made only for well-packed columns. A good column is characterized by low values of the reduced plate height h, typically around 2 at optimal velocity.[11] To test the quality of the packed columns prepared, we carried out electrochromatographic separation of a test mixture of fluorescent aromatic hydrocarbons and calculated the theoretical plate number N and reduced plate height h for each compound. Figure 2 shows electrochromatograms obtained at the field strengths between 45 and 61 kV/m, with a mixture of 75% (v/v) acetonitrile and 25% (v/v) aqueous solution of sodium phosphate (4 mM, pH 7.0) as the mobile phase. The neutral aromatic compounds including anthracenecarbonitrile, anthracene, and fluoranthene are well-resolved and eluted as highly symmetric peaks in all the cases. On average, the h values less than 2 were obtained (see Table 2), suggesting that these columns were well-prepared and suitable for conductivity studies.

Prior to electrical conductivity measurements, the effects of column preconditioning and electrode polarity on column conductivity were investigated. It was found that, upon the application of an electric field, the values of the current noted at the start of the experiment decreased with time for newly prepared packed columns. After about 30 min elapsed, it
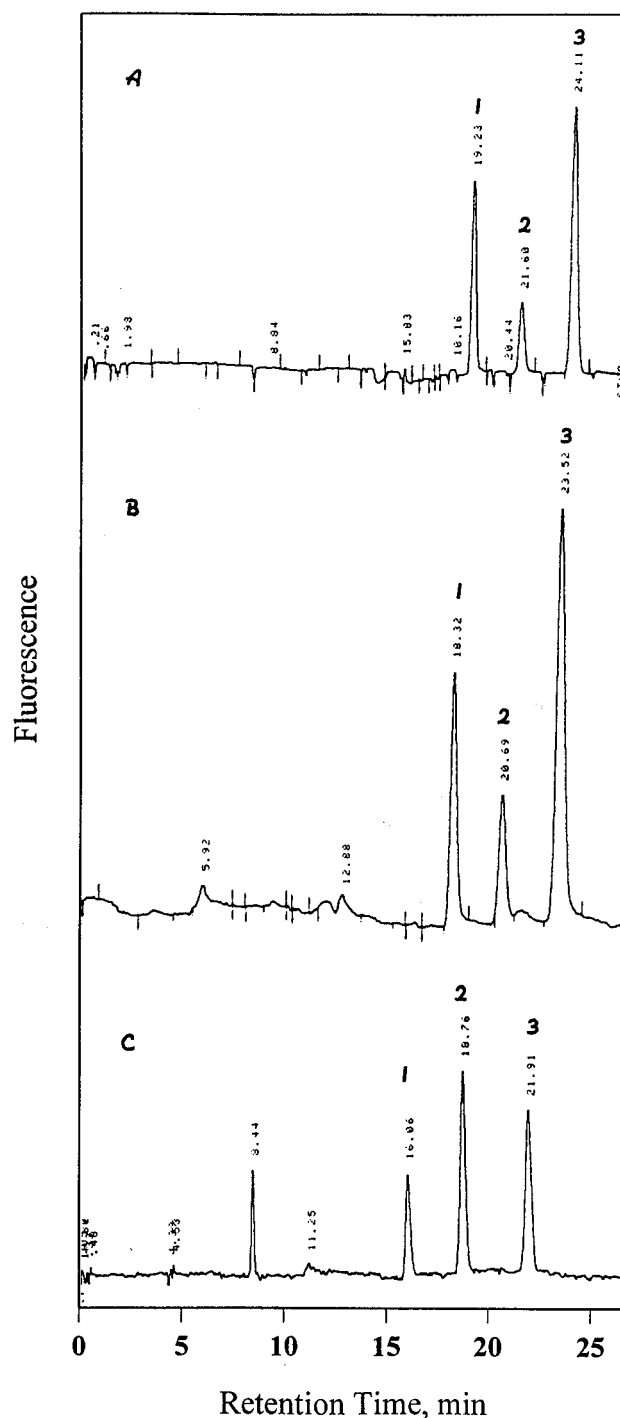
Figure 2. Separation of polycyclic aromatic hydrocarbons by capillary electrochromatography. Eluent, 75% (v/v) acetonitrile:25% (v/v) aqueous solution of sodium phosphate (4 mM, pH 7.0); detection, He−Cd laser induced fluorescence. (a) Column, 44 cm × 75 μm i.d., Zorbax BP C8 (7 μm), effective column length, 25 cm, applied voltage, 20 kV. (b) Column, 44 cm × 100 μm i.d., Zorbax BP C8 (7 μm), effective column length, 22 cm, applied voltage, 20 kV. (c) Column, 53 cm × 75 μm i.d., ODS-Hypersil (5 μm), effective column length, 34 cm, applied voltage, 32.5 kV. Solutes: (1) anthracenecarbonitrile, (2) anthracene, and (3) fluoranthene.

TABLE 2: Experimental Data on Theoretical Plate Number and Reduced Plate Height

solute	column 1		column 2		column 3	
	N	h	N	h	N	h
anthracenecarbonitrile	42 327	0.84	32 968	1.08	27 858	1.28
anthracene	20 659	1.52	20 515	1.53	19 154	1.64
fluoranthene	35 722	1.90	33 849	2.01	33 922	2.00
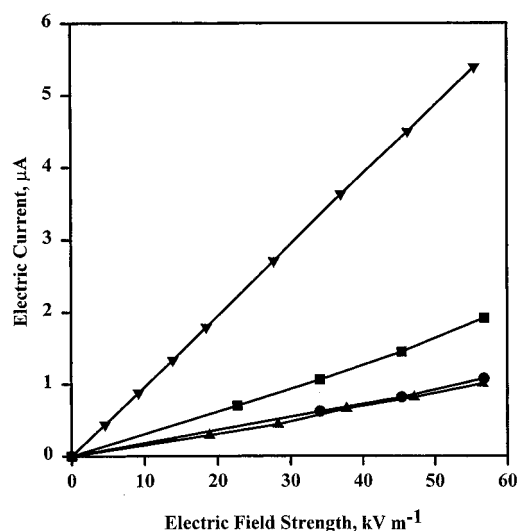
Figure 3. Dependence of electrical current upon electric field strength for open tubular and packed columns filled with 75% (v/v) acetonitrile: 25% (v/v) aqueous solution of sodium phosphate (4 mM, pH 7.0). ● = column 1, ■ = column 2, ▲ = column 3, and ▼ = column 4.

became constant and changed little thereafter when it was followed for a period of more than a week. The stabilized values of electrical conductivity were 10–30% lower than those observed at the beginning of the experiment. The variation of electrical conductivity with time was attributed to a change in packing structure induced by strong electrostatic interactions between the electrodes and the charged particles. This was supported by the observation that reversal of electrode polarity caused a dramatic change in column conductivity. Experiments with preconditioned columns showed that, upon reversing the electrode polarity, the current trace went up gradually until reaching a maximum value and then began to fall afterward. After a typical delay of 30–40 min, the current trace became stable again with a value close to that before the polarity was reversed. This behavior is explicable in terms of restructuring of the packing materials under the influence of the electric field.

Measurements of electrical conductivity were carried out on columns preconditioned and equilibrated with the mobile phase. Figure 3 shows experimental values of current I as a function of applied electric field strength E. While the I–E plot for open tube is a straight line passing through the origin, all the plots for packed columns are slightly curved, particularly at high electric field strengths. The curvature of I–E plots has been noted previously by several workers and was attributed to the slow dissipation of the Joule heat from the column.[19,20] In our opinion, however, the heating effect noted here was largely associated with the heterogeneity of the column packing. Because of the low electrolyte concentration and narrow bore columns used, the average heating effect would be insignificant over the range of electric field strengths investigated. This is evident by noting the straight I–E plot for the open tube which should produce more heat than all the packed columns studied here at the same field strength. However, the local heating effect occurring in dense packed regions where a higher electrical resistance is anticipated can be significantly higher than the

average, thus contributing to the upward deviation from linearity. In extreme cases, the local heating effect was found to be responsible for the problem of bubble formation and subsequently the breakdown of the eluent flow.

Specific κ and relative λ conductivities were calculated from the I–E plots, and the results are given in Table 1. The packed columns have λ values ranging from 0.31 to 0.34. The relatively insignificant variations of the λ values appear to confirm the theoretical expectation that the relative conductivity is essentially a structural constant and thus independent of column dimensions, particle size, and field strength.

Although van der Put and Bijsterbosch[21] reported more than 10 years ago electrical conductivities for porous plugs composed of uniform, nonporous polystyrene spheres, our work represents the first attempt to measure the relative conductivities of columns packed with chromatographic materials. Since the packing materials are porous silica gels, the current flowing through the particles is expected to contribute to the observed conductivity. Because of a lack of knowledge about the particle conductivity, we cannot interpret the results in quantitative terms concerning the relative contributions of interparticle and intraparticle conduction. A comparison with van der Put and Bijsterbosch's values ($\lambda = 0.28 \pm 0.02$), however, leads us to believe that the ionic flux flowing around the particles may play a major role in determining the electrical conductivity of porous chromatographic packings.

With a role similar to the flow resistance parameter in conventional chromatography, the relative conductivity is of diagnostic value in carrying out electrochromatographic experiments. If a relative conductivity of 0.33 is assumed for a good column, then an observed value for a given column that deviates strongly from 0.33 probably suggests a poorly packed column. Low values result from either partial blockage or bubble formation whereas high values are indicative of loosely filled columns or loss of end frits. Obviously, more work is required to establish the ranges in which the relative conductivities vary for different packing materials and packing methods.

5. Conclusions

The present approach to column characterization, which involves the determination of electrical conductivities for open tubular and packed columns, is promising when applied to quality control of column preparation in capillary electrochromatography (CEC) and for use as a diagnostic tool for columns operated under the CEC conditions. The application of the method is not necessarily limited to the situation considered in this work. For instance, the method with appropriate modification should be applicable to capillary gel electrophoresis where information on the uniformity of the gel framework is valuable in column preparation and operation.

Although the results clearly show a correlation between the electrical conductivity and the permeability of the packing structure, more studies need to be carried out to identify factors that influence the electrical conductivity of an electrochromatographic column. Of particular interest are effects of electrolyte composition and concentration, packing method, particle shape and porosity, and particle size distribution. Recently, we[22] reported a theoretical analysis of the effect of electroosmotic flow on the electrical conductivity of packed columns. It is shown that, under typical conditions used in the current practice of CEC, the contribution of electroosmtic flow accounts for less than 5% of the bulk conductivity and, therefore, can be neglected for practical purposes. Given their relevance to our understanding of electroosmotic flow and current in porous structure, we see these conductivity studies as a rich area for further exploration.

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References and Notes

(1) Giddings, J. C. *Dynamics of Chromatography*; Marcel Dekker: New York, 1965; Chapters 2 and 5.

(2) Pretorius, V.; Hopkins, B. J.; Schieke, J. D. *J. Chromatogr.* **1974**, *99*, 23−30.

(3) Jorgenson, J. W.; Lukacs, K. D. *J. Chromatogr.* **1981**, *218*, 209−216.

(4) Knox, J. H.; Grant, I. H. *Chromatographia* **1987**, *24*, 135−143.

(5) Knox, J. H. *Chromatographia* **1988**, *26*, 329−337.

(6) Knox, J. H.; Grant, I. H. *Chromatographia* **1991**, *32*, 317−328.

(7) Yamamoto, H.; Baumann, J.; Erni, F. *J. Chromatogr.* **1992**, *593*, 313−319.

(8) Stevens, T. S.; Cortes, H. J. *Anal. Chem.* **1983**, *55*, 1365−1370.

(9) Wan, Q. H. *Anal. Chem.* **1997**, *69*, 361−363.

(10) Wan, Q. H. *J. Chromatogr.*, in press.

(11) Bristow, P. A.; Knox, J. H. *Chromatographia* **1977**, *10*, 279−289.

(12) Bear, J. *Dynamics of Fluids in Porous Media*; American Elsevier: New York, 1972; Chapter 4.

(13) Maxwell, J. C. *A Treatise on Electricity and Magnetism*, 3rd ed.; Dover: New York, 1954; Vol.1, Part 2, Chapter 9.

(14) Slawinski, A. *J. Chim. Phys.* **1926**, *23*, 710−727.

(15) Bruggeman, D. A. G. *Ann. Phys.* **1935**, *24*, 636−664.

(16) Amyx, J. W.; Bass, D. M., Jr.; Whiting, R. L. *Petroleum Reservoir Engineering*; McGraw-Hill: New York, 1960; Chapter 2.

(17) Rice, C. L.; Whitehead, R. *J. Phys. Chem.* **1965**, *69*, 4017−4024.

(18) Tock, P. P. H.; Boschoven, C.; Hoppe, H.; Kraak, J. C.; Unger, K. K. *J. Chromatogr.* **1989**, *477*, 95−106.

(19) Terabe, S.; Otsuka, K.; Ando, T. *Anal. Chem.* **1985**, *57*, 834−841.

(20) Bruin, G. J. M.; Tock, P. P. H.; Kraak, J. C.; Poppe, H. *J. Chromatogr.* **1980**, *517*, 557−572.

(21) Van der Put, A. G.; Bijsterbosch, B. H. *J. Colloid Interface Sci.* **1980**, *75*, 512- 524.

(22) Wan, Q. H. *J. Phys. Chem. B* **1997**, *101*, 4860−4862.