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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 ($-T\Delta S^\circ_{ads}$) indicates that the adsorption of anionic surfactants onto sepiolite is entropically governed.

Keywords: Sepiolite; Anionic surfactant; Sodium dodecylbenzenesulfonate (SDBS); Sodium dodecylsulfate (SDS); Adsorption density; Thermodynamics

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)
$\Delta G^\circ_\mathrm{ads}$	change in free energy of adsorption (kJ/mol)
$\Delta H^\circ_\mathrm{ads}$	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)
$-T\Delta S^\circ_\mathrm{ads}$	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_2O	0.33
AI_2O_3	1.52
MgO	24.20
TiO_2	0.08
Fe_2O_3	0.70
Na_2O	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]:

$$\Gamma = \frac{(C_\mathrm{i} - C_\mathrm{r}) \times V}{m \times S \times 1000} \quad (1)$$

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