



Characterization of wettability alteration of calcite, quartz and kaolinite: Surface energy analysis

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ABSTRACT

The paper addresses wettability alteration of calcite, quartz and kaolinite powders, with stearic acid (SA), N,N-dimethyldodecylamine (NN-DMDA) and asphaltene as oil soluble additives. It is a challenge to convert silicate based mineral surfaces from strongly water-wet to more oil-wet. Thermogravimetric analysis (TGA) of the modified powders is used to quantify the monolayer adsorption and is suggesting the possible molecular orientation on the mineral surfaces. Characterization of the mineral surface hydrophilicity/hydrophobicity due to modification is determined by the enthalpy of the water vapor adsorption isotherm. From the quantity and the affinity to water vapor adsorption, a new wettability index is suggested. The enthalpy of water adsorption relative to liquefaction enthalpy shows that stearic acid and asphaltene deeply modify the calcite toward more oil-wet for treated humidified surfaces. It is interesting to observe that although the presence of a water film on quartz and kaolinite surfaces, enhance the adsorption of N,N-dimethyldodecylamine (NN-DMDA), does not eliminate but reduces the asphaltene adsorption.

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1. Introduction

It is well documented that the presence of asphaltene and natural polar components (acids and bases) soluble in the crude oil and their interaction at solid surface are important factors in altering solid surface wettability to more oil-wet and enhanced retention of crude oil in reservoir rock pores [1–5]. The analysis of crude oil from Norwegian continental shelf showed that carboxylic acids with carbon number ranging from 16 to 20 are the most abundant acids in the crude oil, thus they can play a critical role in oil recovery by water flooding [6]. The systematic study on the stability of aqueous films between oil and silica showed that in the presence of amine, below a defined pH, the aqueous film becomes unstable and oil phase can spread at the silica/water interface [7]. The heavy ends in the crude oil (asphaltene and resins) also contain surface active components which adsorb on reservoir rock and clay minerals [8]. Adsorption of asphaltene on clays can change the wettability and reduces swelling, effective surface area and cation exchange capacity [9]. Liu and Buckley (1994) also reported that the wettability alteration has often been ascribed to the adsorption of asphaltene,

which was further supported by the observation that de-asphalted crude oils cannot adsorb on minerals surface [10,11].

Hamouda and colleagues in series of work dealing with calcite, water and oil revealed that the adsorption of long chain fatty acids on the calcite surface depends on several factors such as chemical structure of fatty acid, pH, brine composition and temperature [5,12–16]. They have also shown a synergistic effect between asphaltene and fatty acids for alteration of chalk to more oil-wet [5]. Recent publications for wettability characterization using surface energy data shows that combination of thermogravimetric analysis (TGA), microcalorimetry and vapor adsorption isotherms are suitable alternative techniques comparing to contact angle, relative permeability and capillary pressure measurements [12,13,17–20].

Thermo gravimetric analysis provides a quantification of the adsorbed material as well as a measure of the adsorption enthalpy. This method has advantages comparing to other techniques (such as spectroscopy) since it can be applied to all organic adsorbates and it does not require aromaticity or a certain functional group for detection [21,22].

Microcalorimetry can be used also to characterize a surface in terms of hydrophilicity/hydrophobicity by measurement of interaction energy between adsorbed water vapor and solid surface [17,23,24]. The obtained values can be compared to the water latent heat of liquefaction and from this comparison, the wettability

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alteration of solid surfaces and the heterogeneity/homogeneity of surface modification can be assessed [25].

From the shape of adsorption isotherms one can determine the wetting state of a solid [19,26]. For a high energy solid surface, the amount of adsorbed vapor is infinite at saturation pressure, and the area under the adsorption isotherm is large. Such behavior is defined as complete wetting behavior when vapor at saturation pressure forms a macroscopically thick film and spreads on the solids [19]. For a low energy surface, the area under saturation isotherm is finite and the amount of vapor adsorption is low. This case is defined as partial wetting when a thin film (with the thickness of one or few monolayers) is formed at saturation [19].

The combination of these techniques is presented in this work to draw possible reliable conclusions on the adsorption of asphaltene, natural surfactant (fatty acid and amine) and co-presence of these organic components over carbonate, silicate and clay minerals. The purpose of the work is to investigate the consequence of surface modification with organic compounds on hydrophilicity/hydrophobicity of minerals surface in the presence or the absence of humidity. Characterization of the wettability of modified minerals has been performed using a dimensionless index.

2. Materials

2.1. Solids

Three types of powdered solid were used in this work; quartz, calcite and kaolinite which represent sandstone rock, carbonate rock and clay minerals, respectively. Quartz and kaolinite were supplied by Sigma–Aldrich and their chemical compositions are SiO_2 and $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, respectively. Calcite was provided by Norwegian Talc AS.

2.2. Liquids and additives

Normal decane ($n\text{-C}_{10}$) and toluene (C_7H_8) are used in this study as base solvents for added polar components. Both liquids were supplied by Chiron AS in HPLC grade (purity >99%). The water was purified through Milli-Q Millipore and was used in adsorption isotherm experiments. Stearic acid (SA) and N,N-dimethyldodecylamine (NN-DMDA) were used as oil soluble additives to mimic natural fatty acid and amine in the crude

Table 1
Polar components.

Components	Supplier and purity	Structural formula
Stearic acid (SA)	Aldrich $\geq 99\%$	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
N,N-Dimethyldodecylamine (NN-DMDA)	Fulka $\geq 99\%$	$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_2$

oil. Their structural formula, suppliers and purities are shown in Table 1. Asphaltene precipitated from crude oil in excess of normal heptane (1:40) is used to represent the polar and heavy fraction of crude oil. After 48 h of equilibrium between crude oil and normal heptane, the solution was filtered through a 0.22 mm filter (Millipore) to separate the asphaltene and then asphaltene was dried for 24 h under vacuum at room temperature.

3. Methods

3.1. Surface modification

Two types of modification were carried out. One is dry modification where both solid and liquid were dried and the other is the wet modification. In the first case the powder was dried at 150°C for at least 48 h under vacuum condition and the liquids (normal decane or toluene) were dried over molecular sieves (0.4 nm) for one night before modification. In the second case the dried solids were first placed in a desiccator in the presence of a saturated solution of K_2SO_4 for a period of 10 days at 25°C . The saturated solution of a salt provides constant relative humidity and vapor pressure [27]. For K_2SO_4 solution, the relative humidity reaches near 97% at 25°C which provides a sufficient amount of water on the solid surface to investigate its effect on subsequent adsorption of organic adsorbates [12]. For both types of modification, 0.01 M solution of stearic acid (SA) and N,N-dimethyldodecylamine (NN-DMDA) in normal decane were prepared. To investigate the role of asphaltene and co-presence of asphaltene and natural surfactants on wettability alteration of minerals, 0.35 wt% of asphaltene was dissolved in toluene and added to 0.01 M solution of stearic acid and N,N-dimethyldodecylamine (NN-DMDA).

Two grams of powder were weighted in stopper glass tubes and 20 ml of solution were added. The samples were stirred with a slowly rotating agitator (50 rpm) for 24 h. This period of time was

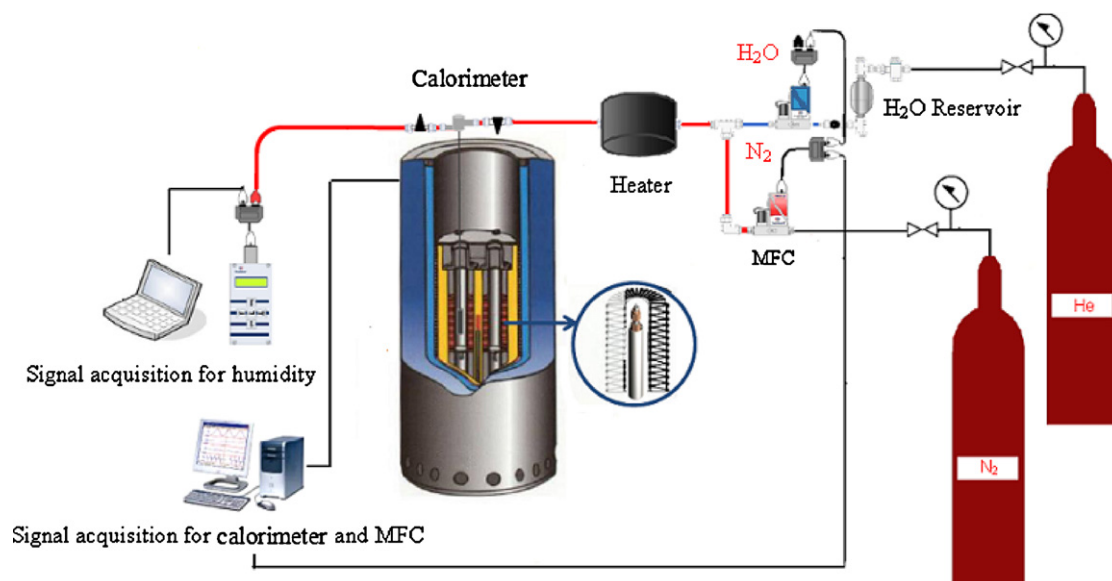


Fig. 1. Schematic representation of the microcalorimetric set up.

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