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Effect of pH on adsorption and desorption of hexadecyl trimethyl ammonium bromide from silicate surface

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Abstract: Hexadecyl trimethyl ammonium bromide (HTAB), a cationic surfactant, is physically adsorbed on negatively charged silicate surfaces due to electrostatic forces. This reversible adsorption process is important for surfactant regeneration in some industrial applications such as waste water treatment. Cationic surfactant adsorption and desorption from silica surfaces were studied using several methods such as UV, FTIR, XPS, and XRD. However, most of these methods are time independent and ex situ in nature. Quartz crystal microbalance with dissipation monitoring (QCM-D) is a power tool that can determine the amount and thickness of the deposited material on the surface in situ as a function of time. In this study, the adsorption and desorption characteristic of HTAB was studied on the silica sensor surface by using QCM-D. The adsorption and desorption tests were performed at a constant HTAB concentration ($5 \cdot 10^{-4}$ M, close to CMC of HTAB) at different pH values (3, 5.5, 6.5 and 10). The results obtained from these studies clearly showed that pH is a critical factor determining the adsorption and desorption processes.

Keywords: adsorption, silica sensor, hexadecyl trimethyl ammonium bromide, quartz crystal microbalance with dissipation monitoring

Introduction

Based on needs for living of growing number of people in a remarkable ratio, the world is experiencing a rapid increase in industrial activities, resulting in deleterious impacts on the environment such as pollutions of soil and air. In near future draughts of drinking water are expected due to increasing water pollution. Therefore, researches related to cleaning waste water and its recycle as drinking water are gaining great momentum.

Waste water discharged from industrial activities contains cationic and anionic ions, oils and organics that could disrupt ecosystems and damage the environment. In order to remove pollutants from waste streams or reduce polluting activities, biological

oxidation, adsorption, flotation, chemical coagulation, UV photodecomposition and electrochemical processes are suggested (Bajpai and Rajpoot, 1999; Lakherwal, 2014). Some of these techniques are quite costly, while others may be evaluated as more economic and applicable. Various studies on utilization of natural minerals as adsorbents are reported to be less expensive than other methods (Ismadji et al., 2015; Novikova and Belchinskaya, 2016).

Silicate minerals such as zeolites have unique natural features such as high cation exchange capacity, porosity, negative surface charge etc. that allow them to adsorb cations (heavy metals, ammonia, and others) effectively, while ineffective in adsorbing anions (Ozdemir et al., 2004; Yapar and Yilmaz, 2004; Indra et al., 2006; Bhattacharyya and Gupta, 2008; Bello et al., 2013; Zhu et al., 2016). For silicate minerals, surface modification with cationic reagents is becoming an important research subject lately. Wang and Peng (2010) published a review on the use of zeolites as an adsorbent in waste water treatment. Cationic reagents such as tetramethyl ammonium, cetyltrimethyl ammonium (CTMA), hexadecyl trimethyl ammonium (HDTMA), octadecyl dimethyl benzyl ammonium (ODMBA), n-cetyl pyridinium (CPD), benzyl tetradecyl ammonium (BDTDA), stearyl dimethyl benzyl ammonium (SDBAC) and etc. have been used for surface modification in various studies. Atkin et al. (2012) reviewed the mechanism of cationic surfactant adsorption at the solid–aqueous interface. In addition to zeolite, other clay minerals such as montmorillonite and sepiolite are modified with cationic chemicals so that they could be used in waste water treatment (Sabah et al., 2002; Karatas et al., 2013; Yesilyurt et al., 2014). It is a well-known that modified minerals used for waste water treatment in industrial applications usually require regeneration of a spent adsorbent. Although adsorption mechanisms have been studied extensively, there is only a limited level of studying desorption phenomena.

Cationic surfactant adsorption onto mineral surfaces has been studied by the titration methods and UV-Visible spectrophotometer (UV) analysis of a clear supernatant obtained after solid-liquid separation at the end of adsorption, while X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and X-Ray Diffraction (XRD) analyses have been applied to the dried adsorbent material (Ruthland and Parker, 1994; Horr et al., 1995; Churaev et al., 2000; Chernyshova et al., 2000; Zdziennicka et al., 2009; Kou et al., 2010). As a result, most of these measurement methods are time independent and ex situ in nature. Quartz crystal microbalance with dissipation monitoring (QCM-D) can determine in situ the amount and thickness of the deposited material from the surface as a function of time. There are only few studies about cationic surfactant adsorption on the sensor that mimics a mineral surface in QCM-D. Kou et al. (2010) investigated adsorption characteristics of dodecylamine hydrochloride (DAH) on the quartz surface using QCM-D. In another study, Kou and Xu (2016) investigated the adsorption behavior and kinetics of the zinc sulfide (ZnS) coated quartz crystal sensor by QCM-D. In this

study, adsorption as well as desorption of HTAB on the SiO₂ sensor surfaces was studied by using the QCM-D method.

Materials and methods

Materials

A quaternary amine, hexadecyl trimethyl ammonium bromide (HTAB, C₁₉H₄₂BrN) purchased from Sigma Aldrich and specified to be of 99% purity with a molecular weight of 346.46 g/mol, was used for the QCM-D experiments. The surfactant stock solutions at different concentrations between 1·10⁻⁴ and 1·10⁻² mol/dm³ were prepared in Milli-Q water. The acid (HCl) and base (NaOH) obtained from Fluka were used for pH adjustment.

The quartz samples of high purity used in electrokinetic (zeta) potential experiments were obtained from the Aydin-Cine region of Turkey. The SiO₂ content in the samples was around 97%.

Methods

The quartz coated sensor (QSX-302) used in the QCM-D analysis was an AT cut quartz disc (14 mm in diameter and 0.3 mm in thickness with an active sensor crystal area of 0.2 cm²) with 5 nm Cr, 100 nm Au, 50 nm Ti, and 50 nm SiO₂, sputter-coated onto the crystal surface successively. The sensors and Q-sense E4 system were supplied by Q-Sense Co-Goteborg (Sweden).

Prior to their use in the QCM-D tests, the SiO₂ sensors were soaked in the sodium dodecyl sulfate SDS solution (2 wt%) for 15 min and sonicated in Milli-Q water and ultra-pure Milli-Q water for 15 min, each followed with 15 min UV-ozone treatment. The sensors were dried in a flow of nitrogen gas. The flow modules and tubings were cleaned with the 2% Hellmanex II solution (an alkaline cleaning liquid from Hellma GmbH & Co. KG, Germany). All cleaning procedures were applied as recommended by Q-Sence Company.

Adsorption measurements were performed with HTAB at varying concentrations and pH by QCM-D at 23±0.5 °C. The solutions were pumped through the QCM-D using a peristaltic pump at a constant flow rate of 0.150 cm³/min. For each experiment, the data were produced with rinse when it became stable with the baseline solution (Milli-Q water).

In this study, thickness of the adsorption layer was calculated from the Saubrey equation based on the change in mass (Δm) on the crystal surface (Saubrey, 1959):

$$\Delta m = -\frac{\rho_q t_q \Delta f}{f_0 n} = -\frac{\rho_q v_q \Delta f}{2 f_0^2 n} = -\frac{c \Delta f}{n} \quad (1)$$

where C is the mass sensitivity constant equal to $17.7 \text{ ng cm}^{-2} \text{ Hz}^{-1}$ with $F = 5 \text{ MHz}$, n is the overtone ($n = 3, 5, 7$ or 9) of the resonance frequency of the applied voltage across the electrodes.

The zeta potential was measured using a Nano ZS instrument (Malvern Inst). The solution used in the measurements was prepared by placing 0.1 g of particles into a 100 cm^3 beaker under the magnetic stirrer for 10 min. The prepared solution was kept for 2 min after mixing. The aliquot (2 cm^3) was taken from the top section of the suspension for zeta potential measurements by placing such suspension into the Nano ZS measurement cell.

Results and discussion

In order to represent modification of natural silicate minerals with HTAB, the time-dependent adsorption was measured using the QCM-D set up. The frequency change Δf obtained from the experiments performed at different HTAB concentrations around natural pH (pH 6.5) is shown in Fig. 1. Figure 1 also shows the real-time experimental data of the frequency change of the third overtone, i.e., Δf_3 . Figure 1 shows a decrease in Δf_3 values with increasing the HTAB concentration at natural pH, indicating increased adsorption of HTAB on the silica sensor surface. There are many proposed models to explain the surfactant adsorption mechanism on mineral surfaces by using contact angle, zeta potential measurements, surface force and thickness of adsorption layer calculation techniques (Rutland and Parker, 1994; Horr et al, 1995; Ersoy and Celik, 2003; Zdzennicka et al., 2009; Karakas and Vaziri Hassas, 2016). Generally, monolayer and bilayer models are proposed for adsorption of the surfactants onto the mineral surfaces (Churaev et al., 2000). However, the idea of individual, hemi-micelle and admicelle- micelle forms are developed for increasing surfactant concentration (Rutland and Parker, 1994). Rutland and Parker (1994) indicated that bilayer formation occurred at the critical micelle concentration (CMC) ($1 \cdot 10^{-3} \text{ mol/dm}^3$ CTAB) for low pH, and below the CMC at increased values of pH. Dermott et al. (1994) indicated that the bilayer form occurred when the thickness of layer was 3.4 nm for HTAB adsorption on the quartz surface using the neutron reflection technique. In this study, the thickness of adsorbed HTAB layers calculated by the Sauerbrey equation was determined to be 0.8, 2.3, and 3.0 nm for HTAB concentration of $2.5 \cdot 10^{-4}$, $5 \cdot 10^{-4}$, and $1 \cdot 10^{-3} \text{ mol/dm}^3$, respectively. It is estimated that the adsorption forms are individual hemi-micelle and admicelle in the increasing reactive concentration using the QCM-D data of the present study and calculated layer thickness. Also, under these conditions, it is possible to occur bilayer formation of surfactant on the sensor as already shown in literature (Karakas and Vaziri Hassas, 2016).

The complete desorption of HTAB by rinsing occurred rapidly at HTAB concentrations under CMC ($0.92\text{--}1 \text{ mmol/dm}^3$), whilst only a partial desorption was achieved when HTAB adsorbed at concentrations above its CMC. The organic materials partially migration from the sensor surface is described in Fig. 1 right after

1200 sec of the experiment. There is a decelerated surfactant movement from the surface with the increased loading concentration. However, even at the highest loading rates, the rinsing water will eventually clear the sensor, and it will be obviously present if the experiment period increased over 1600 sec. It is understood from the QCM-D frequency data that the adsorption intensity increases with the increase in HTAB concentration due to electrostatic and strong chain-chain interactions on the sensor surface. It can be concluded that HTAB adsorption on the silica sensor is fully reversible, thus compile one of the conditions of physical adsorption, and there is a probability of hydrogen bonding, which was coped by the drag force of rinsing water with the organic structures formed at concentrations over CMC (Atkin et al., 2003). Figure 2 shows reactive adsorption and rinse results for the various pH and $5 \cdot 10^{-4}$ mol/dm³ HTAB concentration using the frequency.

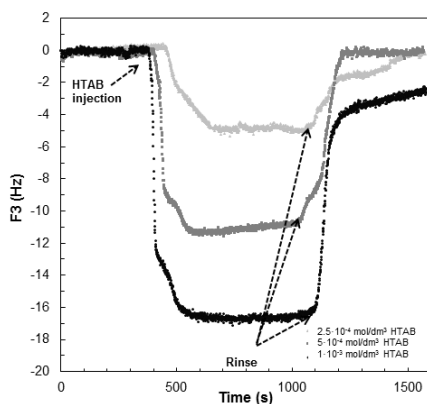


Fig. 1. Displays the real-time experimental data of the frequency Δf_3 from the third overtone associated with HTAB adsorption onto quartz surface for different HTAB concentrations at natural pH (6.5)

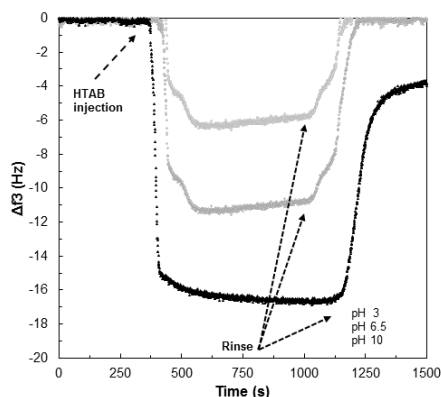


Fig. 2. Real-time experimental data of frequency shifts for different pH (3, 5.5, and 10) at constant HTAB amount ($5 \cdot 10^{-4}$ mol/dm³)

For a given HTAB concentration of $5 \cdot 10^{-4}$ mol/dm³, the results in Fig. 2 show a more rapid and stronger adsorption of HTAB at higher pH than at lower pH. In order to reveal the true desorption phenomena (without the interference of hydrogen ion concentration effect etc.) of surfactant rinsing water was prepared at the same pH conditions as the feed solution. As a result, only partial desorption of HTAB was observed at high pH than lower pH. Considering electrostatic attraction being the driving force for HTAB adsorption on silica surfaces, this observed adsorption characteristics of HTAB at different pH can be better explained if we know the surface charge of silica. As shown in Fig. 3, the silica is negatively charged at pH above 3, becoming more negative at higher pH. The results obtained in Fig 3 can be verified with literature findings such as Alves Junior and Baldo (2014). Figure 3 also includes the results of Alves Junior and Baldo (2014) on the zeta potential of different quartz and silica particles. With cationic nature of HTAB over the pH range studied, it is not surprising that HTAB adsorbed more strongly on the silica surface at pH 10 than pH 3 and 5. In fact, the amount of HTAB from $5 \cdot 10^{-4}$ mol/dm³ solution at pH 10 is the same as the amount of HTAB adsorbed from $1 \cdot 10^{-3}$ mol/dm³ HTAB solution at its natural pH of 6.

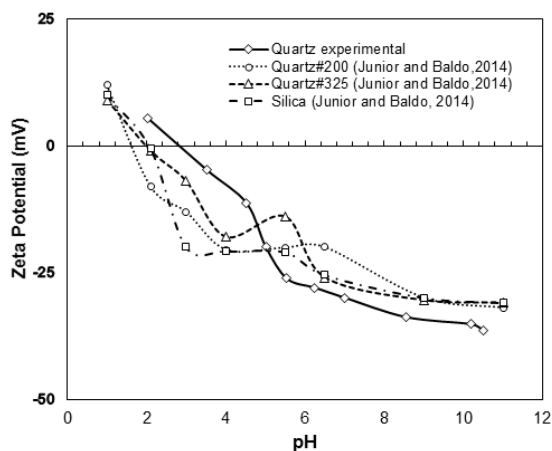


Fig 3. Zeta potential of quartz with compare Junior and Baldo 2014 for variation pH

Conclusions

The experimental results showed an increased amount of cationic HTAB adsorbed on negatively charged silica surfaces with increasing HTAB concentration. Although a complete desorption of HTAB adsorbed from the solutions of HTAB concentrations below its CMC, only a partial desorption of HTAB could be achieved when HTAB was adsorbed from solutions at the concentrations higher than its CMC.

Due to electrostatic attraction as the driving force for HTAB adsorption on silica, the amount of HTAB adsorbed increased with the increasing solution pH, mainly due to increasing negative charge of silica with increasing suspension pH.

Desorption of HTAB was highly influenced by pH of washing/rinsing solutions, more favorable at lower pH than high pH.

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