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ADSORPTION MECHANISM OF SODIUM OLEATE ON TITANIUM DIOXIDE COATED SENSOR SURFACE USING QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION

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Abstract: Quartz Crystal Microbalance with Dissipation (QCM-D) was firstly applied to investigate the adsorption mechanism of sodium oleate on TiO_2 coated sensor surface. The effects of pH value, sodium oleate concentration, and temperature on TiO_2 coated sensor surface were evaluated systematically using the QCM-D technique. Zeta potential, surface tension, adsorption isotherms, and adsorption thermodynamics were employed to characterize the adsorption process. The results showed the advantages of QCM-D on the investigation of the adsorption process. Additionally, the electrostatic equilibrium adsorption data was well matched to the Langmuir isotherm. Based on the thermodynamic analysis, adsorption was a spontaneous and endothermic physisorption process.

Keywords: *QCM-D, TiO_2 coated sensor surface, sodium oleate, adsorption mechanism*

Introduction

Titanium is an important raw material for space industry, nautical engineering, and medicine (Li et al., 2006; Omidvar et al., 2012; Parker and Stec, 2012). Flotation, as an efficient physicochemical technique, is widely used in rutile and ilmenite upgrading (Hacifazlioglu and Sutcu, 2007; Santana et al., 2012). In flotation systems, adsorption mechanism between titanium minerals and collectors is the key for flotation (Fan and Rowson, 2000; 2002). Evaluation of adsorption behavior is essential and helpful for developing efficient collectors, thereby to understand the adsorption mechanism well (Kou et al., 2010). Generally, sodium oleate is used as a collector for flotation of ilmenite (Fan et al., 2014), talc (Yakovleva and Chyong, 2013), fluorite, and hematite (Chanturia and Kondrat'ev, 2014), and so on. However, quantitative analysis on the

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adsorption of sodium oleate is a tough work because of low adsorption mass and difficulties in detection (Alagha et al., 2013; Irwin et al., 2005).

Quartz Crystal Microbalance with Dissipation (QCM-D) is a technique to detect minute mass changes (nanogram range) on the surface of an electro-acoustical sensor device, mainly in a form of a thin slice of quartz crystal, by detecting changes of its resonance behavior (Buttry and Ward, 1992; Vittorias et al., 2010). Recently, *in situ* QCM-D is known as a reliable method to monitor the adsorption kinetics of nanoparticles (Strydom et al., 2014), DNA (Song et al., 2014), artificial skeleton (Lilja et al., 2013), proteins (Ebara and Okahata, 1994), and polymers (Marx, 2003). QCM-D is also a powerful tool for investigating the interactions between solids and surfactants in solution (Bereket and Yurt, 2002; Simbeck et al., 2011).

In this work, the adsorption process of sodium oleate on TiO_2 coated sensor surface was studied using QCM-D in order to reveal the adsorption mechanism of sodium oleate on titanium mineral. The effects of pH value, sodium oleate concentration, and temperature of sodium oleate solution on TiO_2 coated sensor surface were evaluated. Finally, the adsorption isotherms and adsorption thermodynamics were analyzed to explain the adsorption process.

Experimental

Material and reagents

The quartz crystal sensors with TiO_2 coatings crystals were purchased from Q-Sense (BiolinScientific, Q-Sense, Sweden). Analytical grade (99.70%) sodium oleate ($C_{17}H_{33}COONa$), sodium acetate, acetic acid, and sodium dodecyl sulfate (SDS) were purchased from Sinopharm Group of China. Generally, flotation of titanium minerals is performed under acidic conditions (Fan et al., 2009). Therefore, electrolyte solution with pH values of 3.5, 5.0, 6.0, and 7.5 were prepared using sodium acetate (0.2 mol/dm^3) and acetic acid (0.2 mol/dm^3). Then, sodium oleate was dissolved in the electrolyte solution at concentrations of 20, 50, 100, 150, and 200 mg/dm^3. The ultrapure water (resistivity is 18.25 MΩ·cm) was prepared using water purification system (Millipore, USA).

The 97% pure rutile was obtained from natural rutile sample after a series of purification. For the zeta potential measurement the rutile sample was crushed to −2 μm.

QCM-D measurements

The QCM-D measurements were performed with a Q-Sense E4 unit, which simultaneously monitors the changes in frequency (Δf) and energy dissipation (ΔD) of a quartz crystal sensor. The QCM-D technique were reported in literature (Sakai et al., 2006; Yang et al., 2007). For rigid and thin adsorption layers ($\Delta D < 10^{-6}$), Δf is direct proportion to mass through the Sauerbrey (1959) relationship:

$$\Delta m = -\frac{C \cdot \Delta f}{n} \tag{1}$$

where C is the mass sensitivity constant with its value of 17.7 $ng \cdot cm^{-2} \cdot Hz^{-1}$ (Sauerbrey, 1959; Lilja et al., 2013). The Δf is the shift in frequency. The n parameter is the overtone (n = 1, 3, 5, 7, 9, 11 or 13) of the resonance frequency of the applied voltage across the electrodes. Normalized frequency shifts at the third overtone are used to interpret the adsorption result (Deng et al., 2014). However, the Sauerbrey equation is limited for the case of thick and/or viscoelastic films. Fortunately, a new model for QCM-D operation in liquid was proposed by Kanazawa and Gordon (Kanazawa and Gordon, 1985; Schumacher et al., 1985). The resonant Δf can be described as:

$$\Delta f = -\frac{f_0^{3/2}}{\sqrt{\pi \rho_q \mu_q}} \sqrt{\eta_l \rho_l} \tag{2}$$

where f_0, μ_q and ρ_q are the characteristic resonant frequency, shear modulus and density of the quartz crystal, respectively, while the ρ_l and η_l are the density and viscosity of the liquid.

The ΔD is proportional to the power dissipation in the oscillatory system, which provides information on rigidity of the attached materials. The dissipation is defined as:

$$\Delta D = \frac{E_{lost}}{2\pi E_{stored}} \tag{3}$$

where E_{lost} is the energy lost during one oscillation cycle, E_{stored} is the total energy stored in the oscillator. Because the ΔD is a ratio of energies, it is dimensionless, and is reported as 10^{-6} dissipation units.

However, while adsorption causes a great shift in the ΔD value ($\Delta D > 10^{-6}$), as a result of the adsorption of a viscous and soft layer. The adsorbed mass was fitted based on the Voigt model with the Q-tools software from Q-Sense AB. According to the Voigt model for viscous adsorption layer, Δf and ΔD depend on the density (ρ), thickness (h), elastic shear modulus (μ), and shear viscosity (η) of the adsorption layer (Alagha et al., 2013).

The $-\Delta D/\Delta f$ means the energy dissipation per unit resonant frequency, which is used for characterizing the adsorption strength (Nezu et al., 2008). A more rigid and compact adsorption layer attached to the quartz crystal gives a low $-\Delta D/\Delta f$ value. In contrast, a soft and dissipated layer gives a higher $-\Delta D/\Delta f$ value.

For each experiment, the TiO_2 coated quartz crystals were cleaned in a UV-Ozone chamber for 10 min prior to use. The TiO_2 sensors were then mounted in four separate QCM-D flow chambers. A stable baseline was achieved firstly using sodium acetate and acetic acid electrolyte solution at the pH of interest, and then followed by introducing sodium oleate solutions. The baseline solutions were pumped into the flow

chamber when the frequency shift reaches plateau to remove loosely adsorbed or deposited layers. The TiO_2 sensors were first ultra sonicated for 20 min in 5% SDS solution. Then, they were rinsed with the ultrapure water, and cleaned using UV O-zone for 20 min. Finally, they were rinsed thoroughly with the water again, and dried with nitrogen.

Zeta potential measurements

The zeta potential values of rutile particles at different pH values were obtained from electrophoretic mobility measurements using a Brookhaven ZetaPALS (USA). The experiments were repeated at least three times (prepared on different days). In the tests, the concentrate of rutile suspensions was 100 mg/dm^3 in the pH range of 3.0 ~ 8.0, and conditioned for 24 h to reach the adsorption equilibrium. The experiments were carried out at 298 K.

Surface tension measurements

The surface tension measurements for the sodium oleate solution were performed using a Kruss K100 (Germany). The tensile force acting on the plate when in contact with the solution interface is measured and used to calculate the surface tension (Ryu and Free, 2003).

Results and discussion

Effect of pH value of sodium oleate solution on TiO_2 coated sensor surface

The pH value of sodium oleate solution has significant impact on the adsorption of TiO_2 coated sensor surface (Fig. 1).

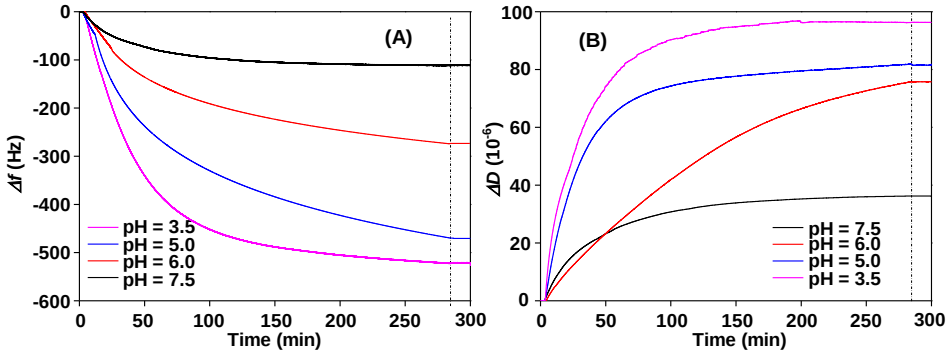

Fig. 1. QCM-D Δf and ΔD response of third overtone as a function of time of the adsorption of sodium oleate on TiO_2 surface with different pH values (sodium oleate concentration = 100 mg/dm^3, T = 298 K)

For a certain pH value, a rapid decrease in Δf (Fig. 1A) accompanied with a rapid increase in ΔD (Fig. 1B). The changes of Δf and ΔD at different pH values follow this

order: pH 3.5 > pH 5.0 > pH 6.0 > pH 7.5 from 0 to 285 min. The ΔD is related to the thickness and viscoelasticity of the adsorbed layer. A lower pH value causes a much larger ΔD, owing to the higher energy dissipation. In addition, a positive ΔD indicates a soft structure. From 285 to 300 min, Δf and ΔD were stable while the baseline solution was pumped into the system.

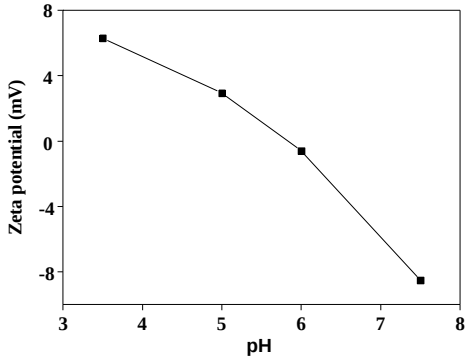

Fig. 2. Effect of pH values on zeta potentials of rutile

Figure 2 shows that the relationship between the zeta potentials of rutile and pH values. The isoelectric point of TiO_2 is located at pH 5.9, implying TiO_2 coated sensor surface is positively charged with pH < 5.9 and negatively charged with pH > 5.9. The carboxylate radical is the active site of sodium oleate, *i.e.* sodium oleate is negatively charged. Therefore, an electrostatic interaction occurred between TiO_2 and sodium oleate solution. A remarkable adsorption on TiO_2 coated sensor surface at pH 3.5 due to the electrostatic attraction between the positively charged TiO_2 coated sensor surface and the negatively charged sodium oleate (Nezu et al, 2008). The adsorption behaviors at pH 6.0 and 7.5 are weaker than those at pH 3.5 and 5.0 because of the electrostatic repulsion between the negatively charged TiO_2 coated sensor surface and the negatively charged sodium oleate.

Effect of concentrate of sodium oleate solution on TiO_2 coated sensor surface

As Fig. 3 displays, the Δf changes sharply while sodium oleate was injected into the measurement chamber. Decreases of the Δf was observed with the increases of sodium oleate concentrate at one time. However, the Δf tends towards stable while sodium oleate concentrate is 200 mg/dm^3. As demonstrated in Fig. 3B, the adsorbed sodium oleate layer on TiO_2 coated sensor surface is more rigid as the sodium oleate concentrate increases. In other words, the sodium oleate adsorption on TiO_2 coated sensor surface is stronger as the concentrate strength increases.

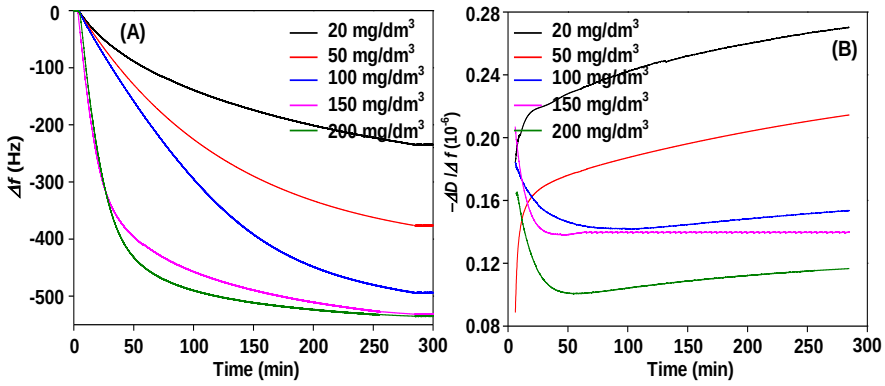

Fig. 3. QCM-D Δf and $-\Delta D/\Delta f$ response of third overtone as a function of time of the adsorption of sodium oleate on TiO_2 surface in different concentrate (pH = 5.0, T = 298 K)

Adsorption isotherms

Adsorption isotherms are of importance because they can reflect the surface characteristics of the adsorbent at micro level, as well as the adsorption characteristics of adsorption mass and absorption state. As shown in Fig. 3A, the adsorption equilibrium is nearly reached at 285 min. As Fig. 4 describes, the adsorbed mass with different sodium oleate concentrate was performed using the Voight model. Adsorption equilibrium data (at 285 min) was fitted by Langmuir and Freundlich equations as follows:

$$\frac{C_e}{\Gamma_e} = \frac{C_e}{\Gamma_m} + \frac{1}{K_L \Gamma_m} \tag{4}$$

$$\ln\Gamma_e = \ln K_f + \frac{1}{n}\ln C_e \tag{5}$$

where Γ_e (mg/m^2) and Γ_m (mg/m^2) represent the equilibrium absorption mass and the saturation absorption mass, respectively; K_L (dm^3/mg) is the Langmuir constants involved in adsorption rate; C_e (mg/dm^3) is the equilibrium concentration; K_f (mg/m^2) and n are Freundlich constants.

The Langmuir and Freundlich isotherms are shown in Fig. 5. K_L, Γ_m, K_f, and n were determined from the two isotherms, and the values were presented in Table 1. The R^2 (0.9977) of Langmuir model is very close to 1, and larger than that of Freundlich model (0.9766), indicating a good agreement with Langmuir model. The saturation adsorption mass calculated from the Langmuir isotherm is 111.47 mg/m^2, which approaches the experimental data (109.90 mg/m^2 from Fig. 4). Therefore, the adsorption layer is considered as physical absorption of monolayer adsorption which is consistent with electrostatic adsorption (Padilla-Ortega et al., 2014; Cui et al., 2014).

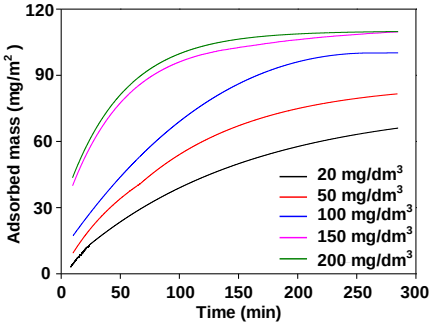

Fig. 4. The fitting adsorbed mass change with time
with different sodium oleate concentrate (pH = 5.0, T = 298 K)

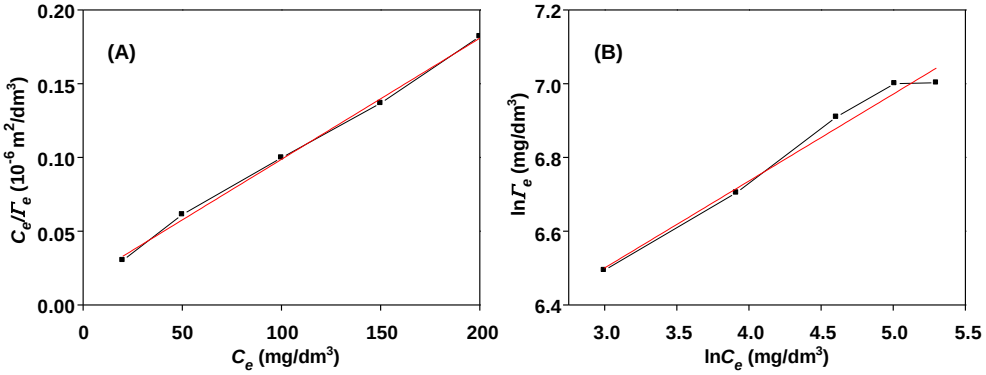

Fig. 5. Langmuir (A) and Freundlich (B) isotherm for the adsorption
of sodium oleate on TiO_2 surface at 298 K

Table 1. Isotherm parameters for sodium oleate adsorption on TiO_2 at 298 K

Isotherms	Parameters	R^2
Langmuir	Γ_m = 111.47 (mg/m^2) K_L = 0.5407 (dm^3 /mg)	0.9977
Freundlich	K_f = 328.27 (mg/m^2) n = 4.2445	0.9766

Critical micelle concentration (CMC) of sodium oleate solution

Surfactant adsorption is affected by hydrocarbon chain length and solution ionic strength (Kim et al., 1998; Somasundaran and Huang, 2000; Fleming et al., 2001). As the surfactant concentration increases, the monomers tend to aggregate, resulting in lower surface tension. Adsorption of surfactant molecules at air-liquid interface is related to the lowering of surface tension according to the Gibbs adsorption equation:

$$\Gamma_i = -\frac{C}{RT}\left(\frac{\partial\gamma}{\partial C}\right)_{T,P} \quad (6)$$

where γ, Γ_i, R, T, and C are surface tension (mN/m), adsorbed mass (mg/m^2), molar gas constant (8.314 J/(mol·K)), absolute temperature (K), and surfactant concentration (mg/dm^3), respectively.

As stated, the Langmuir adsorption layer is considered as monolayer adsorption. Thus, monolayer-level adsorbed mass increases as surface tension decreases. As monolayer coverage at the air-liquid interface is completed, the surface tension reaches a minimum plateau value. This point is considered as CMC. As demonstrated in Fig. 6, the surface tension decreases with the sodium oleate concentrate increases. The CMC of sodium oleate surfactant is 173.42 mg/dm^3. Therefore, the adsorbed mass little or nothing changes while the sodium oleate concentrate is greater than 173.42 mg/dm^3. This could provide a good explanation for Figs. 3A and 4, both of Δf and adsorbed mass only have a tiny change, when sodium oleate concentrate are 150 mg/dm^3 and 200 mg/dm^3.

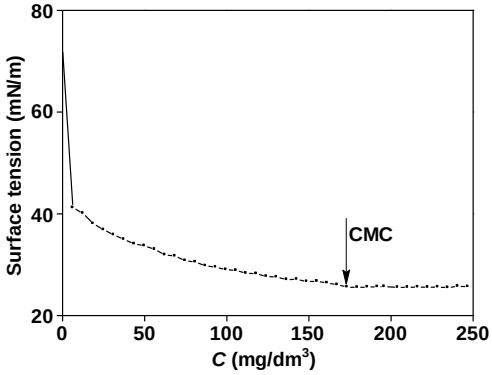

Fig. 6. Surface tension of sodium oleate solution

Adsorption thermodynamics

Adsorption thermodynamics shows the energy effects in the process of adsorption, reflecting whether an adsorption process takes place under certain conditions (Guerra et al., 2014; Fu et al., 2015). The adsorption thermodynamics of sodium oleate (100 mg/dm^3) on TiO_2 coated sensor surface were carried out at different temperatures (298, 303, 308, 313, and 318 K) at pH = 5.0. The data was fitted by the Voigt model and depicted in Fig. 7. The adsorbed mass is favored by increasing temperature because the adsorption reaction is endothermic. This increment value tends to a plateau while the temperature increases from 313 to 318 K.

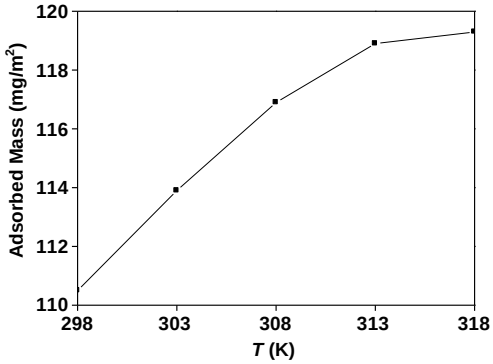

Fig. 7. Effect of temperature of sodium oleate on TiO_2 surface
(sodium oleate concentrate 100 mg/m^3, pH = 5.0)

The standard Gibbs free energy of adsorption value (ΔG), standard enthalpy of adsorption (ΔH), and entropy change (ΔS) were calculated as follow:

$$\Delta G = -\mathrm{R}T\ln K \tag{7}$$

$$\ln K = \frac{\Delta S}{\mathrm{R}} - \frac{\Delta H}{\mathrm{R}T} \tag{8}$$

where K is the Langmuir equilibrium constant (K_L), and T is the temperature (K). ΔH and ΔS were calculated from van't Hoff's equation and represented in Table 2 from the slope and intercept of the linear plot of $\ln K_L$ versus $1/T$ (Fig. 8).

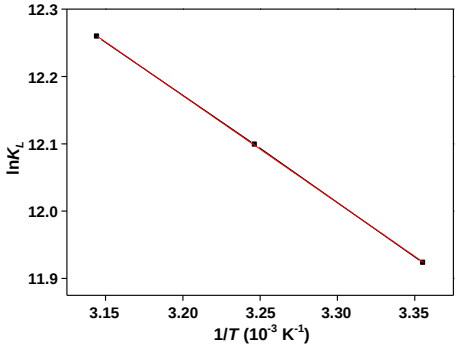

Fig. 8. Van't Hoff's regressions for determination of thermodynamic parameters

As shown in Table 2, the values of ΔG confirm the spontaneous nature and feasibility of the adsorption (Auta and Hameed, 2014). Besides, the decrease value of ΔG with an increase in temperature suggests the adsorption is more favorable at higher temperature. Researchers have reported that the ΔH of physisorption is smaller than 40

kJ/mol (Yao et al., 2010). The value of ΔH is 13.23 kJ/mol, indicating sodium oleate adsorption onto TiO_2 coated sensor surface is a physisorption process and the adsorption reaction is endothermic. Meanwhile, the ΔS illustrates the randomness of solid-solution interface increased during the sodium oleate onto the active sites of TiO_2 coated sensor surface.

Table 2. Thermodynamics parameters for the adsorption mass of sodium oleate on TiO_2 surface

Temperature (K)	$1/T$	$\ln K_L$	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol·K))
298	0.00336	11.92	–29.53		
308	0.00325	12.10	–30.97	13.23	143.47
318	0.00315	12.26	–32.40		

Conclusions

Substantial adsorption of sodium oleate solution on TiO_2 coated sensor surface was attributing to electrostatic adsorption with QCM-D analysis. The Langmuir model is suitable to explain the adsorption process, instead of the Freundlich model. The saturation adsorption mass is 111.47 mg/m^2. The adsorption mass does not change when sodium oleate concentration is greater than CMC. The thermodynamic analysis showed that adsorption is physical, spontaneous and endothermic. The QCM-D technique is a valuable contribution to characterize the adsorption phenomena such as surfactant on solid surface.

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