The Zeta Potential of PMMA in Contact with Aqueous Electrolyte-Surfactant Solutions

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ABSTRACT

A comprehensive study of the zeta potential of Poly(methyl methacrylate) (PMMA) in contact with aqueous solutions containing an anionic, a cationic, or a zwitterionic surfactant at different pH and ionic strength values is conducted. The zeta potential values are inferred from electrophoretic mobility measurements of particulate PMMA along with permittivity and viscosity measurements of the continuous phase. Various types of behaviors are observed for each type of surfactant which is related to the different surfactant adsorption mechanisms on PMMA. For the anionic surfactant, we propose that hydrophobic-based adsorption and, at higher concentrations, the competing micellization process influences the zeta potential. The addition of cationic surfactant results in an isoelectric point where the negative PMMA surface charge is neutralized by a layer of adsorbed cationic surfactant. The zeta potential in presence of zwitterionic surfactant is influenced by adsorption due to hydrophobic interactions between surfactant tail and PMMA surface but there is less influence compared to the ionic surfactants. For all three surfactant types, the zeta potential changes to more negative or less positive values when the media becomes alkaline. An increase of the ionic strength decreases the absolute value of the zeta potential.

KEYWORDS: Zeta Potential, PMMA, Surfactant Adsorption, Adsorption Mechanism, Hydrophobic Surface

INTRODUCTION

The zeta potential (ZP) is the key parameter of all electrokinetic phenomena and is generally relevant for systems with high surface-area-to-volume ratios, e.g. for the stability of colloids. A plot of the total interaction energy vs the separation distance of two particles indicates their energy barrier that has to be overcome to get in contact. Here, the ZP represents the electrostatic interaction and is considered as one of the factors determining the energy barrier.¹⁻³ The ZP is a result of the intrinsic surface properties and the characteristics of the contacting liquid; i.e., the pH value, the electrolyte concentration, the valency and size of the counter-ions, and the temperature.⁴⁻⁵ Additionally, the adsorption of other species such as molecules, ions, or surfactants can significantly impact the electrical surface characteristics. Understanding these effects and processes is crucial for designing the surface for a desired application.

One of the main applications where the control of electrical surface properties is important is the capillary zone electrophoresis and its equivalent in microfluidics, the so-called microchip electrophoresis, which can be applied for (bio)chemical separations such as protein and DNA analysis.⁶⁻¹¹ The separation is based on the different residence times of the analytes if subjected to an electrical field.¹² Here, the control of the electroosmotic flow (EOF) is important to obtain an accurate analysis, especially in polymeric substrates.¹³⁻¹⁴ Furthermore, it is desirable to tune the surface chemistry of the channel substrate to suppress any analyte-wall interactions in order to improve resolution and reproducibility.^{6, 8} In this regard, several techniques have been proposed to manipulate EOF including altering the background electrolyte (pH and ionic strength) and permanent and dynamic coating.^{6, 8, 14} Among these techniques, dynamic coating is perhaps the most convenient way to control EOF and analyte-wall interactions. It comprises the addition of

surface active polymers or surfactants to the system which can cause suppression, decrease or increase of the EOF as well as a change of the substrate wettability.^{6, 8, 15} Due to availability, low cost, easy concentration control and the simple removal step, surfactants may be considered as the best choice for dynamic coatings in capillary zone and microchip electrophoresis.^{12, 16}

Surfactants also play a significant role in other important applications such as droplet microfluidics,¹⁷⁻¹⁸ emulsion polymerization,¹⁹⁻²¹ and stabilization of colloidal systems.^{3, 22-26} The term surfactant refers to amphiphilic macromolecules, possessing a hydrophobic tail and a hydrophilic head. They can be classified into four categories according to their formal charge present in the hydrophilic head: (i) anionic; (ii) cationic, (iii) non-ionic and (iv) zwitterionic (amphoteric) (cf. e.g., ref ²⁷). Anionic and cationic surfactants consist of negatively- and positively-charged polar groups, respectively. Zwitterionic surfactants comprise a positive and a negative polar group while nonionic surfactants feature no net electrical charge.

Surfactants can significantly impact the interfacial properties due to surface adsorption changing the hydrophobicity along with electrical charge and other properties.^{1, 28-30} Here, various adsorption mechanisms can be involved such as covalent bonding or chemical adsorption, electrostatic interactions, hydrophobic interactions between a hydrophobic surface and the hydrophobic tail of a surfactant, as well as hydrogen bonding, just to name a few.²⁹⁻³⁰

The aim of the present work is to explore the interaction between different surfactant types and the electrical surface properties. Our motivation is twofold: On the one hand, surfactants are added to increase stability of dispersed systems, mainly by steric effects. This can also change the ZP of the particle surfaces and therefore the (electrostatic) interaction energy. On the other hand,

surfactants are often used to generate and stabilize droplets in microfluidics, cf. e.g., ref³¹, where droplet flow, breakup, sorting and coalescence can be influenced by applying an electric field.³² The electric field can interact with the EDL located at the channel wall and, in case of in oil-in-water emulsions can induce EOF which can be disadvantageous for the intended droplet manipulation.³³

We choose poly(methyl methacrylate) (PMMA) as a model substrate since it is extensively used in microfluidics due to its good mechanical, electrical and optical properties.^{14, 34} The ZP of PMMA in aqueous electrolytes, without the addition of surfactants, was extensively investigated in our previous work.³⁵ Here, we investigate the influence of anionic, cationic, and zwitterionic surfactants. This article continues with a description of the experimental methodology and the materials. Then, we present the experimental findings and the adsorption mechanism that we propose to explain the change in ZP. Finally, this article is concluded with a summary section.

EXPERIMENTAL

In this section, we introduce the materials and methods that we use to explore the ZP of PMMA in contact with aqueous electrolyte-surfactant solutions.

Surfactants. Three surfactants are chosen in this study: i) the anionic sodium dodecyl sulfate (SDS), ii) the cationic hexadecyltrimethylammonium bromide (CTAB), and iii) the zwitterionic 3-(N,N-dimethylmyristylammonio)propanesulphonate (TDAPS). The molecular structures and selected material data of these surfactants are given in the Supporting Information in Figure S1 and Table S1, respectively. An SDS molecule consists of a sulfate polar head attached to a 12-

carbon hydrocarbon chain while the CTAB's polar head is a quaternary ammonium group which is connected to a 16-carbon chain tail. The TDAPS molecule consists of a cationic quaternary ammonium group and an anionic sulfonate group along with a 3-carbon chain and the 14-carbon chain tail.

Chemicals. Spherical PMMA particles with a diameter of 1 μm are purchased from Sigma Aldrich, Canada, in form of surfactant free suspensions in pure water with the concentration of 10% solids. For the pH adjustment in the range of 5 to 7, buffer solutions containing citric acid $\text{C}_6\text{H}_8\text{O}_7$ ($\geq 99.5\%$) and disodium hydrogen phosphate Na_2HPO_4 ($\geq 99.0\%$) are used. For pH 9, a buffer solution of bicine acid $\text{C}_6\text{H}_{13}\text{NO}_4$ ($\geq 99.0\%$) and sodium hydroxide NaOH ($\geq 98.0\%$) is utilized. Finally, the pH 11 is controlled with NaOH and Na_2HPO_4 . The ionic strength (IS) of the samples is adjusted using sodium chloride, NaCl ($\geq 99.5\%$). All chemicals for pH and IS adjustment are purchased from Sigma Aldrich, Canada. The cationic, anionic, and zwitterionic surfactant CTAB $\text{C}_{19}\text{H}_{42}\text{BrN}$ ($\geq 99.0\%$, Acros Organics, India), SDS $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$ ($\geq 95.0\%$, MP Biomedicals, LLC, France) and TDAPS $\text{C}_{19}\text{H}_{41}\text{NO}_3\text{S}$ ($\geq 98.0\%$, Fluka, Switzerland) are investigated, respectively. Millipore deionized (DI) water with a conductivity of $< 1 \mu\text{S}/\text{cm}$ is used to prepare all samples.

Sample Preparation. All samples are prepared by adding the desired amount of buffer solution, NaCl , surfactant, and PMMA suspension to DI water. From previous work, we know that 75 μL of PMMA suspension added to 100 mL of the aqueous solution is adequate for electrophoretic mobility measurements. The sample IS is calculated according to $I = 1/2 \sum c_i z_i^2$, where c_i and z_i are the concentration and valency of each ionic species i , respectively. The contribution of added

buffer to the ionic strength is also accounted for based on the dissociation equilibrium of the buffer. The range of IS studied here is limited by the experimental methodology. The minimum IS is based on the (unavoidable) addition of the pH buffer without NaCl. The maximum IS is limited by electrode polarization and joule heating with the practical limit being around 0.1 M. Prior to each electrophoretic mobility measurement, the sample is allowed to equilibrate for at least 24 h to ensure that the surfactant adsorption equilibrium is reached. Before each measurement, the sample is sonicated at a high frequency for at least 5 min to avoid particle aggregation. The pH and conductivity is tested using a combined pH and conductivity meter type SevenExcellence (Mettler-Toledo, Switzerland).

Zeta Potential Measurement. We measure the electrophoretic mobility of the particles by electrophoretic light scattering using a Zetasizer Nano ZS (Malvern, United Kingdom). From the electrophoretic mobility values, we can infer the ZP according to

$$\zeta = \frac{u_{EP}\mu}{\varepsilon} \quad (1)$$

where u_{EP} is the electrophoretic mobility, and μ and ε are the dynamic viscosity and the permittivity of the continuous phase, respectively. The latter two properties can be considerably influenced by the medium composition and have to be measured separately; a fact that is mainly neglected in literature. For performing the electrophoresis measurements, a voltage of 20V is applied to the cell. Each measurement is repeated at least 5 times to obtain an average value. The according standard deviation is then calculated using the standard deviations of all parameters; that is, permittivity, viscosity and electrophoretic mobility. Further details about the electrophoretic mobility measurements can be found in Ref. ³⁵.

Permittivity Measurement. Generally, the permittivity of an electrolyte in a solution is smaller than the permittivity of the solvent. The difference can be attributed to the screening effects of the ionic species on the dipole moment of the solvent molecules.³⁶ When the conductivity of the electrolyte solution increases, the permittivity cannot be measured using the parallel plate capacitor method. This is due to the increase in induction effects which results in a short-circuited system.³⁷⁻
³⁸ We measure the complex permittivity of the samples in a frequency range of 200 MHz to 14 GHz with an open ended coaxial probe connected to a N5247A vector network analyzer (Agilent, USA).

Viscosity Measurement. The viscosity of samples containing zwitterionic surfactant are performed using a Gilmont falling-ball viscometer at 25 °C. For the other surfactants, the viscosity is measured using an AR 2000 rheometer (TA Instruments, USA) at 25 °C. The measurements are performed using a steady state ramping of the shear stress ranging from 0.1-1 Pa.

RESULTS AND DISCUSSION

First, the results of the permittivity and viscosity measurements are shown. Next, the influence of surfactant, IS and pH on the ZP is discussed.

Permittivity

The static permittivity of the samples ϵ_s is required to calculate the ZP from electrophoretic mobility data. First, we measure the complex permittivity of a sample over a wide frequency range.

The static permittivity is then extrapolated based on a simplified Havriliak-Negami model of the complex permittivity,³⁹⁻⁴⁰ which can be expressed by the Cole-Cole equation according to

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + (j\omega\tau)^{\alpha}} - j \frac{\sigma(\omega)}{\varepsilon_0 \omega} \quad (2)$$

Here, $\varepsilon(\omega)$ is the complex permittivity at the angular frequency ω ; ε_{∞} and ε_s are the permittivity limits at high and low frequencies, respectively; τ is the characteristic relaxation time; $\sigma(\omega)$ is the ionic conductivity at ω ; ε_0 is the free space permittivity; j is the imaginary unit; and α is the shape parameter of the relaxation peak. This model takes into account the effects of the lossy medium for which the capacitive and resistive components are not ideal and the conductivity depends on the frequency. We take advantage of the fact that an analog of equation (2) could also be used to describe an electrical harmonic oscillator. Hence, we utilize the Multiple Electrical Impedance Spectroscopy Parameterization (MEISP) 3.0 software from Kumho Chemical Laboratories, which is a free complex nonlinear least squares program for fitting, simulation, and inversion of frequency and time domain data sets, to compute the static sample permittivity. In detail, equation (2) has the same mathematical form as an equivalent electric circuit $R_s(R_p Q_p)C_s$ consisting of an ohmic resistor R_s in series with a parallel arrangement of an ohmic resistor R_p and a constant phase element Q_p which are in series with a capacitor C_s as depicted in Figure 1. Therefore, $\varepsilon(\omega)$ represents the equivalent impedance $Z(\omega)$ of the circuit, R_s corresponds to ε_{∞} , R_p represents the term $\varepsilon_s - \varepsilon_{\infty}$, $(R_p Q_p)^{1/n}$ corresponds to τ , n is an equivalent of α , and C_s is a representation of $\varepsilon_0/\sigma(\omega)$.

Figure 1 shows the measured absolute permittivity of four representative samples along with the results of the respective nonlinear regression using the MEISP software. For the DI water sample, the permittivity remains constant in the lower frequency range. However, for samples containing surfactants the electrode polarization effect results in a considerable deviation in the same range of frequencies. This effect is considered in the model by the conductivity containing term. Overall,

it is shown that we are able to get high quality regressions to extract accurate static sample permittivities.

Figure 1. Absolute permittivity vs frequency of four representative samples. Symbols depict measured values while lines represent the results of the nonlinear regression.

The computed static permittivity for samples with different concentrations of SDS, CTAB, and TDAPS are shown in Figure 2. We find that surfactant concentrations below 10 mM merely affect the static permittivity. At higher surfactant concentrations, the static permittivity can considerably decrease with increasing concentration. For example, a 100 mM aqueous SDS sample has around

a 10% lower permittivity compared to DI water. The effect of adding NaCl to the sample on the permittivity values is also investigated. Here, we perform comparable permittivity measurements and data regressions for each of the investigated surfactant sample with a NaCl content of 30, 50, or 100 mM (data not shown but considered for the calculation of the ZP). Generally, for the maximum NaCl concentration used in this work, the decrease in permittivity is less than 2%. The effect of the buffer on the permittivity is neglected due to its small concentration. Nevertheless, our results demonstrate that neglecting the influence of surfactants on the permittivity can result in a considerable error.

Figure 2. Computed static permittivity vs the surfactant concentration for three surfactants. Standard deviations are smaller than the size of the symbols. Lines are guides to the eye.

Viscosity

From our previous study,³⁵ we know that adding NaCl up to 100 mM does not significantly affect the sample viscosity. Hence, we only investigate the influence of the surfactant on the viscosity; results are shown in Figure 3. We find that the viscosity remains almost constant up to a surfactant concentration of around 1 mM. For higher concentrations than that, the viscosity increases with increasing surfactant concentration. For the highest surfactant concentrations studied in the electrophoresis experiments, the SDS, CTAB, and TDAPS sample viscosities compared to DI water increase for 38%, 12%, and 17%, respectively. The results clarify that using the viscosity of pure water to calculate the ZP can result in a considerable error.

Figure 3. Viscosity of the samples vs surfactants concentration for the different surfactants. Lines are guides to the eye.

Zeta Potential

We present zeta potential results for different concentrations of surfactants dispersed in aqueous electrolytes of 4 different pH and various IS values. In total, about 2000 electrophoretic mobility measurements are conducted. For each parameter, selected data sets are discussed that represent general trends. Remaining data is provided in the Supplementary Information to this article.

A. Influence of Anionic Surfactant Concentration

Figure 4 shows the ZP vs the SDS concentration for samples with a pH of 9 and for different IS values. Generally, we observe curves with the same trend. At zero surfactant concentrations, the ZP is negative. At very low SDS concentrations of around 10^{-5} M, there is hardly any impact on the ZP. However, for concentrations higher than that, the SDS addition results in an increase of the absolute ZP.

Figure 4. Zeta potential of PMMA vs SDS concentration for various ionic strengths at pH 9.

Figure 5. The adsorption mechanism of SDS molecules on PMMA at different surfactant concentrations: a) below CMC, b) around CMC, and c) above CMC. d) Schematic of the electrical potential distribution as a function of the distance from the surface for cases a) – c).

When we inspect Figure 4 in more detail, we can divide the general behavior into two different regions that are roughly separated by the CMC. Each of the two regions starts with a plateau followed by an increase of the absolute ZP as the concentration further increases. In the following, we identify mechanisms that can explain the observed ZP for the different surfactant concentration ranges; these proposed mechanisms are schematically depicted in Figure 5.

At very low SDS concentrations of around 10^{-5} M, the ZP is hardly affected by adding surfactant. Similar behavior was reported by Kayes for electrophoretic mobility measurements of hydrophobic, negatively-charged polystyrene particles at very low SDS concentrations. The author

claimed that ionic species in the Stern layer are exchanged with the surfactant molecules which results in an unaltered ZP.⁴¹ In terms of PMMA, there is no adsorption of simple electrolytes, such as NaCl, but there is indirect evidence that hydroxide ions adsorb in an alkaline milieu.³⁵ However, our results show that the ZP difference of a neutral to a mildly alkaline sample at pH 9, is more or less within the standard deviation of the experiments. Hence, we cannot support the hypothesis of a Stern layer molecule exchange in case of PMMA and just conclude that very low SDS concentrations have no noticeable impact on the ZP.

At SDS concentrations higher than around 10^{-5} M up to the CMC, the absolute ZP considerably increases with increasing concentration. The increase is even higher when we consider that still very few surfactant is added; the specific ZP change is on the order of magnitude of 10,000 mV/mol for all given IS. Generally, the alkyl chain side of an SDS molecule has the affinity to adsorb on negatively-charged hydrophobic surfaces such as polystyrene,⁴¹⁻⁴² polycarbonate,⁴³ as well as PMMA.^{14, 44-45} The physiochemical explanation of the ZP change in the presence of a sufficient amount of SDS, but below the CMC, can therefore be linked to the surfactant adsorption. In detail, the negatively-charged polar head of the adsorbed molecule increases the negative charge density and therefore the absolute ZP. The negative net charges of SDS molecule and PMMA surface result in a repulsive electrostatic interaction. Hence, the SDS adsorption is rather related to the van der Waals and/or the hydrophobic interaction between the hydrophobic surfactant tail and the hydrophobic PMMA surface. There are two possible configurations of such adsorbed SDS molecules: i) A vertical adsorption where the hydrophilic head faces the bulk; and ii) A lateral adsorption that is only possible if the hydrophobic interactions are strong enough to overcome the

electrostatic repulsion. The respective adsorption mechanism along with the two feasible molecular orientations are depicted in Figure 5a.

Within the range near CMC up to around 0.02 M, the ZP remains more or less constant. For higher concentrations than that, we find again a range where the absolute ZP increases. The specific ZP change is on the order of magnitude of 100 mV/mol, much less than in the range below the CMC. We explain the plateau as follows: At the CMC, two processes involving the surfactant occur; i.e., the adsorption and the formation of micelles. Note that micellization is a bulk while adsorption is an interface phenomenon and they may be considered as independent of each other.⁴⁶ Based on the correlations provided in Ref.⁴¹, we estimate the Gibbs energy change of SDS adsorption below and above the CMC to be -17 and -9 kJ/mol, respectively. Likewise, we can calculate the Gibbs energy change of micellization according to

$$\Delta G_{mic} = RT \ln \left(\frac{CMC}{mol/L} \right), \quad (4)$$

where R is the universal gas constant and T is the temperature.³⁰ For a CMC range of 1 to 8 mM (cf. Supporting Information), the Gibbs energy change of adsorption ranges from -17 to -12 kJ/mol. Evidently, adsorption and micellization processes around the CMC have very similar Gibbs energy changes and compete with each other. Consequently, when micellization occurs less surfactant is available for adsorption and the ZP remains almost constant even if more surfactant is added. The corresponding mechanism is depicted in Figure 5b.

As the micelle concentration increases with further increase of the surfactant concentration, the magnitude of the Gibbs energy change of micellization decreases.⁴⁷ Consequently, in the concentration range well above the CMC, adsorption is preferred over micellization which triggers a further increase of the absolute ZP. Nevertheless, if the amount of surfactant molecules is sufficient, they should participate in both processes. The increase in ZP also implies that around the CMC, not all adsorption sites on the PMMA surface are occupied. Hence, it is likely that the adsorbed surfactant molecules solely arrange in the vertical orientation. This conclusion is based on the work of Brown and Zhao who observed that for SDS adsorption on polystyrene, the particle size increased by approximately the surfactant size.⁴² Since polystyrene is also hydrophobic and negatively-charged, we assume a comparable behavior for PMMA. The corresponding mechanisms for concentrations well above the CMC are depicted in Figure 5c. A schematic of the potential distribution within the EDL for each concentration range is given in figure 5d. Here and for all following potential distributions, we made the simplification that the adsorbed surfactant layer always has the same thickness. Generally, the absolute value of the electrical potential linearly increases due to surfactant adsorption from the surface potential to the ZP located at the shear plane. Within the diffuse layer part of the EDL, the potential exponentially decreases to the bulk potential. This figure shows that increasing adsorption of SDS (case a to c) can increase the ZP while the surface potential remains constant.

B. Influence of Cationic Surfactant Concentration

Results for samples with CTAB concentrations ranging from 1 μ M to 27 mM for pH 9 and an IS of 3, 30, and 100 mM are shown in Figure 6. Likewise to the SDS adsorption, we again see similar

trends for all IS values. Generally, we distinguish between two regions. Below the CMC, any cationic surfactant addition increases the initially negative ZP. The correlation between ZP and the logarithm of the surfactant concentration up to the CMC appears linear. The respective slope is on the order of magnitude of 10^6 mV/mol. In this linear regime, we find an isoelectric point (IEP), where $ZP = 0$ mV, at around 10^{-6} - 10^{-5} M. This range is well below the CMC and agrees with the observation of electroosmotic flow reversal in a PMMA chip in the presence of CTAB.^{14, 45} Further surfactant addition increases the (positive) ZPs until a plateau-like region at concentrations around and well above the CMC is observed. These results demonstrate that a defined tuning of the PMMA ZP is possible by CTAB addition.

Figure 6. Zeta potential of PMMA particles vs the CTAB concentration for various ionic strengths at pH 9.

Figure 7. The adsorption mechanism of CTAB molecules on PMMA at different surfactant concentrations: a) below IEP, b) at IEP and below CMC, c) around and above CMC. d) Schematic of the electrical potential distribution as a function of the distance from the surface for cases a–c.

We assign the trends seen in Figure 6 to different mechanisms. First, for concentrations ranging from the lowest ZP (no surfactant) to the IEP (well below CMC): The electrostatic interaction between the cationic surfactant and the negatively-charged surface is attractive. Hydrophobic interaction between surfactant tail and surface can be present as well. Therefore, we assume that both vertical and lateral orientations of CTAB molecules on the surface are possible, cf. Figure 7a. This assumption is supported by the work of Bisio et al. who investigated the molecular orientation of adsorbed (cationic) DTAB (dodecyltrimethylammonium bromide) surfactant on a hydrophobic polycarbonate membrane.⁴⁸ At very low concentrations, similar to the one considered here, they did not find a change in hydraulic membrane resistance (pore size) as a result of the surfactant adsorption. However, as the DTAB concentration increased, the resistance (thickness of the

adsorbed layer in the pores) noticeably increased as well.⁴⁸ Based on the analogy between the cationic surfactant and the hydrophobic polymeric surface of the present study and their work, we conclude that at higher concentrations the vertical orientation of the CTAB molecules is more likely to occur. At the IEP, the initial negative surface charge is completely neutralized by a layer of counter-charged surfactants as sketched in Figure 7b.

The second mechanism is proposed for concentrations ranging from the IEP to the ZP plateau present around the CMC. Here, the surface charges are still neutralized by the formerly-adsorbed surfactant layer. Nevertheless, lateral hydrophobic interactions between the surfactant tails lead to further CTAB adsorption in form of a surfactant bilayer which explains the increase in ZP, cf. Figure 7c. Such a bilayer formation was also proposed by Bisio et al. for DTAB adsorption on polycarbonate in a comparable concentration range.⁴⁸ The third mechanism occurs above the CMC where the ZP remains more or less constant. We assume that all adsorption-related processes are saturated and further surfactant addition is consumed by micellization.

A sketch of the interface potential distributions for the different concentration range is depicted in Figure 7d. The initial adsorption of CTAB on the negatively-charged PMMA results in a less negative ZP. Case b demonstrates the IP where the potential drops from surface potential to zero at the shear plane since the entire surface charge is neutralized by a surfactant layer. The curve c represents the third concentration range where the ZP changes sign due to formation of the bilayer.

C. Influence of Zwitterionic Surfactant Concentration

Figure 8 shows the ZP over the TDAPS concentration at pH 9 and for three different IS values. Again, we observe that, for a given IS, all ZP vs surfactant concentration correlations share a similar trend. The addition of a very small amount of 10^{-5} M TDAPS, considering the standard deviations of the experiment, has a very weak influence. It seems that the absolute ZP somewhat increases. If more surfactant is added, the absolute ZP gradually starts to decrease. Well above the CMC, the ZP remains more or less constant independent of further concentration increases. Compared to the ionic surfactants, the impact of this zwitterionic surfactant is generally low which is related to the lack of net charge.

A literature review on the interaction of zwitterionic surfactants with (hydrophobic) surfaces shows that adsorption takes place in different ways. Grant and Ducker investigated the aggregate formation of DDAPS (3-(N,N-dimethylaurylammonio)propanesulphonate) on hydrophilic (silicon nitride and silica) as well as on hydrophobic (graphite) surfaces.⁴⁹ They proposed that on hydrophobic surfaces a monolayer or low curvature structure aggregates (hemi-cylinder) is formed, compared to spherical aggregates in case of a hydrophilic surface. The reason for this is that the relatively-high free energy of the hydrophobic interface decreases when the surfactant tail adsorbs with the hydrophilic head directed towards the liquid bulk. Hence, this preferred molecule orientation along with lateral hydrophobic interactions between surfactant tails can trigger the formation of a monolayer or hemi-cylinder aggregates on the surface. Similar behavior is proposed by others for TDAPS¹⁶ and DDAPS⁵⁰⁻⁵¹ in contact with hydrophobic surfaces other than PMMA.

Since we deal with a zwitterionic surfactant and a hydrophobic surface as well, we assume that the adsorption of TDAPS on PMMA takes place in a similar fashion as discussed above. Hence, at very low concentrations ($< 10^{-5}$ M), surfactant molecules adsorb due to hydrophobic interactions of surface and tail as sketched in Figure 9a. In this case, the very small increase of the absolute ZP probably results from the exposure of the anionic part of the surfactant head towards the bulk liquid while the influence of the cationic part is diminished by the much large number of negative surface charges.

As the concentration increases, the observed decrease of the absolute ZP is still related to the surfactant adsorption due to the lateral hydrophobic interaction. However, when the density of adsorbed molecules is high, the hydrophobic tail-tail attraction of neighboring molecules is getting more important which triggers surface aggregate formation. Here, we propose that due to the hydrophobicity of PMMA, the most feasible aggregate configuration is a low curvature structure. That is, monolayer and hemi-cylinder for low and high surface densities, respectively. A semi-spherical structure of the surface aggregates is rather unlikely due to the lack of affinity of the hydrophobic surface and the hydrophilic surfactant head.

A sketch indicating surfactant adsorption and surface aggregate formation is shown in Figure 9b. Here, the decrease in ZP can be related to two different effects. The presence of the many cationic surfactant heads in a surface aggregate shield the fewer number of PMMA surface charges beneath while still neutralizing the anionic part of the head. Another influence is the decrease of the permittivity in the adsorbed layer, cf. Figure 2, which increases the potential drop. Therefore, the overall effect is that the absolute ZP decreases with increasing surfactant concentration.

When the surfactant concentration reaches and exceeds the CMC, the micellization consumes surfactant which is not available for adsorption anymore resulting in the plateau-like ZP behavior, cf. Figure 9c.

Figure 9d represents the potential distribution in the EDL at different concentrations of the TDAPS according to Figures 10a-c. At very low concentrations (case a), the absolute potential, starting from surface potential, increases to a higher value at the shear plane and then gradually decreases over the diffuse layer. In case b, the potential remains more or less constant over the adsorbed layer. Case c represents the formation of aggregates that causes the potential drop over the adsorbed surfactant layer.

Figure 8. Zeta potential of PMMA particles vs the TDAPS concentration for various ionic strengths at pH 9.

Figure 9. The adsorption mechanism of TDAPS molecules on a PMMA surface at different surfactant concentrations: a) below CMC at very low concentrations, b) below CMC at higher concentrations, c) around CMC. d) Schematic of the potential distribution as a function of the distance from the surface for cases a – c.

D. Influence of pH

To demonstrate the influence of the pH value, we present selected measurements in acidic and alkaline milieu which represents the general trends that we observe.

To obtain a better insight, it is common to plot the ZP scaled with the negative logarithm of the ionic strength over the pH value. If the counter-ion adsorption does not play an important role, all ZP vs pH values collapse to a single curve as can be seen for various examples, cf. refs. ^{5, 35, 52}.

This theory is supported by our current experiments in an inverted form. All our attempts to normalize the ZP data are mainly not successful but for samples with very low surfactant concentrations where adsorption has practically no impact.

Figure 10 shows the ZP vs the concentration of cationic, anionic and zwitterionic surfactant at $IS = 30 \text{ mM}$ and for pH 5 and 11. We find that for a given surfactant species and concentration, the ZP in the alkaline milieu is always lower than in the acidic one. This effect can probably be attributed to the increased presence of adsorbed hydroxide ions on the PMMA surface at higher pH values.³⁵ We also assume that the resulting higher negative charge density impacts the electrostatic interaction between surfactant and surface and increases the CTAB adsorption and decreases the SDS adsorption. However, this question cannot be definitively answered in the current study.

Figure 10. Zeta potential vs different surfactant content in acidic and alkaline milieu and an ionic strength of 30 mM. Lines are guide to the eyes.

E. Influence of Ionic Strength

To demonstrate the effect of the electrolyte's ionic strength on the ZP values, we show selected concentrations of each surfactant (below and above CMC) at pH 9 in Figure 11. As a general trend for all three surfactants, as well as for the case of no surfactant, we observe that the absolute ZP decreases with an increase of the IS. Furthermore, we can see that the correlation between ZP and the logarithm of the IS, at a given surfactant concentration, is linear to good approximation.

Figure 11. Zeta potential vs ionic strength for different surfactant contents. Lines are linear regressions of zeta potential and $\log(I)$.

Generally, the change in counter-ion concentration affects the Debye length of the EDL resulting in a direct change in ZP due to shielding. In detail, when the Debye-Hückel approximation can be

applied ($|\zeta| < 25.7$ mV for a dilute aqueous solution and 1:1 electrolyte), the change of the absolute ZP is proportional to $1/\sqrt{I}$. However, when Debye-Hückel approximation is not an adequate assumption, the proportionality is typically according to $\zeta \propto \log(I)$.⁵² We recover the latter proportionality, to good approximation, as can be seen by the regression lines of our data in Figure 11.

In addition, in case of ionic surfactant adsorption, higher electrolyte concentrations lower the electrostatic interactions between adsorbent and adsorbate.⁴⁷ This can affect the cationic and anionic surfactant adsorption in different ways. On the one hand, it facilitates the adsorption of the anionic surfactant on the PMMA due to a diminished repulsive electrostatic interaction. On the other hand, it impedes the adsorption of cationic surfactant by decreasing the attractive electrostatic interaction. When we take a closer look at the SDS concentration range of 10^{-5} - 10^{-3} M in Figure 4, this statement is supported. Here, the change in ZP per surfactant concentration for an IS of 3, 30, and 100 mM is roughly -10, -20, and -30 V/mol, respectively. The increase of the absolute change in ZP per surfactant concentration with increasing IS indicates a compensation of the repulsive electrostatic interaction which facilitates the SDS adsorption on PMMA. Similar behavior is observed in Figure 6. In a concentration range of 10^{-6} - 10^{-5} M, the change in ZP per CTAB concentration for an IS of 3, 30, and 100 mM is around 6000, 4000, and 3000 V/mol, respectively. This reduction in ZP change per surfactant concentration indicates a diminished attractive interaction at higher IS values.

Nevertheless, for the range of IS studied in this work - i.e., up to 100 mM - we still conclude that shielding is the dominant mechanism. This conclusion is based on the linear correlation of the ZP and the $\log(I)$ that we recover for all samples. However, sole ZP measurements do not provide

enough insights to quantify the individual effects of shielding and change in adsorption mechanisms.

SUMMARY

In this article, the zeta potential of PMMA in the presence of an anionic, a cationic, and a zwitterionic surfactant is reported. The ZP values are inferred from electrophoretic mobility measurements along with measurements of the permittivity and the viscosity of the medium. We find that the surfactant addition can have a considerable influence on the viscosity and the permittivity which is mainly neglected in the respective literature.

The results of the electrophoretic measurements clarify the effects of different concentrations of each surfactant, ionic strength and pH of the aqueous electrolyte on the ZP. Respective adsorption mechanisms are proposed that explain the relation of ZP and surfactant for different concentration ranges.

In the presence of the anionic SDS surfactant, the negative ZP of the PMMA becomes more negative. This is probably due to the adsorption in form a monolayer that is triggered by hydrophobic interactions between the surface and the surfactant tail. In case of the cationic CTAB surfactant, we observe an isoelectric point where the ZP changes from negative to positive values. This indicates that a combination of electrostatic and lateral hydrophobic effects most likely results in formation of an adsorbed surfactant bilayer. In comparison, we generally observe less impact of the zwitterionic TDAPS surfactant on the ZP values which is related to the lack of net electrical charge. Hence, TDAPS adsorption likely occurs by hydrophobic interactions between surfactant tail and surface as well as by lateral hydrophobic interactions among the molecule tails.

Our results show that the ZP decreases at higher pH which should be related to the adsorption of hydroxide ions on the surface. Furthermore, studying the effect of IS indicates that the ZP changes are mainly related to the shielding effect of the EDL.

Finally, the current work provides reliable values for the zeta potential of PMMA in the presence of three common surfactants. The results can be applied for various process design in microfluidic chips made of PMMA or, in a broader context, made from a hydrophobic polymer. In future work, the combined effects of mixtures of different surfactants could be studied.

ASSOCIATED CONTENT

Supporting Information. The molecular structure and properties of surfactants as well as the zeta potential results of PMMA in the presence of SDS, CTAB and TDAPS at pH 5, 7, 9 and 11 for different ionic strength of the medium.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support from DuPont Canada and the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Prof. Brian Amsden for the use of the rheometer.

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Table of Contents Graphics