

Mineral surface monitoring, understanding and modification at molecular level

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Determination of the adsorbed layer composition and structure at molecular and atomic levels and understanding adsorption mechanisms and dynamics are vitally important for the preparation of surface layers with specific functions. Direct information at a molecular level about mineral surface composition, its structure and surface distribution is crucial to perform an efficient separation processes for mineral beneficiation. This information is equally important for modification of surface properties of industrial minerals for various specific applications such as: fillers, composites, weathering resistance, etc. The understanding of the mechanisms and kinetics of interaction of the first adsorbed organic molecules with mineral surfaces is the fundamental requirement to make possible the prediction and control of the macroscopic surface properties that govern the efficiency of separation technologies or new material formulations. The developed infrared external reflection technique has a very unique ability to study interface phenomena at a molecular level on heterogeneous substrates. The variety, precision and reliability of information about interface phenomena delivered by this technique are superior to other single techniques. The experiments are fast and non-destructive. High sensitivity (starting from 20% of monolayer), in situ collected information in a multiphase system even in the region of a strong absorption of substrate, makes this technique a very valuable experimental tool. The complexity of the recorded reflection spectra, their sensitivity to any variations of the optical properties of all bulk and surface components and their spatial distribution in the system under investigation, are in fact the major strength of the technique. In this presentation a few examples of application of this multidagnostic technique

for monitoring surface modifications of semisoluble minerals for selective flotation will be discussed in detail.

1. INTRODUCTION

Selective separation of mineral components is achieved in flotation process by addition of specific collectors, activators, depressants or modifiers and manipulation of solution conditions (pH, Eh, aeration). All these actions are performed in one aim, to produce different surface properties for valuable mineral components and gangue components. The flotation behaviour of ore components depends on the nature and structure of produced surface hydrophobic or hydrophilic species. The possibility of monitoring surface phenomena at molecular and atomic levels at the interfaces of natural minerals contacted with aqueous solution is vitally important for the understanding of the surface phenomena that govern selective and efficient flotation. This requires application of the appropriate experimental techniques.

Infrared spectroscopy is functional group selective, so it is particularly well suited to detect small changes of the molecular microenvironmental properties as those emerging at the interfaces at a molecular level. Experiments can be performed in situ in both gas-mineral and aqueous solution-mineral interfaces. There is only very gentle interaction of the infrared beam with the examined sample with an energy level lower than 0.3 eV. The recent instrumental development of infrared spectroscopy is contributing significantly to the increased emphasis being placed on molecular level surface characterization. To perform the proper interpretation of reflection spectra for a more detailed picture of the interfacial structure, it is vitally important to combine spectroscopic measurements with a spectral simulation technique. The importance of such combination is reinforced by the anticipated sensitivity of surface infrared absorbance not only to surface concentration but also to adsorbate structure, molecular orientation, surface distribution, lateral interaction, surface diffusion, molecular recognition, and so-called optical effects. Some of them are overviewed in this presentation.

A wide range of mineral optical properties requires specific spectroscopic flexibility to make successful the design and completion of surface characterization experiments. The development of special experimental techniques and procedures was required to follow all important surface processes. This presentation is focused on the recently developed infrared external reflection technique which is a solid basis for tremendous gain in understanding surface and interface phenomena which take place at mineral interface. Single reflection spectra from any mineral surface at three chosen

incident angles and two polarizations are sufficient to propose a reliable three dimensional « picture » of the nature and structure of mineral surface layer. Surface phenomena at multicomponent and heterogeneous mineral samples can be investigated by a spatially resolved spectroscopic procedure. All solid minerals with all known optical properties, from transparent such as fluorite to non-transparent as native gold, could be examined. The unique advantages of the developed method are discussed on different fluorite-aqueous solution systems for which detailed qualitative and quantitative evaluations of the produced surface layers were performed. Fluorite – collector interactions were already subject of intensive studies by infrared transmission [5, 7, 27, 29] and attenuated total reflection (ATR) [3, 6, 9] techniques.

2. EXPERIMENTAL

Materials. The natural mineral samples of fluorite (procured from Ward's) with dimensions of about of 13 x 20 mm² was used in this study. X-ray diffraction confirmed the crystal structure of fluorite with (111) orientation for cleaved samples. In these experiments, two types of fluorite sample were employed: a sample cut and polished before use, and a sample with cleavage plane, prepared immediately before the sample was contacted with oleate solutions. Fluorite was pure with traces of Cl, Si, Mg at a few thousand ppm, and Y, Nb, Fe on a level of a hundred parts per million.

More than 98% pure sodium oleate (cis-9-octadecenoic acid salt), supplied by Aldrich-Chemie, was used. Other reagents used were all of an analytical grade. Distilled water from the Millipore (Milli-Qplus) system was used throughout the experiments.

Adsorption studies. The mineral samples were polished with emery paper and alumina powder. The final polishing was made with the use of 0.05 mm alumina and the polished sample was washed with water. The samples with surface prepared by cleavage were contacted with solution instantly without any additional treatment. Typically the mineral sample was immersed in 200 ml of oleate solution at pH 10.0 ± 0.1 for a period of 1 min to 20 h. The solution concentration varied from 2 x 10⁻⁶ to 5 x 10⁻⁴ M. Immediately after contact with oleate solution, the sample was immersed in water with a pH of 10 for about 1 s and then placed instantly in an FTIR spectrophotometer to record the reflection spectra. Other experimental details can be found in a previous paper [13].

Infrared analysis. The infrared reflection spectra of slab samples were recorded on a Bruker IFS55 FTIR spectrometer equipped with an MCT or DTGS detector and a reflection attachment (Seagull). A wire-grid polarizer was placed before the

sample and provided p- or s-polarized light. These accessories were from Harrick Scientific Co. For each adsorption layer sample usually three reflection spectra were recorded by the use of s- and p-polarized light and different angles of incidence. An optimized optical reflection system permits to detect adsorbed amounts as low as about 20% of a statistical monolayer of calcium oleate on a fluorite surface, which is equivalent to a 0.4 nm thick uniform layer of calcium oleate. The unit of intensity was defined as $-\log(R/R_0)$, where R_0 and R are the reflectivity of the systems without and with the investigated adsorbed layer, respectively. Both sample and reference spectra are averaged over the same number of scans, from 200 to 2000 scans, depending on energy throughput.

Developing of the infrared external reflection technique. One of the major problems to solve was developing proper experimental procedures for collecting representative and useful information directly from mineral surfaces contacted with aqueous solution of organic and inorganic species. The complexity of the system under investigation, heterogeneity of mineral samples and the produced surface species and their low stability require application of the appropriate experimental techniques. During these studies an infrared external reflection technique were developed that let to overcome experimental problems and collect reliable data to monitor and understand surface phenomena at a molecular level.

A schematic diagram of the interaction of electromagnetic waves with a simple three-phase system is presented in Figure 1. For polarization perpendicular to the plane of the incident beam (s - polarization) there is only one electric vector, $E_{\perp Y}$, parallel to substrate plane. Hence, only molecular groups of the adsorbed species having a dipole transition moment parallel to the interface in y direction can interact with the incident radiation and produce an absorbance band $A_{\perp Y}$. For example, in the case of the adsorption of oleate molecule involving both oxygen atoms with the same distance from interface (Figure 1) and assuming a uniaxial system (no difference in orientation in x - y plane), it is expected that the absorbance assigned to the asymmetric vibration of the OCO group, $A_{\perp Y}$, will show the highest value. This results from the most favourable configuration for interaction of the asymmetric stretching vibration of the OCO group and electric field vector $E_{\perp Y}$. For a molecule inclined to interface the interaction is lower and the recorded absorbance will decrease depending on the orientation of this molecular group versus interface. No interaction and obviously no absorbance band due to the asymmetric stretching vibration is observed when the OCO group is turned 90° from the position presented in Figure 1 when the dipole transition moment of the asymmetric vibration of the group becomes vertical to interface. However, at this time the most active will be the symmetric stretching vibration of the OCO group.

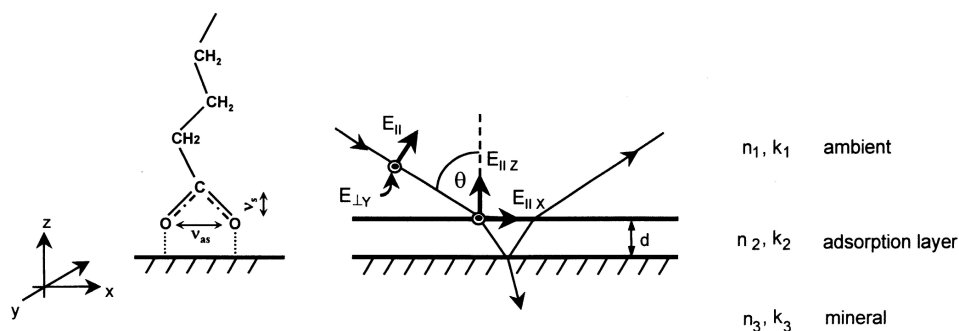


Fig. 1. Schematic diagram of the interaction of electric field vectors in three directions with a simple three-phase system. Oleate molecule with marked dipole transition moments of the asymmetric stretching vibration of OCO group (parallel to interface) and of the symmetric stretching vibration of OCO group (vertical to interface) is also presented.

For parallel polarization (p - polarization) there are two electric field vector components at the interface, one parallel E_{IIx} and one perpendicular E_{IIZ} to the substrate plane (Fig. 1). Therefore, for p - polarization the molecular groups showing dipole transition moments parallel and vertical to interface in x and z directions can produce absorbance bands. Using the example of carboxylic group of oleate molecules at the surface presented in Figure 1 two absorbance bands: the A_{IIx} for the asymmetric stretching vibration of the OCO group and the A_{IIZ} related to the symmetric stretching vibration of the OCO group will be presented in the recorded spectrum. It is also possible to distinguish these two components because they show reverse absorbance, whereas one produces positive absorbance the second one is negative, depending on the angle of incidence. The intensities of the absorbance band recorded for the two polarizations A_{\perp} and A_{\parallel} , depend on the nature of the vibration of the particular molecular group, the amount of surface species, the angle of the incident beam and the orientation of molecules in the surface layer. These together allow determining orientation of each molecular group of the adsorbed collector based on the recorded two spectra at different conditions. The type of the produced surface species and their orientation at interface determine the level of hydrophobicity that governs the selectivity of separation process [12, 15, 16, 18, 19, 21, 22, 25, 26].

The incident infrared beam reflected from mineral surface carries all the information about surface composition and structure. The recorded reflection spectra of the investigated sample at different incident angles and polarizations of the incident beam are sufficient to describe qualitatively and quantitatively the surface phenomena taking place at mineral surfaces. Each spectrum recorded under different optical conditions carries specific spatial information about the

composition and structure of the surface layer. With proper manipulation of the experimental optical conditions (incident angle and polarization) it is sufficient to record three spectra which together give a three dimensional "picture" of the species present at the mineral surface. The technique is based on the comparison of the experimental spectra with the simulated spectra of the hypothetical surface layer with the assumed composition and structure as is shown below. The good agreement (fitting) between all recorded experimental spectra and the simulated ones allows us to evaluate qualitatively and quantitatively the investigated surface structure. Lack of good agreement requires continuation of spectral simulation with different assumed composition, structure or adsorbed quantity.

It is also important to underline that the simulation of isotropic adsorbed layer on natural minerals could be performed before any experiments are carried out [11-17, 20, 25, 26], allowing to predict the best experimental conditions that ensure optimal spectral sensitivity and the maximum confidence in the interpretation of experimental results. This also significantly speeds up the experimental procedure.

The developed technique has unique properties compared with other known infrared techniques such as transmission, diffuse reflectance, attenuated total reflection, or photoacoustic. This technique supported by the spectral simulation of surface species allows obtaining almost all the details about the mineral-aqueous solution interactions, including:

- the nature of the adsorbed products (by which functional group adsorption takes place),
- the adsorbed quantities of different surface products (starting from 20% of monolayer),
- the surface distribution of the adsorbed species (uniform layer or patches with determined thickness),
- molecular orientation of the adsorbed species (orientation of particular functional groups),
- molecular recognition (selective adsorption on specific surface sites),
- dynamic phenomena such as kinetics of adsorption/desorption, stability of surface products, surface mobility of the adsorbed species.

All of this information leads to the determination of the mechanisms and dynamics of surface phenomena and the proposition of surface modifications for numerous applications where mineral surface properties play important roles.

This multidagnostic technique shows important advantages in the study of the surface phenomena on solids: (i) the experiment is fast and non destructive, (ii) any type of mineral sample can be investigated; there is no limitation, from the transparent to non-transparent for infrared radiation (iii) multicomponent and

heterogeneous mineral systems was successfully investigated (spatially resolved spectroscopic analysis).

All of the mentioned features were experimentally evaluated in our original studies. Examples of optical considerations and spectra simulations for different multilayer stratified systems on solid substrate can be found in several papers [1, 4, 10, 12-16, 20, 26, 28, 32].

This multidagnostic technique has been applied extensively to study of interaction of different solids such as: semisoluble minerals [13, 18, 20, 21; 24, 25], and sulfides [14-16, 17, 19] with various aqueous solutions.

3. RESULTS AND DISCUSSION

Surface composition. The reflection spectra of fluorite sample contacted with 9×10^{-6} M oleate solution recorded at the same optical conditions, at an angle of incidence of 45° and p-polarization, after different adsorption times are presented in Figure 2. It can be seen that the amount of the adsorbed surface product, calcium oleate, at first increases and then decreases with an increase of adsorption time. Two absorbance regions, at $3200\text{--}2700\text{ cm}^{-1}$ characteristic of the stretching vibration of the aliphatic chain, and at $1800\text{--}1300\text{ cm}^{-1}$ due to the stretching vibration of the carboxylate group and bending vibration of aliphatic group, are mainly discussed in this work. The amount adsorbed after 1 h is estimated, on the basis of comparison of the experimental with the simulated spectra, to reach about a statistical monolayer (Fig. 2a). At this coverage two well separated absorbance bands at 1575 and 1538 cm^{-1} due to carboxylate stretching vibration are observed, indicating two types of conformations of the adsorbed molecules, unidentate-like and bidentate-like, respectively [13, 18, 20, 21]. Prolongation of the adsorption time results in a gradual increase of the adsorbed amount, after 4 h of adsorption the adsorbed amount was about 4 statistical monolayers (Fig. 2b). After 19 h of adsorption the surface species undergo dissolution and the adsorbed amount is about 0.2 of a monolayer (Fig. 2c). At this very low coverage a broad band centred at about 1560 cm^{-1} due to the asymmetric stretching vibration of the COO^- group was observed. The large broadening of the band indicates a wide distribution of different conformations of the carboxylate groups of the adsorbed oleate molecules. This is in agreement with the expected surface structure where separate oleate molecules as well as very small patches, with a high ratio between the number of external (less oriented) and internal (with high lateral interaction) molecules in the patches, are mainly present. At a diluted concentration of 5×10^{-6} M the adsorbed amount does not exceed about 0.25 of monolayer after 2 and 6 h of adsorption and the recorded spectra are similar to that presented in Figure 2c.

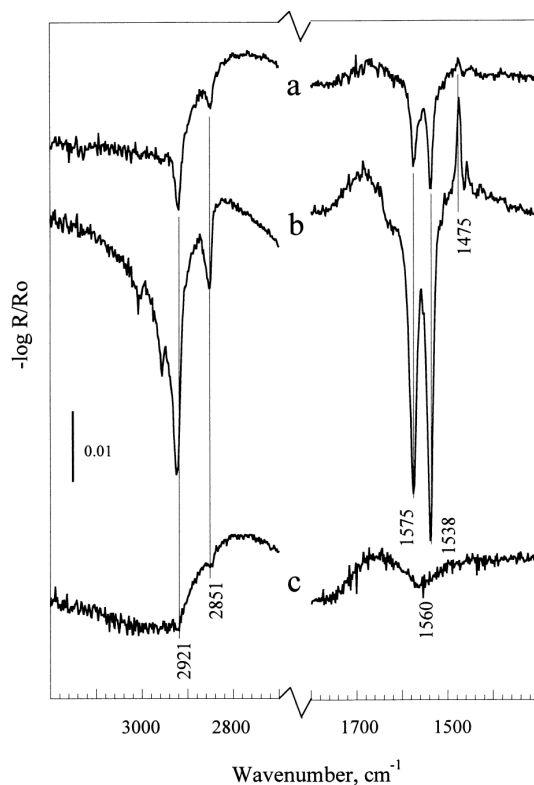


Fig. 2. Reflection spectra of fluorite after adsorption from a 9×10^{-6} M oleate solution, recorded for p- polarisation at angle 45° , after different adsorption times: 1h (a), 4h (b), 19h (c).

At a concentration about 5×10^{-4} M of sodium oleate in solution an additional adsorption product was observed. The carboxylate absorbance region shows a doublet at 1574 and 1537 cm^{-1} , similar to those observed at lower oleate concentrations, and an additional band at 1561 cm^{-1} (Fig. 3a). The presence of the sharp band at 1561 cm^{-1} (fwhm 18 cm^{-1}), which is partly overlapped with the band due to surface calcium oleate unidentate-like form at 1574 cm^{-1} (Fig. 3a), could indicate the presence of sodium oleate in the surface structure. The band at about 1560 cm^{-1} was already assigned [7, 29] to adsorbed sodium oleate by simple comparison with spectrum of pure sodium oleate. The spectroscopic observations (Fig. 3a) allow to conclude that mixed calcium-sodium oleate surface species are produced on mineral surface. It implies that at higher sodium oleate concentrations in solution sodium ions are trapped in the surface calcium oleate structure. Sodium

ions which at first are electrostatically adsorbed on negatively charged fluorite surface are exchanged for calcium ions when the adsorption time is increased.

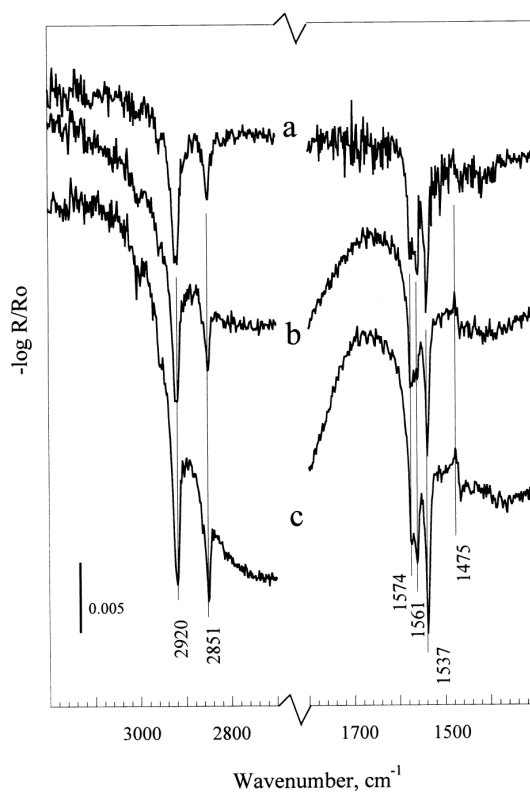


Fig. 3. Reflection spectra of the adsorption layer on fluorite from a 5×10^{-4} M oleate solution, after different adsorption times: 20 min (a), 1h (b), 4h (c). Spectra recorded for p-polarisation at angle of 45° .

At this high concentration the same adsorption products are observed after shorter and also after longer adsorption times. After 4 h of contact with oleate solution there are still sodium ions in the surface structure (Fig. 3c). The total amount of oleate adsorbed on fluorite surface does not exceed a statistical monolayer coverage. It can be proposed that at higher sodium oleate concentrations a steady state is reached with some level of sodium ions usually present in the surface layer. For this explanation the formation of mixed calcium-sodium oleate micelles in solution is the fundamental issue. It was already suggested [30] that the presence of calcium ions in solution will decrease the cmc of sodium oleate which is about 7×10^{-4} M.

Molecular Surface Recognition. An adsorbed monolayer of oleate on fluorite shows two conformations, i.e., bidentate and unidentate, of carboxylate groups (the bands at 1575 and 1538 cm^{-1} , Figs 2 and 3) present in similar amounts. The molecular recognition effect of the adsorption of oleate on fluorite was investigated [18] on mineral surface prepared by cleavage. In an ideal situation, the fluorite cleavage plane (111) has only one type of calcium atoms uniformly distributed with an equal interatomic distance of 0.386 nm . This suggests that in the case of perfect conditions for a well-organized monolayer only one type of carboxylate group, i.e., bidentate form with an absorbance band at about 1537 cm^{-1} , should be observed. The experiments repeated for several cleaved fluorite samples show that the intensity ratio between the unidentate and bidentate conformation (Fig. 4) varied significantly from sample to sample though the solution conditions are the same. The expected bidentate conformation with an orientation angle of 80° is the dominating observed adsorption product at below and nearly monolayer coverage. This indicates that the molecular recognition effect of the surface calcium atoms of fluorite by adsorbed oleate molecules from solution takes place. However, the unidentate conformation is also present. This is explained by the fact that the real surface of the cleaved fluorite on a microscopic scale is not perfect, showing local perturbations, presence of steps, dislocation, etc., although the X-ray diffraction shows an ideal (111) cleavage plane. It was found that the amount of the unidentate conformation is related to the amount of crystallographic defects on the real cleavage plane of the mineral sample.

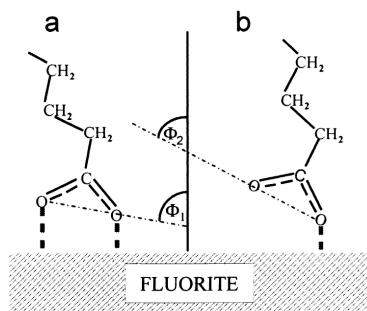


Fig. 4. Two molecular conformations: a – bidentate, b – unidentate of adsorbed oleate molecules.

Adsorption Oleate on Fluorite Sample After Its Different Pre-treatments. The importance of mineral surface structure on the surface layer formation was clearly documented in the earlier publications [13, 18]. In the present study, the influence of mineral surface structure (varied with the help of pre-treatments) on the amount

of adsorbed oleate as well as the structure of surface layer produced was investigated. As a standard treatment, the mineral sample was immersed in oleate solution immediately after polishing and brief washing with water. Obviously polishing of the sample causes distortion of the crystalline structure of the outermost atomic layer of fluorite, which does influence the structure of the adsorbed oleate layer. In Figure 5 the spectra of the adsorption layer produced on fluorite are presented. Experimental conditions for this set of adsorption tests include an initial concentration of 3.3×10^{-5} M at pH 10 for 5 min, with different pre-treatments of the sample. The recorded spectrum (Fig. 5a) is characteristic of submonolayer coverage; it is about 0.7 of a statistical monolayer. A quantitative estimation of the adsorbed amount was made on the basis of the intensity of the aliphatic absorbance bands at about 2920 and 2850 cm^{-1} (Fig. 5) [18]. Two preferential, unidentate- and bidentate-like, conformations of carboxylate groups with absorbance bands at 1574 and 1538 cm^{-1} were observed (Fig. 5) with the intensity ratio of these bands nearly 0.7. If the mineral sample was held 5 min in 200 ml of water at pH 10, and then was immersed in oleate solution, the amount adsorbed (Fig. 5b) was significantly lower (about 50%) in comparison to the spectrum obtained after a standard preparation (Fig. 5a). Moreover, the intensity ratio of the bands at 1574 to 1538 cm^{-1} increased to around 0.85 under the new condition (Fig. 5b).

The different kind of adsorption layer was produced if the mineral sample after polishing was held in water for 30 min before immersion in oleate solution (Fig. 5c). The amount of oleate adsorbed increased significantly to 1.3 of a monolayer, and the intensity ratio of the doublet components was found to be 0.45. The absorbance band at 1536 cm^{-1} was much stronger as compared with the samples with no pre-treatment (Fig. 5a). This indicates a preferential formation of the calcium carboxylate bidentate-like conformation. The high intensity of this band and a strong positive band at 1477 cm^{-1} (Fig. 5c) suggest that the oleate molecules in the adsorption layer are strongly oriented. Similar results were observed for the adsorbed oleate layer produced on the cleaved surface of a fluorite sample. As reported earlier for the cleaved sample [18] the intensity ratio between doublet components decreases to a value about 0.3 indicating the formation of about twice more bidentate- like than unidentate-like conformation. This observation suggests that the mineral surface after 30 min in water undergoes modifications resulting in the formation of a smooth mineral surface similar to that obtained after cleavage.

Conditioning of the mineral sample in water at pH 10 for 10 min in an ultrasonic bath did not produce a well organized surface structure of fluorite. The amount adsorbed was found to be 1.3 times the monolayer coverage (Fig. 5d) and the intensity ratio for the doublet is 0.6. The ultrasonic pre-treatment thus helped to

remove the outermost few amorphous atomic layers of fluorite but is probably too strong to ensure a more organised mineral surface structure.

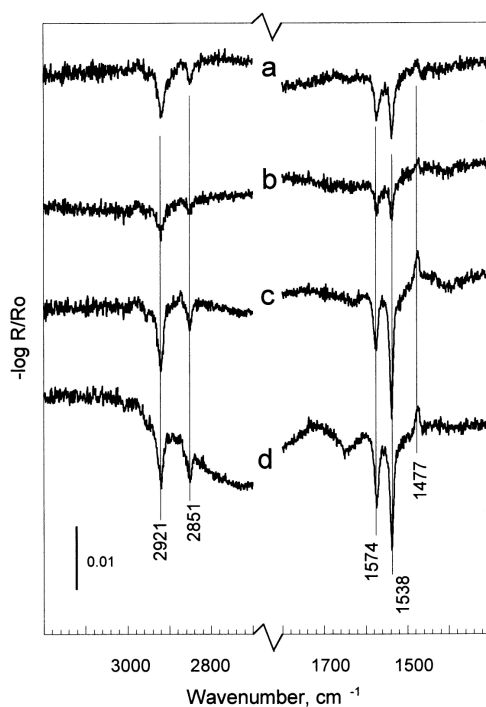


Fig. 5. Reflection spectra of fluorite after 5 min of adsorption from a 3.3×10^{-5} M oleate solution (pH 10), recorded for p-polarisation at angle of 45° , after different pre-treatments: immersion in oleate solution directly after polishing (a), conditioning 5 min in water at pH 10 before immersion in oleate solution (b), conditioning 30 min in water at pH 10 before immersion in oleate solution (c), conditioning 10 min in water at pH 10 in ultrasonic bath before immersion in oleate solution (d).

The positions of the bands of the asymmetric and symmetric stretching vibrations of the CH_2 groups at 2921 and 2851 cm^{-1} indicate a strong lateral interaction between the adsorbed molecules in the surface layer [8, 31]. This observation suggests a compact and rigid surface structure for all fluorite samples. As a result, the adsorbed molecules at the sub-monolayer coverages form a patch-like structure with a strong lateral interaction between the adsorbed molecules. At higher than monolayer coverage the adsorbed species form a rigid structure (Fig. 5c, 1.3 of statistical monolayer).

These results clearly demonstrate that the adsorption kinetics as well as the structure of the adsorbed layer depends strongly on the structure of fluorite surface available for adsorption.

Mechanism of Interaction of Fluorite with Oleate Solution. Kinetics of adsorption of oleate on fluorite at pH 10 shows very interesting features [21]. The maximum of adsorbed oleate are observed at an initial concentration in solution of 3.3×10^{-5} M after 6 hours of adsorption (Figure 6). The amount adsorbed versus time shows also a lower maximum at higher concentrations as shown in Figure 6. These findings indicate complex phenomena taking place at fluorite surface contacted with oleate aqueous solutions, such as: fluorite dissolution and interaction with water, ion exchanges, adsorption/desorption of oleate ions and other oleate aggregates from solution. The surface composition and structure result from these competitive processes. Fluorite immersed in oleate basic solutions shows surface phenomena dependent on initial oleate concentration if other solution conditions (pH, agitation, etc.) are constant.

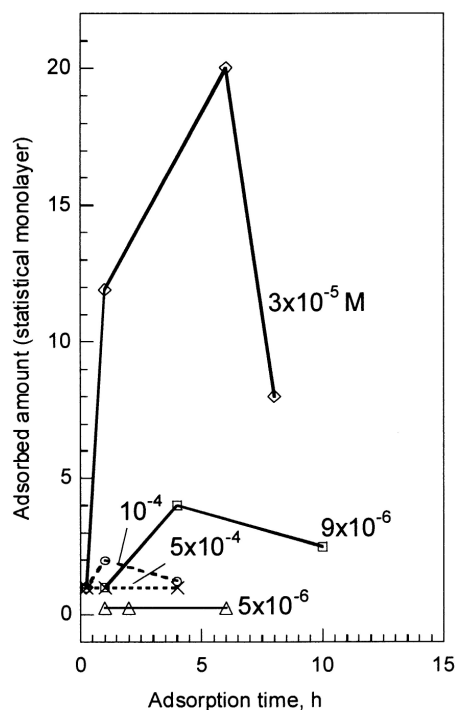


Fig. 6. Kinetics of oleate interaction with fluorite at different oleate concentrations in solution (marked at each curve) revealed by spectroscopic study of the mineral surface.

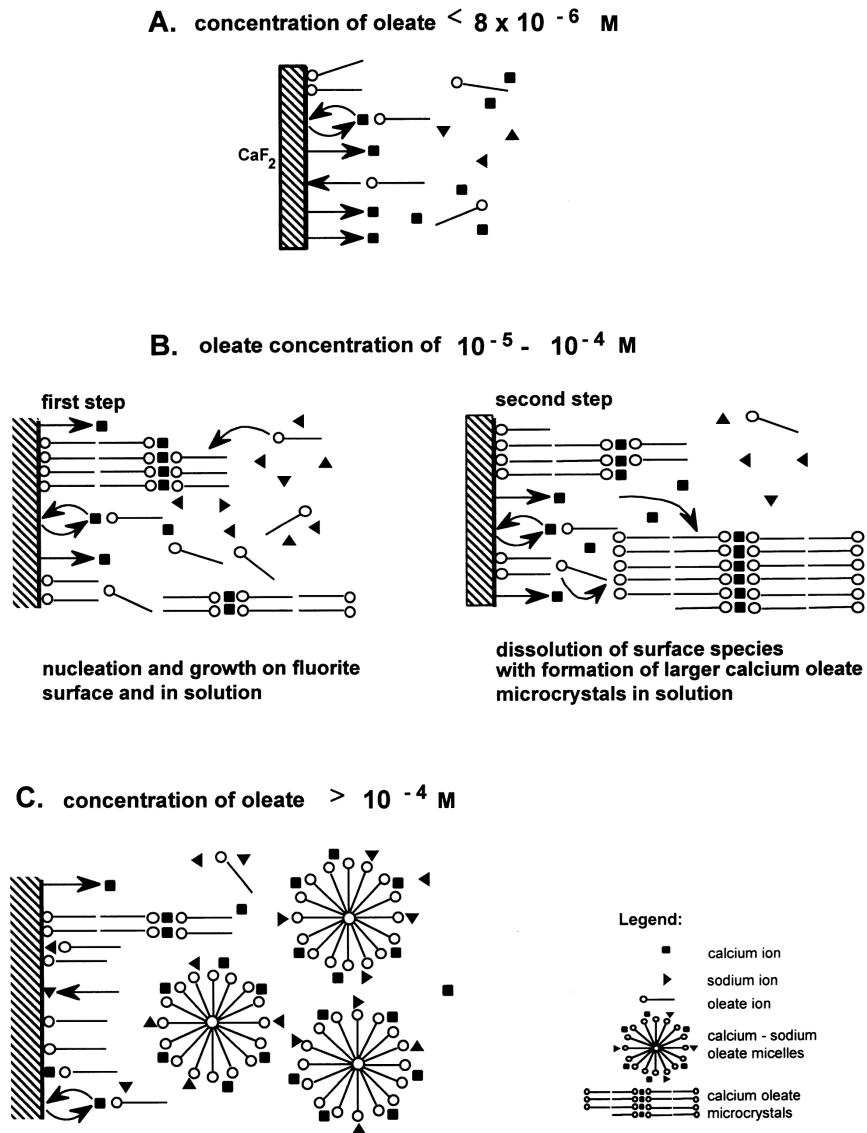


Fig. 7. Proposed mechanism of interactions of fluorite with oleate solution at pH 10 at different solution concentrations.

Based on detailed interpretation of all reflection spectra (not all shown here) three characteristic regions of adsorption related to oleate concentration can be distinguished (Fig. 7). In diluted solutions, below 10^{-5} M, a steady state is

reached. The amount of surface calcium oleate surface species does not exceed 0.3 of a statistical monolayer.

At concentrations between 10^{-5} and 10^{-4} M the most dynamic interactions between fluorite - oleate aqueous solutions were observed. The adsorbed amount shows a maximum. The level of the maximum (up to 20 statistical monolayers) and the adsorption kinetics are strongly related to initial oleate concentration. There are clear evidences that the thicker coverage is produced by a nucleation and growth mechanism. Dissolution of the produced surface calcium oleate with an increase of adsorption time is caused by the Ostwald ripening which transfers the calcium and oleate from fluorite surface to solution where fine particles of calcium oleate are produced. Above oleate concentration of 10^{-4} M the total adsorbed amount of oleate does not exceed monolayer coverage after a long adsorption time. A steady state is reached; micelles are formed in solution, at concentration lower than cmc of sodium oleate due to the adsorption of calcium ions on the micelles, lowering significantly calcium and oleate concentrations in solution. This prevents the formation of thick three-dimensional patches on fluorite surface. Adsorption kinetics is also very sensitive to other changes, as solution hydrodynamics (agitation), or addition of external calcium (ions or/and solid calcium oleate) to oleate solution.

4. CONCLUSIONS

The composition and structure of fluorite surface contacted with oleate solution were already investigated by numerous authors but only the application of the new developed infrared reflection techniques allows significant progress on monitoring and understanding in detail the complex surface phenomena taking place in the system. The presented results of fluorite-aqueous oleate solution interactions show clearly that the fluorite-oleate system behaves differently from a well described classical surfactant adsorption on oxides. This finding allows the explanation of the discrepancies between the previous published results for this system described in the Finkelstain's review [2] as inconsistent and illogical. It is clear that the surface interactions in the system are very complex and dynamic and that there are no simple relations between the adsorbed amount and solution concentration. Equilibrium is not reached under experimental conditions, whereas different steady states can be achieved.

The surface composition and structure depend on the competitive processes taking place at the interface, such as fluorite dissolution and interaction with water, adsorption of oleate ions and other aggregates from solution. If the fluorite is immersed to pure oleate alkaline solution the observed surface phenomena depend on an initial oleate concentration if other solution conditions (pH, agitation, etc.) are constant. Three characteristic regions of adsorption can be distinguished for

which the formation of very fine calcium oleate particles or mixed calcium-sodium oleate micelles in solution are vitally important.

If the other solution conditions are changed, such as solution hydrodynamics (agitation) or an addition of external calcium (ions or/and solid calcium oleate) to oleate solution, they change the adsorption/dissolution kinetics tremendously. The observations underline again the importance of solution chemistry of calcium/sodium oleate (with fluorite as the source of calcium ion) on the composition, structure and stability of the oleate adsorbed layer on fluorite.

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