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The Surface Properties of Tetradecyltrimethylammonium Bromide Observed by Capillary Electrophoresis

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Abstract

The electroosmotic flow (EOF) is measured as a function of tetradecyltrimethylammonium bromide (TTAB) concentration and is shown to have distinct zones that are pH dependent. The data is correlated with previously proposed surface structures ranging from unimolecular adsorption to hemimicelles and micelles of TTAB adsorbed on the hydrated fused silica. A plot of the TTAB concentration at zero EOF versus pH shows that the zero point of charge (zpc) is pH dependent and that a linear extrapolation of the data intercepts close to the pH value for the zpc of a fused-silica surface. This shows that different surface properties at different pH values at any given TTAB concentration are generally dealt with. Therefore, these pH-dependent structures of the fused-silica surface have to be taken into account while studying these phenomena.

Introduction

The importance of understanding the adsorption of surfactants onto surfaces cannot be overstated because it is involved in environmental remediation (1,2), chromatography (in particular capillary electrophoresis) (3), catalysis (4), mineral processing (5), detergency (6), materials processing (7), and sensor technology (8). However, our understanding of the processes and structures involved is sparse. Capillary zone electrophoresis is a rapidly growing method for the separation of charged species that is performed in a narrow fused-silica capillary filled with electrolyte solution. In the separation of anions, cationic surfactants are often added to manipulate the electroosmotic flow (EOF). Several common cationic surfactants used are tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium chloride (CTAC), and lauryltrimethylammonium bromide (LTAB). TTAB is increasingly used in capillary electrophoresis as a surface active aid in the separation of acid derived anionic species (9,10). It has been observed that TTAB requires a minimum concentration of approximately 0.4mM for best results. This value has been chosen because it is close to its critical micelle concentration (CMC), and it has been projected that this concentration is required for "hemimicelles" to be formed on the inner wall of the capillary (11,12). Since the introduction of the concept of the hemimicelle by Fuerstenau et al. (13–15) to explain electrophoretic mobility and the use of hemimicelle formation in chromatography by Emmer et al. (16), the structure has been differently discussed as island-like, coulombic adsorbed, associated surfactant, adsorbates with the surfactant head groups attached to the surface with a resulting hydrophobic surface presented to the solution (13), and more complicated structures with tail-to-tail three-dimensional interactions with some head groups presented to the solution (11). The original concept of the hemimicelle was one of "patches of associated ions" adsorbed to the surface (14). At the present, it remains an open question as to what is the actual structure of the hemimicelle. However, the critical concentration at which the association has been observed is well-documented for various situations and is referred to as the hemimicelle concentration (C_{HM}). Another structure that forms at higher surfactant concentrations has been postulated as well, which is termed "admicelle" and has a three-dimensional structure that resembles an adsorbed micelle. Supporting this has been the observation that increasing the concentration of TTAB in the electrolyte much beyond the CMC does not make the separation faster because once the hemimicelles and admicelles are formed, the maximum positive ion contribution to the interfacial structure is reached. Thus, the physical structural picture of the interfacial region (using this explanation) would consist of four regions: one being the binding of individual surfactant ions, the second being the formation and growth of the island-like hemimicelles, the third some type of adsorbed micelle structure, and the fourth a saturated zone resembling a monolayer–bilayer. These are similar to those regions observed by Kaneta et al. (11) for CTAC.

In this work, we studied the influence of the pH on the surface structures that can form in the capillary. Although the effect of TTAB has been previously studied (9,10), only very limited pH ranges were covered. In this study, the pH was varied over the whole acidic pH range in order to further explore the effect of pH. Further work is currently underway to cover the basic pH range, too.

Experimental

Capillary electrophoresis has been used to examine the interaction of structures of TTAB with the silica walls of the capillary. The

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EOF has been measured as a function of TTAB concentration and pH. The experiments were performed using a Hewlett Packard (Palo Alto, CA) 3D capillary electrophoresis system and HP 3D CE ChemStation software. A potassium hydrogen phthalate (KHP) buffer was used at pH 2.4, 3.1, 3.8, 4.5, 5.2, 5.9, and 6.6. The neutral marker was dimethylformamide (Sigma Aldrich, St. Louis). In this case, the original silica surface would be expected to be negative (i.e., the zero point of charge (zpc) of silica is approximately pH 2.0 with a pK_a of 5.3 as determined by Schwer and Kenndler (17)). The capillary used was a fused-silica capillary 64.5-cm long with an inner diameter of 50 µm supplied by Hewlett Packard. The experiments were performed using a voltage of –30 kV at 20°C. The capillary temperature was held constant by forced airflow cooling within the HP system. The cooling was efficient enough to prevent joule heating, which was measured to be approximately 5×10^{-3} W/cm without cooling. Before each experiment, a pretreatment with 0.1M NaOH for 8 min and buffer solution for 15 min was performed. The injection time was 1 s at –10 kV using electrokinetic injection. The buffer solutions were made using KHP (Sigma Aldrich), 2-(*N*-morpholine)-ethanesulfonic acid (MES) (Sigma Aldrich), and sodium hydroxide (Hewlett Packard) (e.g., 5mM KHP, 25mM MES, and 0.1M NaOH for pH 5.2). The ionic strength was held constant for all solutions measured. All experiments were performed using multiple runs with different capillaries of the same brand to ensure that the results were reproducible. The number of coils used in our study was 7, and at least 20 runs were done with each coil.

Results and Discussion

Figure 1 shows a plot of EOF versus TTAB concentration at different pH levels. The addition of TTAB at increasing concentrations caused a decrease in the EOF up to the point of charge reversal and then an increase of the reverse EOF (i.e., absolute value of the EOF) beyond that point. This was caused by an increasing positive interfacial potential that was countered by mobile buffer anions that become responsible for the reverse EOF. Figure 1 is divided into three parts by dotted lines that correspond to the three regions shown in Figure 2. The data in Figure 1 indicated that with careful measurement of the EOF as a function of surfactant concentration, the entire range of apparent structural changes can be followed. It has been suggested that coulombic-driven adsorption of a surfactant to specific surface binding sites at the surface acts as seeds for different forms of surfactant aggregation at the surface (18). This can then lead to the structures in the sorption isotherm, as has been observed in this study. The physical significance of these proposed structures is depicted by the drawings shown in Figure 2 and are matched to the respective regions in Figure 1 by numbers I–III. At pH 4.5 and 5.2 (Figure 1) these three regions can clearly be seen. At lower pH the structure in the EOF versus TTAB concentration plots disappeared. At low pH there were not enough surface sites available to form the surface structures shown in Figure 2. In contrast to that, at higher pH (5.9 and 6.6) four regions can be seen in Figure 1. Corresponding to the model from Figure 2, this shows a difference

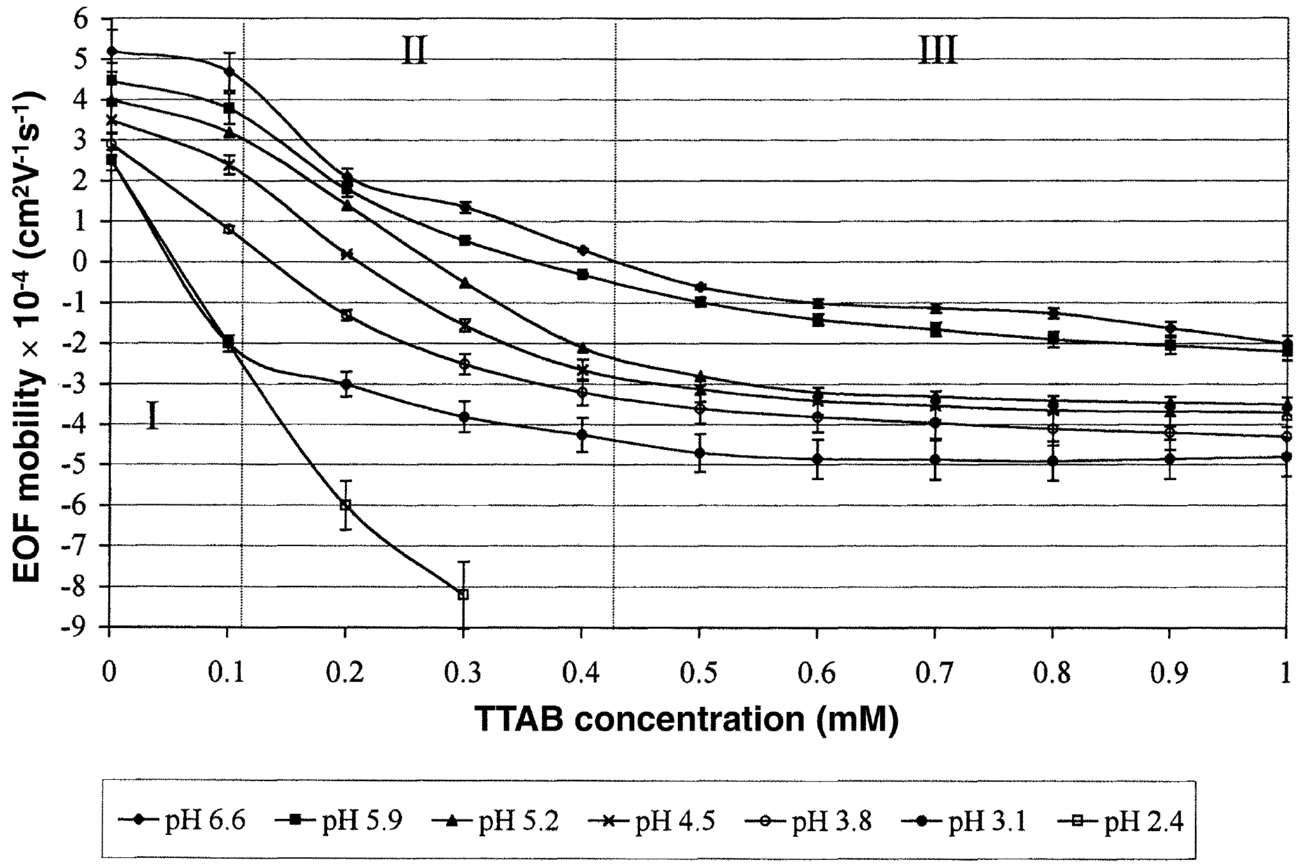

Figure 1. Plot of EOF versus TTAB concentration at different pH levels.

between hemimicelle and admicelle formation. In the first region, the binding of individual surfactant ions occurred. The second region (in which the formation and growth of the island-like hemimicelles and admicelles took place) occurred at approximately C_{HM} = 0.12mM. The third region began approximately at CMC = 0.42mM, in which some type of saturated zone occurred that included the possible monolayer structure as well as the possible bilayer structures. It is apparent from the data that the hemimicelles (if they exist) may appear at the surface well below the CMC (approximately 0.25mM).

In addition, some interesting data can be extracted from the plots in Figure 1 if the points of zero EOF are examined for their pH dependence (see Figure 3). The intercept of the plot with the pH coordinate (dotted line) was at 2.6, a little more than one-half the pH unit above the reported zpc of silica. The value of this intercept has to be viewed with caution because the TTAB concentration at zero mobility was taken from the data of Figure 1, which had an error margin of approximately 10%. If one assumes that the point of zero EOF was the point at which the surface charge was neutral, then the dotted line in Figure 3 should cross the axis at the zpc of fused silica if only coulombic-adsorbed TTAB were in control of the EOF. At the zpc, zero-adsorbed TTAB would be expected. The current data suggests that zpc was overestimated, which indicates that even when the surface charge was zero as demanded by pH there was a positive-charged species attached to the surface. This is an indication that some charge-bearing species, possibly TTAB, was adsorbing by a bonding mechanism other than coulombic interaction. This could possibly be adsorption of the long-chain component of the surfactant to the surface. The effects of organic solvents on the EOF and the zeta potential have been detailed by Schwer and Kenndler (17), in which it was observed that the organic molecules adsorbed to the hydrated silica surface and were involved in the double layer. This adsorption via hydrogen bonding can be visualized using the picture for region one in Figure 2. This noncoulombic adsorption could be aided by the hydrogen bonding of counter anions such as bromide. The effect of anionic counter ions is competitive with the anionic surface sites, as has been shown by Lucy and Underhill (12). Both anionic counter ions and anionic surface sites would be expected to be in interaction with surfactant molecules that were adsorbed by hydrogen bonding or other mechanisms, and counter ions themselves could be hydrogen bound to the surface.

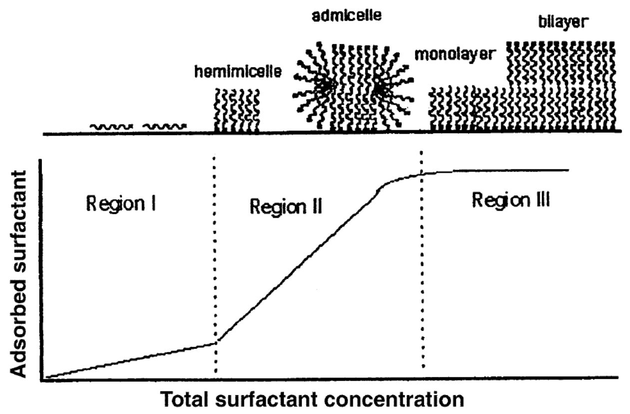

Figure 2. Schematic representation of the adsorption of TTAB showing the orientation of the surfactant molecules and their possible structures as a function of adsorbed surfactant and total surfactant concentration.

Conclusion

Modification of the EOF by cationic surfactant additives in capillary electrophoresis continues to be studied (19) in order to help optimize separations, and with the aid of improved physical models of the interfacial zones continuing improvement can be expected. These studies should continue to contribute valuable data to aid in the formation of improved models and understanding of these structures. It is clear that similar data is produced by different laboratories (11,19) and that the structure shown in the plots of EOF versus TTAB has a relationship to structural changes of the adsorbate at the interface as a function of pH. However, spectroscopic evidence needs to be forthcoming to confirm the nature of the adsorbate structures. Fourier transform infrared spectrometry has been used to examine the structural changes of micelle-like structures on surfaces (20). The complexity of the EOF versus TTAB concentration curves is dependent on the pH. The pH controls the number and strength of the adsorption sites available at the surface for adsorption of a positive surfactant ion and consequently controls the nature of the surface structures that can be accommodated at the silica surface. Therefore, the structure of the resulting adsorption layer is shown to be strongly pH dependent. Plotting the concentration of TTAB at zero osmotic flow versus pH allows the amount of TTAB required to neutralize the surface to be monitored and potentially give the apparent zpc of silica at zero TTAB concentration (intercept).

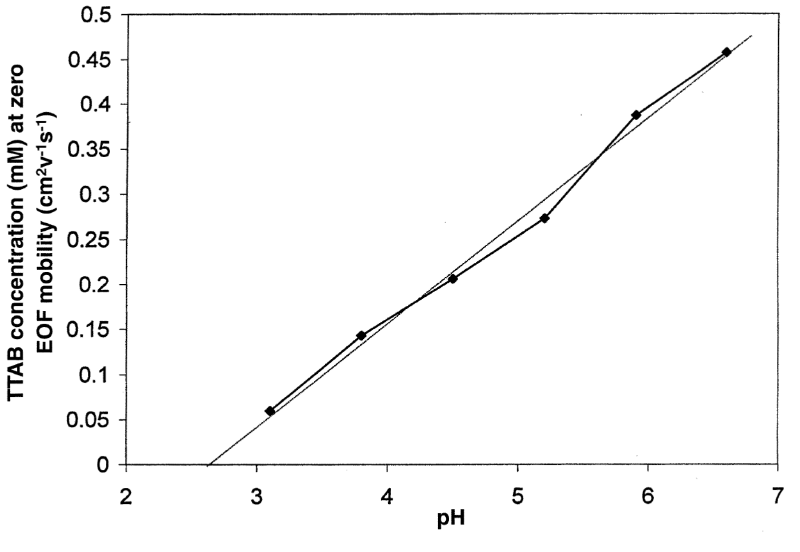

Figure 3. Plot of the TTAB concentration at points of zero EOF taken from Figure 1 versus pH.

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