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Adsorption of anionic surfactants onto sepiolite

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Abstract

Anionic surfactants constitute the main ingredients of detergents and a number of surfactant formulations used in a spectrum of diverse industries. The aim of this study is to examine the amenability of natural sepiolite to the adsorption of anionic surfactants, sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS). Adsorption isotherms exhibit three regions with distinctly different slopes. The first region is characterized by the complexation of anionic surfactants with Mg^{2+} ions at the octahedral sheet or hydrogen bonding between the oxygen groups of anionic head groups of surfactant and H^+ of the bound or zeolitic water. The Mg^{2+} ions released from sepiolite leads to the precipitation of magnesium salt of surfactant in the second region. The third region marks both the beginning of plateau region and micellar dissolution of the precipitate. The effect of temperature on surfactant adsorption for SDS/sepiolite system was utilized to calculate such thermodynamic parameters as the free energy of adsorption (ΔG_{ads}°) and the heat of adsorption (ΔH_{ads}°). The low value of ΔH_{ads}° (1.87 kJ/mol) is an evidence for the physical adsorption of anionic surfactants onto sepiolite. The relatively large value of entropic contribution ($-T\Delta S_{ads}^{\circ}$) indicates that the adsorption of anionic surfactants onto sepiolite is entropically governed.
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1. Introduction

Sepiolite, a hydrated magnesium silicate $[(Si_{12})(Mg_9)O_{30}(OH)_6(OH_2)_4H_2O]$, belongs to a clay family of phillosilicates. It exhibits a fibrous structure and thus finds applications in a variety of areas where sorptive, catalytic and rheological properties are exploited. The sorptive property of sepiolite particularly renders it invaluable as a bleaching and clarifying agent, filter aid, industrial absorbent and a spectrum of uses ranging from cosmetics to paints and even fertilizers. Sepiolite is often found associated with other clay and non-clay minerals such as carbonates, quartz, felsdpar and phosphates. The most important occurrences of sepiolite are found in Vallecas of Spain, Turkey, Madagascar and Tanzania.

Adsorption of various metal ions onto sepiolite (Cd, Cu, and Zn) for the treatment of wastewaters (Ni, Cd and Zn) has been studied [1–3]. Among others including adsorption of dilute thiram on active carbon and sepiolite as a function of temperature [4], interaction of amines on sepiolite and palygorskite by infrared measurements [5], removal of aromatic amines from aqueous solutions by activated sepiolite [6] have been investigated. Uptake of ammonia [7], the access of cationic dye (methylene blue) into the structural micropores of sepiolite [8], adsorption mechanism of organic and inorganic ions by sepiolite [9], adsorption of primary and quarternary amines [10] and adsorption of pyridine derivatives [11] are some other examples pertinent to our study. Anionic surfactants that constitute the main ingredient of laundry detergents are extensively used in cosmetics, dyeing of fabrics in textile industry and flotation applications [12–14]. The presence of such surfactants in the above industries and household uses, if discharged into wastewater, can be detrimental to living species. Elimination of surfactants from wastewater is very important to protect public health [15].

It is therefore the objective of this study to investigate the amenability of uptake of typical anionic surfactants, sodium dodecylsulfate and sodium dodecylbenzenesulfonate by sepiolite and identify mechanisms responsible for their adsorption.

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Nomenclature

a_i	effective diameter of the ion in solution (Å)
A	lateral interaction coefficient
A, B	constants characteristic of the solvent at the specified temperature and pressure
C	equilibrium concentration (M)
C_i	initial concentrations (M)
C_r	residual concentrations (M)
ΔG_{ads}°	change in free energy of adsorption (kJ/mol)
ΔH_{ads}°	heat of adsorption (kJ/mol)
I	ionic strength (M)
K	adsorbability of the surfactant molecule at infinitively low coverage
K_{sp}	solubility product of a compound
m	amount of solid (g)
m_i	molality (M)
n_i	adsorbate loading of component i (mol/kg)
N	size ratio
R	gas constant (1.987 cal mol^{-1} K^{-1})
S	specific surface area of solid (m^2/g)
T	temperature (K)
$-T\Delta S_{ads}^{\circ}$	entropic contribution (kJ/mol)
V	volume of the solution (ml)
z_i	charge of the ith ion in solution

Greek symbols

γ_i	individual ion activity coefficient
Γ	adsorption density (mol/m^2)
θ	degree of surface coverage of the mineral with the collector molecule at Γ/Γmax

2. Experimental

2.1. Materials

The sepiolite sample used in this study was received from Mayas Mining Co. in Sivrihisar, Turkey. This brown sepiolite ground to minus 65 μm produced an average particle size (d_{50}) of 1.98 μm as determined by Zetasizer. The X-ray diffraction and chemical analysis indicates that calcite and dolomite are the major impurities accompanying sepiolite [10]. The surface area of untreated sepiolite was found to be 68 m^2/g by means of the BET method using nitrogen as adsorbent. Complete chemical analysis of the sepiolite is given in Table 1.

Sodium dodecylsulfate (SDS; $C_{12}H_{25}SO_4Na$) and sodium dodecylbenzenesulfonate (SDBS; $C_{12}H_{25}C_6H_4SO_3Na$) as the anionic surfactants, and hexadecyltrimethylammonium bromide (HTAB; $C_{16}H_{33}N(CH_3)_3Br$) was used as titrant in the analysis of anionic surfactants. SDS and HTAB were purchased from Fluka and specified to be of high purity. SDBS, which assayed about 85% sulfonate, was also purchased from Fluka but contained a mixture of different chains (C_{10}: 5%, C_{11}: 45%, C_{12}: 35%, and C_{13}: 15%). Distilled and deionized water with a conductivity value of 2×10^{-6} mho s/cm was utilized in all experiments.

Table 1
Chemical composition of sepiolite

Compound	wt%
SiO$_2$	51.93
CaO	0.12
K$_2$O	0.33
Al$_2$O$_3$	1.52
MgO	24.20
TiO$_2$	0.08
Fe$_2$O$_3$	0.70
Na$_2$O	0.12
LOI[a]	21.00

[a] Lost on ignition.

2.2. Methods

Electrokinetic measurements were carried out with a Zeta Meter 3.0 equipped with microprocessor unit. It automatically calculates the electrophoretic mobility of particles and converts it to the zeta potential. One gram of mineral was conditioned in 100 ml of distilled water for 10 min. The suspension was kept still for 5 min to get larger particles settle. The samples were taken from the actual supernatants following the adsorption tests. About 25 ml of supernatant was removed from the adsorption test vial and introduced into the electrophoresis cell. An appropriate amount of sepiolite particles was pipetted out of the sepiolite bed and placed in the cell. This procedure assured the measurements under in situ conditions. Each data point is an average of approximately 10 measurements.

Adsorption tests were conducted in 20 or 40 ml glass vials. A sepiolite sample of 500 mg was mixed in 10 ml or its multiples with a solid to liquid ratio of 0.05. The vials were shaken for 2 h on a shaker and centrifuged at 5000 rpm for 15 min. The supernatant was analyzed for the anionic surfactant by a two-phase titration technique using dimidium bromide and disulfine blue as indicators [16]. This technique is based on the formation a complex between anionic surfactant and cationic surfactants; this complex is soluble in chloroform and changes from pink to blue in the presence of indicators.

Magnesium ion concentration was determined from the actual supernatants following the adsorption tests either in the absence or presence of surfactant using the Atomic Absorption Spectrometer.

The amount precipitated was determined by contacting solutions of 10^{-3} M/l MgCl$_2$ with varying concentrations of SDS and SDBS. All solutions were centrifuged at 5000 rpm for 15 min or more until a clear supernatant was obtained; the supernatant was analyzed for sulfonate concentration. The difference between initial and residual concentration of the surfactant was converted to the amount of surfactant lost due to precipitation.

The adsorption density was calculated by the following formula [17]:

$$\Gamma = \frac{(C_i - C_r) \times V}{m \times S \times 1000} \tag{1}$$

where C_i and C_r represent the initial and residual concentrations in M, m the amount of solid in grams, V the volume of the solution

in ml, S the specific surface area of sepiolite in m^2/g and Γ is the adsorption density in mol/m^2. The concentration of magnesium was analyzed by atomic absorption spectrometer.

3. Results and discussion

3.1. Elektrokinetic properties of sepiolite

Sepiolite undergoes acid–base interactions in the vicinity of pH 8.5 and thus exhibits a strong buffering capacity, particularly in the acidic pH. It takes less than a minute for a sepiolite suspension adjusted to pH 3 to attain its natural pH of 8.5. Since Mg ions located in the octahedral sheet are conducive to ion exchange, they are released into solution, as the pH is made more acidic. It should be noted that while the Mg concentration at natural pH is about 20 ppm, it is about 400 ppm at pH 3 [18]. Zeta potential measurements conducted as a function of solids concentration revealed significant differences. The zeta potential–pH profile of sepiolite at two different solids concentration is presented in Fig. 1. It is seen that the isoelectric point (iep) of sepiolite at 0.2% solids concentration yields 3.2 and that at 5% gives 6.3. Such difference can be explained on the basis of increased Mg concentration at high solids concentration. Increasing the solids concentration from 0.2 to 5% proportionally shifts the zeta potential values from negative to more positive values; this behavior was also found in the case of colemanite $(Ca_2B_5O_{11}\cdot 5H_2O)$, which yielded an iep of 8.5 at 0.1% solids concentration and 10.5 at 1% solids concentration [19].

3.2. Effect of solids concentration on adsorption

Sepiolite is a good adsorbent for polar molecules such as water and ammonia and non-polar compounds and to a lesser extent methyl and ethyl alcohols [12]. In batch systems, because the volume of the liquid in suspension is fixed, the extent of adsorption is primarily controlled by the conditioning or equilibrium time. Fig. 2 illustrates the effect of solids concentration on adsorption density of SDS and SDBS onto sepiolite. The adsorption density (mol/m^2) decreases at a higher slope with

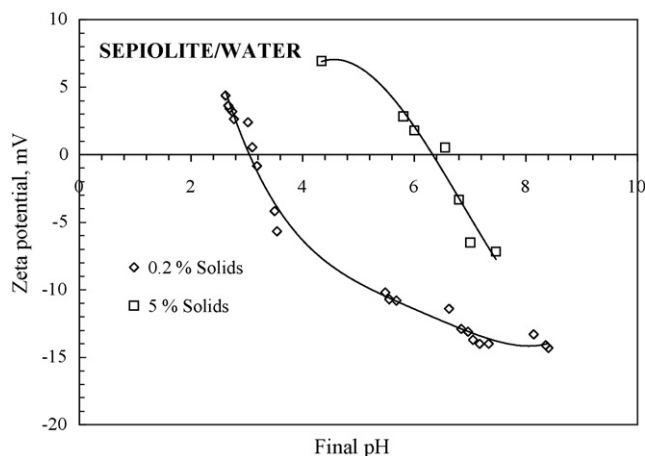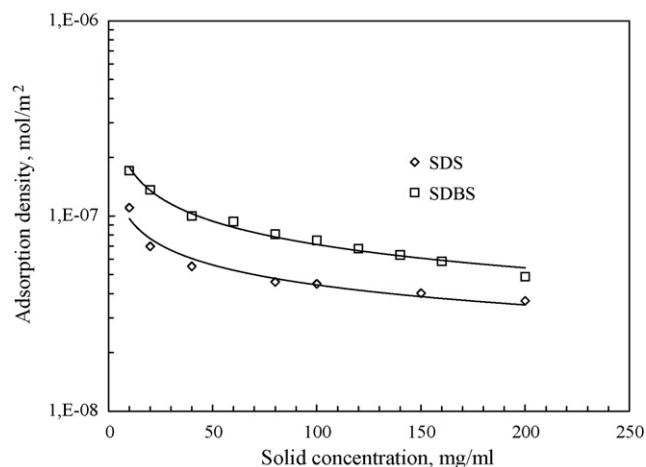Fig. 2. Effect of solids concentration on adsorption density of SDS and SDBS onto sepiolite ($C_i = 1 \times 10^{-3}$, pH 8.25 ± 0.15).

increasing the solids concentration up to 50 mg/ml and proceeds with a lower slope for both surfactants above it. Therefore, the rest of the adsorption tests were conducted at 50 mg/ml (5% by wt) solids concentration.

3.3. Effect of conditioning time on adsorption

Conditioning time in adsorption systems generally reveals the nature of adsorption. Short equilibrium time often reflects the physical adsorption, whereas; longer equilibrium times indicate either chemical adsorption or difficulty to the access of collector to micro pores. The adsorption data in Fig. 3 show that the required time for both surfactants to reach equilibrium is about 60 min; this relatively short time indicates that adsorption is indeed governed by physical interactions. However, adsorption of sulfonate onto kaolinite has been shown to take several days [20].

3.4. Effect of surfactant concentration on adsorption

In order to determine the mechanism of adsorption process, the adsorption of anionic surface-active agents has been studied as a function of residual concentration and the corresponding
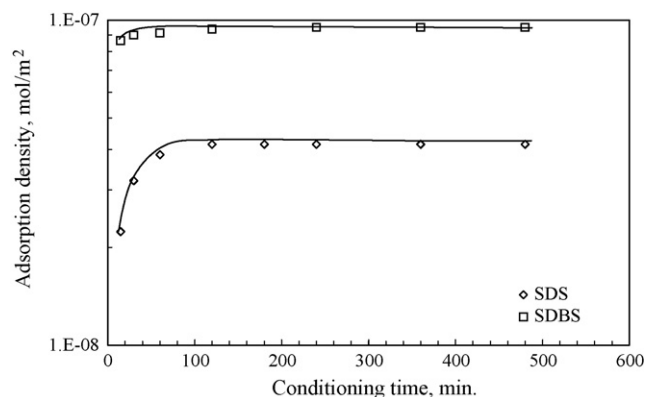

Fig. 1. The zeta potential–pH profile of sepiolite at two different solids concentration.

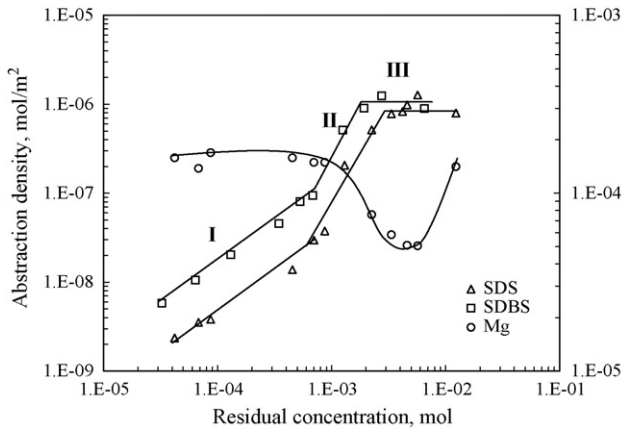Fig. 3. Effect of conditioning time on adsorption density of SDS and SDBS onto sepiolite ($C_i = 1 \times 10^{-3}$, pH 8.2 ± 0.2).

Fig. 4. Abstraction isotherms of SDS and SDBS onto sepiolite at pH 8.5 ± 0.5 along with the variation of Mg ion concentration.

Fig. 5. The ratio of residual and initial surfactant concentration against residual surfactant concentration in the presence of 10^{-3} M MgCl$_2$ sepiolite supernatant at pH 8.5 ± 0.5.

abstraction isotherms for both SDS and SDBS are presented in Fig. 4. Here abstraction refers to the total depletion of surfactant from the solution in the form of both adsorption and precipitation as follows:

$$abstraction = adsorption + precipitation \qquad (2)$$

Accordingly, in order to obtain the net adsorption isotherm precipitation values need to be subtracted from those of abstraction. The abstraction isotherms exhibit three regions of interest. The first region (I), which is characterized by the molecular interactions, e.g. complexation or hydrogen bonding on the sepiolite surface, extends up to approximately 10^{-3} M residual surfactant concentration. The second region (II) marks the onset of precipitation of magnesium alkylsulfate or alkylbenzenesulfonate and/or that of chain–chain interactions. Finally, the third region (III) represents the plateau region.

In the second region, the formation of MgR$_2$ (magnesium dodecylsulfate or magnesium dodecylbenzenesulfonate) precipitate is plausible on thermodynamic grounds. Here R refers to the alkylsulfate or alkylbenzenesulfonate chain. The appearance of precipitation in the bulk is an indication of surface precipitate formation on the sepiolite surface. Surface precipitate and hemimicelles show similarities and are thus thermodynamically indistinguishable [21,22].

Mg ion concentration in the bulk increases with a decrease in pH. While the Mg ion concentration at the natural pH of 8.5 is 3.5×10^{-4} M, it is 10^{-2} at pH 2. In order to determine the onset of precipitation and the corresponding solubility product, a series of precipitation tests were carried out. It is envisaged that the Mg^{2+} ions released from sepiolite into solution interacts with long chain surfactants leading possibly to the formation of MgR$_2$. As seen in Fig. 5, the onset of precipitation for SDS occurs at 1.4×10^{-3} M and that of complete dissolution at 9.5×10^{-3} M. The solubility product of Mg precipitate in the presence of SDS can be calculated assuming the onset of precipitate formation at 1.4×10^{-3} M and Mg ion concentration of 1.49×10^{-4} M at the onset of precipitation.
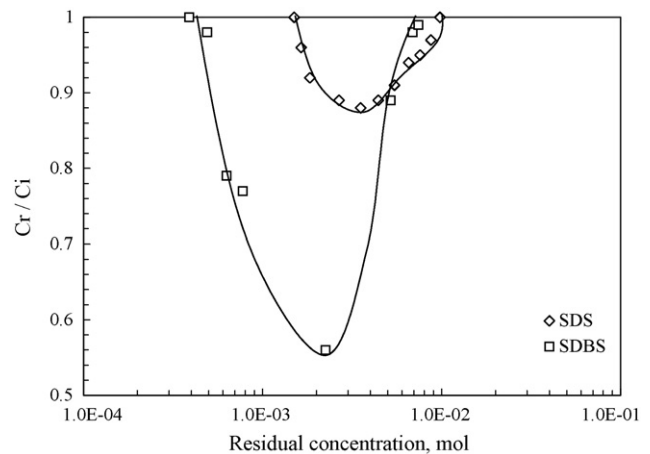
The ionic strength of the solution under these conditions can be calculated as follows:

$$I = \frac{1}{2} \sum m_i z_i^2 \qquad (3)$$

Using the Debye–Huckel equation [23]:

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} \qquad (4)$$

The individual activity coefficient for Mg^{2+} ion can be calculated as $\gamma_{Mg}{}^{+2} = 0.85$ by taking; $A = 0.5085$, $B = 0.3281 \times 10^{-8}$, $a_i = 8 \times 10^8$ for 25 °C. If we make the same calculation for the DS ion using $a_i = 4 \times 10^8$ [24], it comes out as $\gamma_{DS}{}^- = 0.96$ by plugging these values in the solubility product equation:

$$K_{sp} = a_{Mg^{+2}} a_{DS^-}^2 \qquad (5)$$

$$K_{sp} = (\gamma_{Mg^{+2}} C_{Mg^{+2}})(\gamma_{DS^-}^2 C_{DS^-}^2) \qquad (6)$$

The solubility product for MgDS assuming the formation of magnesium dodecylsulfate can be found as $K_{sp} = 2.29 \times 10^{-10}$. Back calculation of the SDS concentration at the onset of precipitation confirms the accuracy of the solubility product and in turn the experimental procedure. This value is also in line with the reported literature value of 2×10^{-10} [25].

Using the same method, the solubility product of MgDBS precipitate was calculated assuming the onset of precipitate formation (4.9×10^{-4} M) and Mg ion concentration (3×10^{-4} M) in solution and found to be 7.2×10^{-11} for MgR$_2$. The previous studies have shown that the dissolution of precipitates begins above the critical micelle concentration (CMC) of the surfactants [26]. It is interesting to note that the benzene ring has been found to be equivalent to 3.5 CH$_2$ groups from the data on adsorption of alkylbenzenesulfonates at the alumina surface [27]. In our study, an average ratio of 3.4 found in region I between the adsorption of SDS and SDBS shows a reasonable agreement between the literature values, though our surfactant is dodecylsulfate rather than dodecylsulfonate.
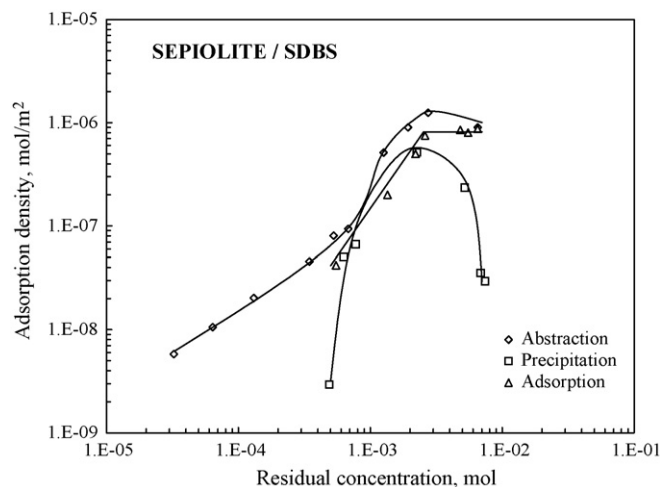
Fig. 6. Abstraction, precipitation and adsorption isotherms in sepiolite/SDBS system at pH 8.5 ± 0.5.

Fig. 8. Adsorption isotherms of sepiolite/SDS system at different temperatures at pH 8.5 ± 0.5.

The effect of precipitation on adsorption has been investigated in Figs. 6 and 7 where adsorption density or surfactant uptake is plotted against residual concentration for abstraction, precipitation and adsorption. As seen from figures, when the precipitation curve is subtracted from the abstraction curve, the adsorption curve with a plateau region is obtained. This indicates the role of precipitate dissolution on adsorption maximum [28]. It should be noted that the onset of region III marks the CMC as determined by surface tension technique using the ring method. The CMC values for SDS and SDBS are respectively 8×10^{-3} and 1.4×10^{-3} M, which are in agreement with our previously reported values [26].

The effect of pH on adsorption was also investigated for both surfactants at 10^{-3} M. Because of the instability of the pH in the acidic pH region, the adsorption measurements in that region as a function of pH were performed as follows: the adsorption experiments were conducted in a beaker containing 2.5 g sepiolite and 50 ml of solution of desired surfactant concentration. The pH was continuously adjusted by introducing appropriate amounts of NaOH for a period of 30 min. It is found that the abstraction density slightly increased with decreasing pH, espe-
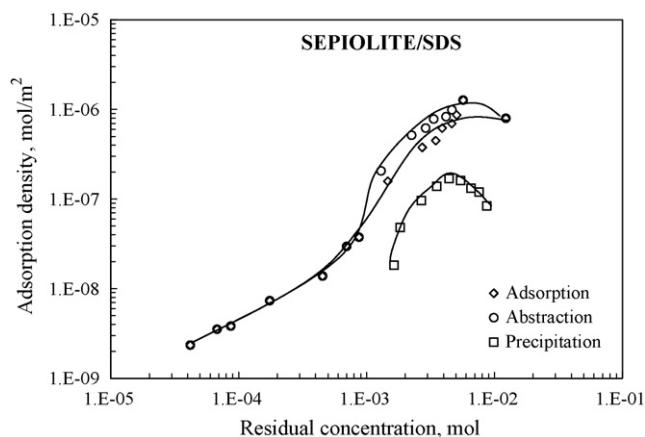

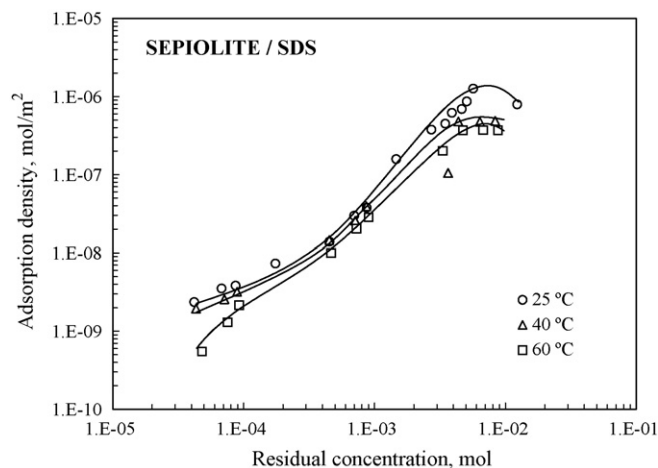Fig. 7. Abstraction, precipitation and adsorption isotherms in sepiolite/SDS system at pH 8.5 ± 0.5.

cially below pH 3.5 indicating the marginal role of electrostatic forces at natural pH of the system. Because sepiolite is a silicate mineral, it carries net negative charges at the natural pH of the system. The presence of zeolitic and bound water and also that of magnesium ion is instrumental in the adsorption process.

3.5. Thermodynamics of SDS adsorption onto sepiolite

The effect of solution temperature on adsorption is generally an important indicator to describe the type of adsorption. The decrease in adsorption with increasing temperature may be indication of physical adsorption and the reverse is generally true for chemisorption. However, there are a number of contradictory cases in the literature [22].

The thermodynamic evaluation was only made for SDS as both surfactants yield similar trend. For this purpose, the effect of solution temperature on adsorption density in sepiolite/SDS system was investigated. The adsorption isotherms of sepiolite/SDS system at different temperatures are presented in Fig. 8. As seen from Fig. 8, the adsorption of SDS on sepiolite decreases with an increase in temperature; adsorption densities at the plateau region reveal significant differences as a function of temperature: 1×10^{-6} mol/m^2 for 25 °C, 4×10^{-7} mol/m^2 for 40 °C and 3×10^{-7} mol/m^2 for 60 °C.

The cross-sectional area of a SDS molecule in Å^2/molecule can be calculated as

$$\text{cross-sectional area} = \frac{10^{20}}{\Gamma_{max} A} \tag{7}$$

where Γ_{max} is the adsorption density at the plateau region, A is the Avogadro number. Table 2 illustrates the effect of temperature on various calculated values [29] (Klimenko and Koganovski, 1973).

Although the decrease in the adsorption of SDS onto sepiolite with increasing temperature may show the presence of physical adsorption, this is not sufficient to say whether the adsorption is physical or chemical in nature. The type of adsorption may be determined through such thermodynamic quantities as free energy of adsorption (ΔG_{ads}°) and the heat of adsorption (ΔH_{ads}°)

Table 2
Thermodynamic data obtained from adsorption isotherms of SDS/sepiolite system as a function of temperature

Temperature (°C)	Plateau ads. density Γ_{max} (M/m^2)	Equilibrium concentration (M)	Cross-sectional area (Å^2)	Degree of coverage (θ)
25	1.6×10^{-6}	6.0×10^{-3}	166	0.18
40	4.0×10^{-7}	4.5×10^{-3}	415	0.07
60	3.0×10^{-7}	4.7×10^{-3}	554	0.05

both of which can be obtained from the adsorption data given in Fig. 8.

A general adsorption isotherm for surfactant adsorption at the solid/liquid interface taking into account the effect of size ratio (n) and lateral interaction coefficient (a) between adsorbed molecules has the following form [30].

$$\frac{0}{(1-\theta)^n}e^{-2a\theta} = KC \tag{8}$$

$$K = \frac{1}{55.5}e^{\Delta G^{\circ}_{ads}/RT} \tag{9}$$

where K is the adsorbability of the surfactant molecule at infinitively low coverage, C is the equilibrium concentration in M, θ is the degree of surface coverage of the mineral with the collector molecule at (Γ/Γ_{max}), R is the gas constant ($8.1314\,\text{mol}^{-1}\,\text{K}^{-1}$), T is the temperature in K. The free energy of adsorption can be calculated from Eq. (8) where the degree of coverage θ was calculated at various concentrations all the way up to the plateau region.

The cross-sectional area of dodecylsulfate molecule is approximately $30\,\text{Å}^2$ [26]. The value of n is defined as the ratio of cross-sectional area of the adsorbate molecule over the cross-sectional area of the water molecule ($12.5\,\text{Å}^2$). The value of n is approximately equal to $30/12.5 = 2$ and thus the modified Frumkin equation takes $n = 2$ in Eq. (8). Accordingly by reordering Eq. (8) and taking the logarithms:

$$\ln\frac{\theta}{C(1-\theta)^2} = 2a\theta + \ln K \tag{10}$$

The values of a and K can be determined graphically from a plot of $\ln \theta/C(1-\theta)n$ versus θ (for $n = 2$). The resultant straight line has a slope of $2a$ and an intercept of $\ln K$ [10].

The fit obtained out of this model yields a R^2 value of 0.98.

While ΔG°_{ads} determines the affinity of the mineral surface towards the surfactant molecule, a represents the strength of lateral interaction forces; a negative value of "a" indicates a repulsive interaction between the polar heads, whereas a positive value of "a" indicates the presence of chain–chain interactions among the non-polar molecules.

Another very important thermodynamic parameter in determining the type of adsorption is the heat of adsorption (ΔH°_{ads}).
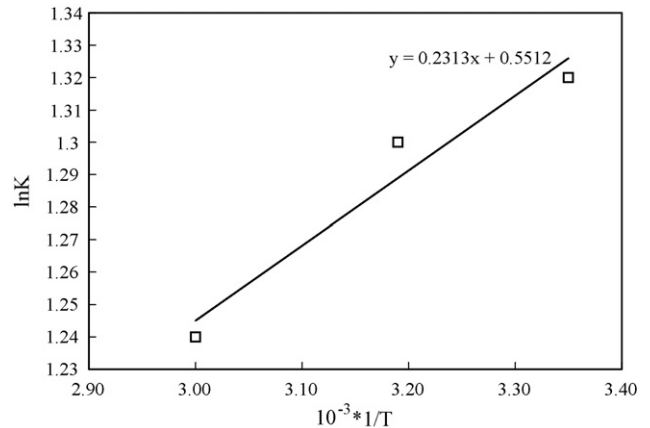

Fig. 9. Heat of adsorption data for sepiolite/SDS system using the modified Frumkin model.

This can be obtained from the Clausius–Clapeyron equation [22] as

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H^{\circ}_{ads}}{R} \tag{11}$$

Using this equation, the plot of $\ln K$ and $1/T$ is given in Fig. 9. The slope of the straight line has been put in Eq. (11) and the ΔH°_{ads} calculated. These results are presented in Table 3 along with the entropy values calculated using Eq. (12) given below:

$$\Delta G = \Delta H - T\Delta S < 0 \tag{12}$$

However, the temperature dependence using the Classius–Clapeyron equation does not yield a good straight line as seen in Fig. 9. Despite discrepancies reported in the literature [31], this is the only available technique for the calculation of heat of adsorption. The error estimate shows that the heat of adsorption data could be as much as 15%.

According to the modified Frumkin model, ΔH°_{ads} is rather small compared to the total adsorption energy. However, the entropic contribution ($-T\Delta S^{\circ}_{ads}$) is approximately equal to the free energy of adsorption. Therefore, it is plausible to say that the adsorption of SDS onto sepiolite is an entropically governed process. This is also evident from the positive values of "a". In addition, because the level of ΔH°_{ads} is much

Table 3
Various thermodynamics parameters calculated using the modified Frumkin model

System	$1/T$ (K)	Γ_{max} (M/m^2)	ΔG°_{ads} (kJ/mol)	ΔH°_{ads} (kJ/mol)	$-T\Delta S^{\circ}_{ads}$ (kJ/mol)	a
SDS/sepiolite	3.35×10^{-3}	1×10^{-6}	−12.93	−1.87	11.06	3.84
	3.19×10^{-3}	4×10^{-7}	−13.54	−1.87	11.67	5.24
	3.00×10^{-3}	3×10^{-7}	−14.22	−1.87	12.35	6.41

lower than 40 kJ/mol, it again indicates the presence of physical adsorption.

3.6. Adsorption mechanism of anionic surfactants on sepiolite

The change in free energy of adsorption (ΔG°_{ads}) is a sum of various contributing forces.

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{elect} + \Delta G^{\circ}_{ion\,exch} + \Delta G^{\circ}_{hyd,bond} \qquad (13)$$

ΔG°_{elect} represents the change in free energy of adsorption of surfactant molecules on the oppositely charged sepiolite via electrostatic forces, $\Delta G^{\circ}_{ion\,exch}$ represents adsorption through ion exchange between surfactant ion and anions in the sepiolite matrix and the $\Delta G^{\circ}_{hyd,bond}$ represents the hydrogen bond or coordination bond between the zeolitic water or bound water and O$^-$ of anionic head groups [32].

At 8.5 where the surface of sepiolite is negatively charged the presence of electrostatic interactions is unlikely. Because spectroscopic techniques such as IR is unable to distinguish between electrostatic interaction and hydrogen bonding. Zeolite, a porous sodium aluminum silicate mineral, for instance does not adsorb SDS. This confirms that the presence of Mg ion in the structure of sepiolite is the key factor for the adsorption of anionic surfactants. In addition, in sepiolite, each structural block is made up of two tetrahedral silica sheets sandwiching a central sheet of magnesium oxide–hydroxide. As the silica sheets are discontinuous, silanol (Si–OH) groups are present on the external surface of the silica particles. The dimensions of the cross-section of sepiolite tunnels are about 11 Å × 4 Å of which they shelter two types of water molecules: (i) coordinated water molecules which are bonded to Mg^{2+} ions located at the edges of octahedral sheet, and (ii) zeolitic water bonded to the coordinated water molecules through hydrogen bonding.

Experimental data show that anionic surfactants adsorb onto the surface of sepiolite in two modes. First is hydrogen bonding between O$^-$ of anionic polar head and H$^+$ of bound or zeolitic water. Second is the coordination bond between Mg ion at octahedral sheet and polar anionic head groups. Mg ion measurements in solution (Fig. 4) show that ion exchange mechanism is not possible. In fact, the value of 1.87 kJ/mol for the heat of adsorption (ΔH°_{ads}) is in agreement with the 1–2 kJ/mol value of heat of adsorption for hydrogen bond [3]. The low surface coverage (18%) observed in this study does not allow the distinction between the interaction of bound or zeolitic water with dodecylsulfate ion over that of water molecules of the solution. The adsorption of SDS on sepiolite in two modes is schematically illustrated in Fig. 10.

It may not be generally practical to use sepiolite to remove long chain anionic surfactants from wastewater. However, since wastewaters contain significant amounts multivalent ions to activate the silicate surface and make it amenable for the adsorption of anionic surfactants, the use of sepiolite may be justified. Otherwise sepiolite can be made positive with various inorganic ions or quaternary amines to make it a better adsorbent for anionic surfactants.
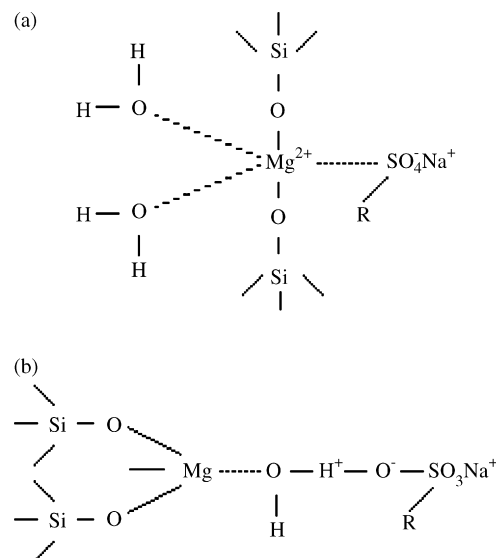

Fig. 10. Adsorption modes of SDS on sepiolite (a) complexation between Mg ion at octahedral sheet and polar anionic head groups (b) hydrogen bonding between O$^-$ of anionic polar head and H$^+$ of bound or zeolitic water.

4. Conclusions

Sepiolite with an isoelectric point of about 6 is negatively charged at natural pH of sepiolite and thus not conveniently amenable to electrostatic attraction of anionic surfactants.

Adsorption isotherms of alkysulfate and alkylbenzenesulfonate onto sepiolite obtained at room temperature exhibit three regions of interest. The first region is characterized by the regular molecular interactions. In the second region, the interaction of anionic surfactants with the Mg^{2+} ions released from sepiolite leads to the precipitation of magnesium salt of surfactant. Using the solubility product expression the contribution of precipitation towards the real adsorption was determined. The third region marks both the beginning of plateau region and micellar interactions.

Experimental data reveal that anionic surfactants in region I of the adsorption isotherm can adsorb onto sepiolite in two modes. First is the hydrogen bond between oxygen groups of anionic head group and H$^+$ of the bound or zeolitic water. Second is the electrostatic attraction between Mg ion at octahedral sheets and polar head and/or complexation between magnesium ions and anionic head groups. In region II, chain–chain interaction leading to hemimicelle formation and/or precipitation of Mg-surfactant species result in the occurrence of fast rising abstraction. Region III marks the plateau adsorption.

The effect of temperature on surfactant adsorption for SDS/sepiolite was utilized to calculate such thermodynamic parameters as the change in free energy of adsorption (ΔG°_{ads}) and the heat of adsorption (ΔH°_{ads}). While the former is calculated to be 13–14 kJ/mol, the latter comes out as 1–2 kJ/mol. The low value of ΔH°_{ads} 1.87 kJ/mol is an evidence for the physical adsorption of anionic surfactants onto sepiolite. The relatively large value of entropic contribution ($-T\Delta S^{\circ}_{ads}$) indicates that the adsorption of anionic surfactants is governed entropically.

Acknowledgements

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