

Acidity -dependent Electro-osmotic Mobility in Surfactant-coated Silica Microchannels

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Abstract: - We have derived a theory to predict the electro-osmotic mobility dependence on buffer pH values in surfactant-coated fused silica capillary. Using the surfactant aggregation density data obtained with atomic force microscopy and dissociation degree data from electro-osmotic mobility in bare channels, we have successfully predicted the mobility tendency at different pH values in the surfactant-coated channel.

Key-Words: - Acidity; Microchannel; Electro-osmosis; Surfactant; Aggregation; Dynamic coating

1 Introduction

Dynamic coating is a popular ancillary technique to modify the surface of capillary electrophoresis microchannels used in biochemical assays.^{1,2} The main purpose of dynamic coating is to enhance the bio-compatibility of microchannels via preventing biochemical analytes, especially peptides and proteins, from absorbing on the fused silica channel walls, when analytes are migrating through the capillary during electrophoretic separation processes. Sample loss due to this absorption is sometimes critical, especially when samples are in very small amount. To accomplish dynamic coating, typically positively charged surfactants are mixed with electrophoretic buffers and then filled into the channel to absorb on silanol groups, which dissociate to anionic functionalities. Negative charge density at the silanol surfaces decreases due to the coverage of cationic surfactants. Therefore, cationic analytes are less likely to interact with negatively charged channel wall. When the charges of absorbed surfactants exceed those of dissociated silanols, the polarity of net charges reverses. The electro-osmotic flow in the channel move toward the opposite direction of that in bare silica channels.

The governing equation of electro-osmotic flow rates is Helmholtz – Smoluchowski equation,³

$$v = - \epsilon \zeta E / 4\pi\eta \dots (1)$$

where v is electro-osmotic velocity under the applied field strength E and the zeta potential ζ due to surface charges on the channel wall. The dielectric constant and viscosity of electrophoretic buffer are ϵ and η respectively.

Under the Debye-Huckel approximation, zeta potential arising because of surface charges is

proportional to charge density. Having rearranged eq (1), we obtain the electro-osmotic mobility ($u = v/E$) which increase linearly with the increase of surface negative charge density. This relation is able to rationalize the mobility change and direction reversal during the course of surfactant titration described in the above.

The pH dependence on the electro-osmotic mobility in bare silica channel is straightforward to understand. The dissociation degrees of silanol group, which governs the surface charge density, depends buffer acidity. How the adsorption mechanism of coating surfactant on the surface varies with pH change, however, is still in need of investigation. In this paper, we use the linear combination of dissociated silanol degree and the surface morphology data cluster of surfactant aggregates such as cluster distance to estimate the net charge density. We also discuss the agreement between observed mobility values in fused silica capillary coated with cetyltrimethylammonium bromide (CTAB) and our theoretical prediction.

2 Problem Formulation

As mentioned previously, the electro-osmotic mobility ($u = v/E$) is proportional to surface zeta potential ζ ,

$$u = - \epsilon \zeta / 4\pi\eta \dots (2)$$

Since ζ is approximated as a linear function of negative surface charge density σ , the mobility values measured in bare silica capillaries filled with a variety of pH buffer solutions directly reflect the relative values of σ , which are due to the

dissociation of surface silanol groups in those solutions.

On the other hand, we use atomic the images of surfactant aggregates acquired with atomic force microscopy (AFM) to estimate the positive charge density since the cationic sites are provided by these aggregates. The linear combination of both positive charge density σ^+ and negative charge density σ^- is expressed as σ_{net} as follows,

$$\sigma_{\text{net}} = \sigma^+ - \sigma^- \dots (3)$$

The net charge density should be proportional to the mobility in the coated capillary.

2.1 Measuring Electro-osmotic Mobility with Current Monitoring Method

Current monitoring method is to measure the current transition duration time during the replacement of a higher conductivity buffer with lower one using electro-osmosis.⁴ Typically dilute buffer is filled in the cathode reservoir to aspirate into the bare capillary using electro-osmosis after the electrophoresis voltage is activated, and the dilute buffer gradually replace the higher concentration buffer filled in the capillary. Current through the capillary is determined via monitoring the voltage drop across a high resistor between the anode electrode and the ground. We use four types of buffer solutions at 25 mM to measure electro-osmotic mobility at pH 3, 5, 7, and 8 respectively. The ratios of negative charge density on the capillary surface between these pH values are obtained from the mobility data.

We also employ current monitoring method to measure the mobility values in coated capillary in the same pH values as those in the above. The coating surfactant cetyltrimethylammonium bromide (CTAB) is at 0.5 mM in all experiments. Since the coated capillary surface is positively charged, the direction of electro-osmotic flow in the capillary is opposite to that in bare capillary. Therefore, dilute buffer is filled in the anode reservoir to aspirate into the capillary to replace higher concentration buffers.

2.2 Morphology of Surfactant Aggregates on Silica Surface

CTAB absorbed on silica surfaces usually form two types of aggregates, spherical hemimicelles and rod-like admicelles.⁵ The first stage accumulation of surfactants absorbed on the surface forms spherical aggregates, which are uniformly distributed on the surface. The excess amounts of surfactants keep laying on the surface to form randomly distributed and rod-like aggregates. These two types of micelle aggregates have been observed with AFM images.⁶ The morphology of aggregates is both pH dependent and ionic-strength dependent. In the ionic strength

condition we use in our experiments, spherical aggregates are formed. As illustrated in Table 1, the distance between each aggregate is pH dependent. Each aggregate is at the same dimension and should contain the same numbers of charges. Therefore, the square of separation distance between aggregates should inversely proportional to the positive charge density on the surface. We use the distance data in Table 1 to obtain the ratios of positive charge density between each pH condition.

Having specified the positive and negative charge densities at pH as σ^+ and σ^- respectively, we are able to obtain the ratio between these two densities, since the net density is proportional to the mobility in coated capillary and σ^- scales to the mobility in bare capillary. We use the ratio σ^+/σ^- to calculate the net charge densities at other pH conditions and to estimate the relative mobility in these conditions.

Table 1. Normalized Charge Density on Silica Surface due to CTAB Aggregation in Different pH Buffers

buffer pH	nearest-neighbor (nm)	normalized charge density (a.u.)
3	13	0.33
5	8.5	0.78
7	7.5	1.0
11	7.5	1.0

3 Problem Solution

At pH 8, the mobility in bare capillary is about four times as much as that in CTAB-coated capillary. Using eq(3), when σ_{net} is only one fourth of σ^- , we obtain the ratio σ^+/σ^- as 1.25.

Using mobility data in bare capillary and spacing distance data in Table 1, we obtain the charge densities in other pH values relative to σ^+ and σ^- in pH 8. The relative values of net charge densities in other pH conditions are given as well. According to eq(2), the trend of relative mobility values should agree with the relative net charge densities.

When the mobility at pH 8 is given, the other mobility values are specified as shown in Figure 1A.

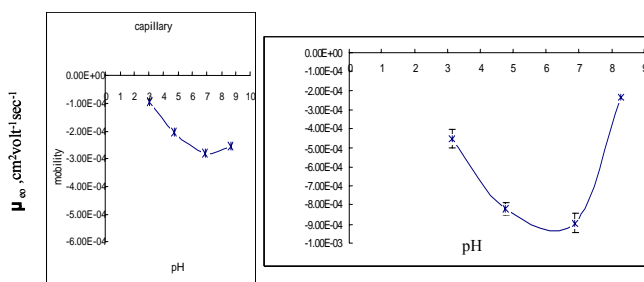
Figure 1B shows the mobility values in coated capillary measured with current monitoring method. The optimum reverse electro-osmotic mobility occurs around pH 7, which agrees with the prediction. The general tendencies of mobility change in these two figures are fairly matched as well.

4 Conclusion

We have successfully used the linear combination model with mobility data in bare capillary and CTAB aggregates separation distance data in AFM images to predict the trend of mobility change in CTAB-coated capillary.

Although both the dissociation degree of silanol and aggregate separation distance become smaller as buffer pH gets lower, the distance change is less sensitive to pH change. Therefore, the net charge density increases firstly, cross a maximum, and then decreases finally, as the buffer solutions change from alkaline to acidic. This change trend reflects on the mobility change too, which have been confirmed with our experimental observation.

Figure 1 A. Left frame: estimated tendency of electro-osmotic mobility change using the data of CTAB (cetyl-tetra-ammonium bromide) aggregate morphology data fused silica surface. B. Right frame: pH dependence of electro-osmotic mobility in fused silica capillary coated with surfactants.



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