

The surface free energy of fluorite in presence of sodium dodecyl sulfate

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Abstract

Measurements of contact angle for water, glycerol, formamide, diiodomethane and bromoform on the surface of fluorite covered with a film of sodium dodecyl sulfate (SDS) were made. From these results the Lifshitz–van der Waals and the acid–base components of the surface free energy of fluorite covered with an SDS film were calculated. The electron-acceptor and the electron-donor parts of the acid–base component were also evaluated. On the basis of the measurements and the calculations carried out, a minimum wettability of fluorite and a minimum contribution of the acid–base intermolecular interaction to the surface free energy of fluorite were found when the fluorite surface was covered with an SDS monolayer. At higher SDS concentrations, a bilayer film can be formed on the fluorite surface, increasing the electron-donor proportion of the acid–base component of the surface free energy.

Keywords: Adsorption; Surface free energy; Fluorite; Sodium dodecyl sulfate

1. Introduction

Interfacial phenomena are of great significance in many fields, ranging from geochemical processes in nature, through the behavior of solids, to the processing of raw minerals.

Among the technological applications of these phenomena, the flotation process is one of the most important. In flotation, finely ground minerals are made hydrophobic so that they can be attached to air bubbles and separated from the rest of the slurry. Most separations by flotation are based on the selective adsorption of amphipathic organic reagents, called collectors, at the mineral/water interface.

Alkaline salts of fatty acids, especially oleic acid, are by far the most effective collectors for recovering fluorite by flotation. The main problem with this type of collector is, however, its low selectivity in the separation of fluorite from other calcium-containing minerals with

which they are usually mixed [1]. Therefore, other collectors have been sought for the flotation of fluorite [2]. Among the anionic collectors, sodium dodecyl sulfate is very often used for recovering minerals [3,4].

The adsorption of sodium dodecyl sulfate at the fluorite/water interface has been the subject of several studies [5,6]. However, there is a lack of information concerning the change in the wettability of fluorite and its surface free energy under the influence of adsorbed sodium dodecyl sulfate.

Knowledge of the surface free energy can be useful for a better understanding of interfacial phenomena related to flotation processes, particularly the adhesion of air bubbles to mineral particles and the stability of particle–air bubble aggregates.

Since it is not possible to directly measure the surface free energy of a solid phase, many indirect methods have been devised to obtain this value based on e.g. the heat of immersion [7], adsorption [8], zeta potential [9] and contact angle measurements [8,10–16]. The methods based on the application of Young's equation to the contact angle measurements are the most popular [8,10–16]. However, one of the problems in the use of

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Young's equation is the formulation of the interfacial solid–liquid free energy in terms of the surface free energy of the solid and the liquid.

There are various approaches to the formulation of the interaction of interfaces, even though some of them have been criticized [14–16] as not being of general applicability. It seems interesting to test the approach, recently formulated by van Oss et al. [14–16] for the determination of the Lifshitz–van der Waals and the acid–base components of the surface free energy of fluorite covered with a sodium dodecyl sulfate film. For this purpose, the contact angles of five different kind of liquids with the surface of fluorite coated with sodium dodecyl sulfate films were measured.

2. Experimental

2.1. Materials

For contact angle measurements the following liquids were used: water (doubly distilled and deionized from a Milli-Q system) (W), anhydrous glycerol (purity >99.5%, from Merck) (G), formamide (purity >99%, from Merck) (F), diiodomethane (purity >99%, from Merck) (D), and bromoform (purity >99%, from Aldrich) (B). Sodium dodecyl sulfate (SDS) for adsorption was obtained from Merck (purity 99%).

The fluorite samples came from Cordoba (Spain). The mineralogical specimens of fluorite were cut into plates, which were polished using abrasive paper of various grades. The plates were then washed several times in doubly distilled and deionized water, placed in an ultrasonic bath for 15 min, dried at 50 °C for 1 h and kept in a desiccator.

2.2. Measurements

SDS was dissolved in doubly distilled and deionized water and a series of solutions in the range of concentration (C) from 5×10^{-6} to 5×10^{-2} M were prepared. The pH of the solutions was non-controlled and ranged from 5.85 to 6.0.

The fluorite plates were immersed in an SDS solution at a given concentration for 24 h, a time verified to be sufficient to ensure equilibrium of adsorption of SDS at a given concentration. Several other fluorite plates were also equilibrated with doubly distilled and deionized water at pH=2.85. The pH of the water was adjusted using HCl and NaOH solutions. After equilibration the plates were dried at 50 °C for 30 min.

All measurements of advancing contact angle were made at 20 ± 1 °C by the sessile drop method [17] using a camera-computer system described elsewhere [18]. For a given SDS concentration at least 30 measurements

of contact angle were made, with an accuracy within 2°.

3. Results

The results of contact angle measurements for water (θ_W), glycerol (θ_G), formamide (θ_F), diiodomethane (θ_D) and bromoform (θ_B) are shown in Table 1. It is seen from Table 1 that θ_W increases in the range of SDS concentration (C) from 0 to 10^{-3} M to a maximum and then decreases as SDS concentration increases further. However, the contact angles for glycerol, formamide, diiodomethane and bromoform on fluorite surface covered with SDS film also increase in the range of C from 0 to 10^{-3} M and then remain almost constant. For a given concentration in the range from 0 to 5×10^{-3} M, the highest values of contact angles are obtained for water and the lowest for bromoform. However at SDS concentrations higher than 5×10^{-3} M, the highest values are for glycerol and the lowest for bromoform.

It is also seen from Table 1 that the contact angles for all the liquids studied on fluorite covered with an SDS film are higher than those on the surface of 'bare' fluorite. However, the maximum difference between them does not exceed 21° for water, glycerol, formamide and diiodomethane and is equal to 29.9° for bromoform.

4. Calculations

Using the contact angle values for the above-mentioned liquids, it is possible to determine the surface free energy of fluorite covered with SDS film using Young's equation:

$$\gamma_S - \gamma_{SL} - \pi e_L = \gamma_L \cos \theta_L \quad (1)$$

where γ_S is the surface free energy of a solid, γ_L is the surface tension (surface free energy) of a liquid,

Table 1
Measured values of the contact angle for water (θ_W), glycerol (θ_G), formamide (θ_F), diiodomethane (θ_D) and bromoform (θ_B) on fluorite covered with an SDS film

| Concentration (M) | θ_W (°) | θ_G (°) | θ_F (°) | θ_D (°) | θ_B (°) |
|--------------------|----------------|----------------|----------------|----------------|----------------|
| 0.0 | 67.9 | 58.5 | 52.1 | 44.8 | 16.0 |
| 5×10^{-6} | 75.4 | 67.7 | 58.7 | 55.3 | 35.8 |
| 10^{-5} | 77.9 | 69.4 | 61.8 | 58.8 | 39.1 |
| 5×10^{-5} | 78.3 | 70.3 | 62.3 | 60.1 | 42.2 |
| 10^{-4} | 81.2 | 73.1 | 65.4 | 60.9 | 43.1 |
| 5×10^{-4} | 82.3 | 74.1 | 66.2 | 61.5 | 45.9 |
| 10^{-3} | 83.5 | 76.3 | 67.4 | 62.9 | 45.9 |
| 5×10^{-3} | 79.1 | 77.4 | 67.6 | 61.3 | 43.1 |
| 10^{-2} | 75.4 | 78.1 | 67.3 | 61.4 | 42.4 |
| 5×10^{-2} | 72.8 | 79.5 | 67.5 | 61.3 | 39.8 |

γ_{SL} is the solid–liquid interfacial free energy, θ_L is the contact angle and π_{eL} is the spreading film pressure.

Recently, van Oss et al. [14–16] have considered the surface free energy of a solid and a liquid as the sum of the γ^{LW} and γ^{AB} components. The γ^{LW} component results from noncovalent long-range Lifshitz–van der Waals intermolecular interactions and the γ^{AB} component from Lewis acid–base interactions [14–16]. Expressing γ^{AB} as a function of the geometric mean of the γ^+ and γ^- parts originating from the electron-acceptor (Lewis acid) and electron-donor (Lewis base), respectively, the total surface free energy can be written as [14–16]:

$$\gamma = \gamma^{LW} + 2(\gamma^+ \gamma^-)^{1/2} \tag{2}$$

According to the van Oss et al. approach, the interfacial solid–liquid free energy (γ_{SL}) can be expressed as [14–16]:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} - 2(\gamma_S^+ \gamma_L^-)^{1/2} - 2(\gamma_S^- \gamma_L^+)^{1/2} \tag{3}$$

Combining Young’s equation Eq. (1) with Eq. (3) gives:

$$\begin{aligned} \gamma_L(\cos\theta_L + 1) + \pi_{eL} \\ = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_S^- \gamma_L^+)^{1/2} \end{aligned} \tag{4}$$

Introducing into Eq. (4) the contact angle values measured for three different liquids on a given solid surface, the values of γ_S^{LW} , γ_S^+ and γ_S^- can be determined if the π_{eL} value for these liquids is known. Usually π_{eL} is assumed as zero when contact angles are higher than zero [8,14–16].

As the contact angle with the fluorite surface has been measured for five liquids, there are ten different combinations to calculate the γ_S^{LW} , γ_S^+ and γ_S^- components from Eq. (4).

Using in Eq. (4) the γ_L^{LW} , γ_L^+ and γ_L^- values for water, glycerol, formamide, diiodomethane and bromoform taken from the literature [8,16,19] (Table 2) and the contact angles measured for these liquids, the Lifshitz–van der Waals, electron-acceptor and electron-

donor components of the surface free energy of fluorite/SDS film were calculated.

According to our previous paper [20] and van Oss et al. [14–16], the values of γ_S^{LW} , γ_S^+ and γ_S^- calculated from the systems of liquids GDW, FDW, GBW and FBW are affected by the lowest error. The γ_S^{LW} , γ_S^+ , γ_S^- and γ_S^{AB} values calculated from Eqs. (4) and (2), respectively, for these three-liquid systems are shown in Table 3.

Table 3
Values of the Lifshitz–van der Waals (γ_S^{LW}), electron-acceptor (γ_S^+) and electron-donor (γ_S^-) components of the surface free energy of fluorite covered with an SDS film calculated from Eq. (4) and the acid–base component calculated from Eq. (2)

| Concentration (M) | Liquid | γ_S^{LW} (mJ/m ²) | γ_S^+ (mJ/m ²) | γ_S^- (mJ/m ²) | γ_S^{AB} (mJ/m ²) |
|--------------------|--------|--------------------------------------|-----------------------------------|-----------------------------------|--------------------------------------|
| 0.0 | GDW | 32.17 | 1.31 | 12.49 | 8.09 |
| | GBW | 31.30 | 1.43 | 12.61 | 8.49 |
| | FDW | 31.86 | 0.87 | 14.18 | 7.02 |
| | FBW | 30.83 | 1.06 | 14.13 | 7.74 |
| 5×10^{-6} | GDW | 27.11 | 0.95 | 10.48 | 6.31 |
| | GBW | 26.76 | 0.99 | 10.54 | 6.46 |
| | FDW | 27.25 | 1.15 | 9.77 | 6.70 |
| | FBW | 27.01 | 1.20 | 9.76 | 6.84 |
| 10^{-5} | GDW | 25.51 | 1.07 | 9.08 | 6.23 |
| | GBW | 26.11 | 0.98 | 9.02 | 5.95 |
| | FDW | 25.53 | 1.11 | 8.96 | 6.31 |
| | FBW | 26.11 | 0.99 | 8.99 | 5.97 |
| 5×10^{-5} | GDW | 24.77 | 1.04 | 9.28 | 6.09 |
| | GBW | 24.87 | 1.03 | 9.28 | 6.18 |
| | FDW | 24.87 | 1.19 | 8.82 | 6.48 |
| | FBW | 25.02 | 1.15 | 8.83 | 6.37 |
| 10^{-4} | GDW | 24.60 | 0.80 | 8.01 | 5.06 |
| | GBW | 24.98 | 0.75 | 7.97 | 4.89 |
| | FDW | 24.64 | 0.87 | 7.78 | 5.20 |
| | FBW | 25.04 | 0.79 | 7.80 | 4.96 |
| 5×10^{-4} | GDW | 24.38 | 0.75 | 7.54 | 4.76 |
| | GBW | 24.03 | 0.79 | 7.58 | 4.89 |
| | FDW | 24.49 | 0.84 | 7.21 | 4.92 |
| | FBW | 24.17 | 0.89 | 7.20 | 5.06 |
| 10^{-3} | GDW | 23.59 | 0.58 | 7.68 | 4.22 |
| | GBW | 24.01 | 0.53 | 7.64 | 4.02 |
| | FDW | 23.79 | 0.84 | 6.75 | 4.76 |
| | FBW | 24.33 | 0.74 | 6.78 | 4.48 |
| 5×10^{-3} | GDW | 23.46 | 0.22 | 13.12 | 3.40 |
| | GBW | 23.38 | 0.23 | 13.14 | 3.48 |
| | FDW | 23.79 | 0.52 | 11.14 | 4.81 |
| | FBW | 23.94 | 0.50 | 11.15 | 4.72 |
| 10^{-2} | GDW | 22.61 | 0.09 | 18.69 | 2.59 |
| | GBW | 22.26 | 0.11 | 18.77 | 2.87 |
| | FDW | 23.09 | 0.47 | 15.20 | 5.35 |
| | FBW | 23.10 | 0.47 | 15.21 | 5.35 |
| 5×10^{-2} | GDW | 22.01 | 0.01 | 24.00 | 0.98 |
| | GBW | 22.07 | 0.01 | 24.00 | 0.98 |
| | FDW | 22.66 | 0.37 | 18.73 | 5.27 |
| | FBW | 23.17 | 0.31 | 18.78 | 4.83 |

Table 2
Values of the Lifshitz–van der Waals (γ_L^{LW}), electron-acceptor (γ_L^+) and electron-donor (γ_L^-) components of the surface tension of liquids taken from the literature [8,16,19]

| Liquid | γ_L^{LW} (mJ/m ²) | γ_L^+ (mJ/m ²) | γ_L^- (mJ/m ²) | γ_L (mJ/m ²) |
|---------------|--------------------------------------|-----------------------------------|-----------------------------------|---------------------------------|
| Water | 21.8 | 25.5 | 25.5 | 72.8 |
| Glycerol | 34 | 3.92 | 57.4 | 64 |
| Formamide | 39 | 2.28 | 39.6 | 58 |
| Diiodomethane | 50.8 | 0.72 | 0.0 | 50.8 |
| Bromoform | 41.5 | 1.72 | 0.0 | 41.5 |

It can be seen from Table 3 that the values for the four systems of liquids, for a given concentration of SDS, are similar. As a consequence, only the values obtained for the GDW system will be taken into consideration in further discussions.

From Table 3 it is seen that the γ_s^{LW} values decrease as the SDS concentration increases from 0 to 5×10^{-2} M. The γ_s^+ values are small and decrease slightly in the SDS concentration range studied. For a given concentration of SDS, the γ_s^+ values are many times lower than the γ_s^- ones. The electron-donor portion of the acid–base component decreases to a minimum at $C = 10^{-3}$ M and then increases with increasing SDS concentration. However, the acid–base component decreases in the range of C from 0 to 10^{-3} M and then remains almost constant.

As mentioned above, there are only small differences among the γ_s^{LW} , γ_s^+ , γ_s^- and γ_s^{AB} values for a given concentration obtained from different systems of three liquids, including water.

5. Discussion

As calcium fluoride is sparingly soluble in water, the presence of calcium and dodecyl sulfate ions in solution leads to the precipitation of calcium dodecyl sulfate (CaDS) if the solubility product of the latter is exceeded. Therefore on the fluorite surface not only adsorption of SDS molecules but also precipitation of CaDS can take place.

Study of SDS adsorption on the fluorite surface [5] has shown a steady increase in the amount of SDS adsorbed with increasing SDS concentration, up to a maximum value which corresponds to a concentration of SDS in solution equal to ca. 10^{-2} M, and then stays constant. The presence of this maximum suggested that a bilayer of SDS can be formed on the fluorite surface at high SDS concentration in solution.

Shergold [21] concluded from an infrared study of the SDS adsorption on calcium fluoride that a chemisorption process takes place leading to the formation of CaDS. It was stated [5] that the adsorption of DS^- ions up to a monolayer coverage probably involves interactions between the adsorbed sulfate groups and the calcium cations, either at the sites of the calcium fluoride surface lattice or at the adsorbed Stern layer. The attainment of close-packed sulfate groups would also lead to nearly close-packed hydrocarbon chains. This statement is confirmed by the values of the surface free energy components of fluorite covered with SDS film (Table 3). In the range of C from 0 to 10^{-3} M (10^{-3} M is close to the concentration which corresponds to the formation of a monolayer of SDS on the fluorite surface [5]) the γ_s^{LW} component decreases from 32.12 to 24.38 mJ/m². The value of 24.38 mJ/m² lies between

the values of the surface tension for decane and dodecane [22]. Simultaneously a decrease in γ_s^+ , γ_s^- and γ_s^{AB} values is observed, minimum values of γ_s^- and γ_s^{AB} being observed at a concentration of SDS equal to 10^{-3} M.

Once the monolayer is complete, with the hydrocarbon chains directed toward the solution, SDS adsorption probably progresses, at concentrations of SDS higher than ca. 10^{-3} M, by the interaction of the hydrocarbon chain of the adsorbed molecules with the chain of new molecules in a reversed orientation with respect to the surface of fluorite, as suggested by the considerable increase in the γ_s^- portion of the acid–base component (Table 3). In the reversed orientation of the SDS molecules, their polar ‘heads’ are directed outwards the fluorite surface. The presence of Ca^{2+} ions in solution leads to the adsorption of Ca^{2+} at the anionic sites of the interface between the bilayer and the adjacent solution [5], leading to at least partial neutralization of charges, with the rest of the DS^- polar heads strongly hydrated, with molecules of water directing the positive sign to the DS^- anion. Therefore at concentrations higher than 10^{-3} M a slight decrease in γ_s^+ and a strong increase in γ_s^- are observed. However the γ_s^{AB} values are almost constant (Table 3).

The suggestion that some of the DS^- heads are bonded by Ca^{2+} ions is confirmed by comparison of the surface free energy components for the surface of fluorite covered with a bilayer SDS film, that is, for an SDS concentration $\geq 10^{-2}$ M, and for ‘hydrated’ SDS.

Introducing into Eq. (4) the literature values of the contact angle for water (46°), glycerol (56°) and diiodomethane (47.25°) [23] on the surface of a ‘thick’ layer of SDS formed on a glass slide, and the γ_L^{LW} , γ_L^+ and γ_L^- values from Table 2 [7,16,19] for these liquids, the γ_s^{LW} , γ_s^+ , γ_s^- and γ_s^{AB} components of the free energy of the polar heads of the surfactant were calculated. It was assumed, after van Oss and Constanzo [23], that at the interface between the air and the ‘thick’ layer of SDS only ‘hydrated’ polar heads of the surfactant are present. The values obtained are: 27.10, 0.76, 42.63 and 11.41 mJ/m², respectively.

This last value of γ_s^{LW} (27.1 mJ/m²) is not too far off for the apolar tail of the surfactant (the γ^{LW} value for tail is equal to the surface tension of decane or dodecane: 23.9–25.08 mJ/m² [22]) and is about 5 mJ/m² higher than the γ_s^{LW} value for fluorite with a bilayer film of DS^- (Table 3). However, the γ_s^- is more than two times higher than γ_s^- for fluorite coated with SDS film. This indicates that not all DS^- heads in the bilayer are hydrated.

It is commonly known that the most stable mineral particle–air bubble aggregate corresponds to the case in which the surface free energy of the mineral is low and results mainly from the dispersion intermolecular

interactions. As a consequence, on the basis of the above-mentioned measurements and calculations it can be stated that from the flotation point of view, the best conditions for the adhesion of air bubbles to the fluorite particles can be obtained when they are put in contact with an aqueous solution of SDS at a concentration of 10^{-3} M, because in that case a monolayer film of SDS molecules is formed on the fluorite surface, and the contribution of the polar intermolecular interactions to its free energy then has a minimum.

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