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Wettability of calcite and mica modified by different long-chain fatty acids (C_{18} acids)

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Abstract

The effect of long-chain fatty acid adsorption on the wetting states of calcite and mica powders is investigated. The selected long-chain fatty acids are saturated or unsaturated aliphatic acids (stearic acid and oleic acid, respectively) and naphthenic acids with saturated or unsaturated aromatic rings (18-cyclohexyloctadecanoic acid and 18-phenoloctadecanoic acid, respectively). The amount of irreversibly adsorbed acid is determined by thermogravimetric analysis. The affinity of water and *n*-decane for these samples before and after modification is deduced from their adsorption isotherm and microcalorimetry. Thermodynamic analysis of surface pressure and spreading tension are performed based on adsorption isotherms. The enthalpy versus coverage curve for water adsorption and its comparison to liquefaction enthalpy is shown to be a meaningful method for characterizing the wettability of a surface. The naphthenic acid with unsaturated aromatic ring deeply modifies the calcite to an oil-wet state. The mica powder was not as strongly modified as calcite by these acid molecules.

Keywords: Wettability; Calcite; Mica; Long-chain fatty acids; Adsorption isotherms; Microcalorimetry; Energy of adsorption

1. Introduction

Many researchers in the area of wettability have shown that the presence of polar components (acids or bases) soluble in crude oil and their interaction at solid surfaces are key factors in altering solid surface wettability to a more oil-wet state, thus increasing the retention of crude oil in the reservoirs [1–4]. The adsorption of these molecules depends on factors such as their chemical composition and the nature of the solid surface and the environment [5–7]. Based on these works, it seems that long-chain fatty acids are the major components responsible for wettability alteration in carbonate reservoirs. Some of these factors were investigated in a previous study focusing on the wettability alteration in carbonate reservoirs [8]. The objective of the present work is to determine the type of long-chain fatty acids that are the most responsible for such behavior. The recently published patent [9] on the analysis of crude oil from the Norwegian continental shelf showed that carboxylic acids with carbon number ranging from 16 to 20 are the most abundant acids in the crude oil. Therefore this work focuses on fatty acids within this range of carbon numbers.

The amount of adsorbed acids on the surface can be detected by different methods. The solution depletion method with solution composition analysis by UV or IR is the most commonly used. To obtain a direct and reliable amount of irreversibly adsorbed acids on the surfaces, thermogravimetric analysis of the solid surface was used in this work [10]. One of our objectives is to analyze the solid surfaces in term of wettability or hydrophilicity/hydrophobicity. The change in surface energy is considered a controlling parameter whose value can help to predict the solid wettability. When such study is performed with powders, vapor adsorption isotherm determination and microcalorimetry are considered as suitable alternative techniques to other available techniques such as contact angle measurement or capillary rise [11,12]. The surface pressure can be derived from the adsorption isotherm through the integration of the Gibbs equation, whereas microcalorimetry can be used to determine the variation of internal energy during the adsorption

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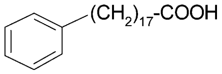
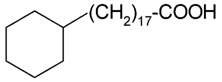
Table 1
Chemical analysis of calcite and mica powders

				Chemical analysis of calcite					
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O	Na_2O	MnO	P_2O_5
0.09	<0.01	<0.01	0.007	0.45	54.74	<0.003	<0.1	<0.002	0.03
				Chemical analysis of mica					
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O	Na_2O	MnO	P_2O_5
47.34	31.67	3.59	0.26	0.64	0.1	9.33	0.85	0.15	0.04

Table 2
Organic components

Organic component	Supplier and purity	Structural formula
Stearic acid (SA)	Aldrich, >98.5%	$CH_3(CH_2)_{16}COOH$
Oleic acid (OA)	Fluka, >98%	$C_8H_{17}CH{=}CH(CH_2)_7COOH$
18-Phenoloctadecanoic acid (PODA)	Chiron A/S, >98%	
18-Cyclohexyloctadecanoic acid (CHOA)	Chiron A/S, –	

process [13]. The combination of techniques allows drawing reliable conclusions on the adsorption of long-chain fatty acids onto minerals and its consequences for their wettability.

2. Materials

2.1. Solids

Two powdered solids were used, mica and calcite, which represent sandstone and carbonate reservoirs, respectively. Both solids were supplied by Norwegian Talc AS. The chemical analyses of samples measured by the NGU (Norwegian Geological Survey) are reported in Table 1.

2.2. Liquids and additives

Two liquids were used: an apolar liquid, *n*-decane, in HPLC grades (purity > 99%) supplied by Aldrich and a polar liquid, water. The water was purified through a Milli-Q Millipore system.

Four long-chain fatty acids were selected. Their structural formulae, suppliers, and purities are shown in Table 2.

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 solids were dried at 150 °C for at least 4 h under nitrogen flow before modification by acids, and the liquid (*n*-decane) was dried over molecular sieves (0.4 Å) for 1 night before use. In the later 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. The saturated solution of a salt provides constant relative humidity [14]. In the case of K_2SO_4 solution, the relative humidity was fixed at 97% at 25 °C, which provides a sufficient amount of water on the solid surface to investigate its effect on subsequent adsorption of fatty acids. For both types of modification 0.01 M solution of each acid in *n*-decane was prepared. Two grams of solid were weighted in stopper glass tubes and 20 ml of solution were added. The samples were stirred with a slowly rotating agitator (45 rpm) for 20 h. This period of time was found to be sufficient to reach equilibrium as reported in literature [7]. The suspension was centrifuged for 30 min at 4000 rpm/min. The solid phase was separated from the liquid, redispersed in *n*-heptane for washing, and centrifuged again for 10 min at 4000 rpm. Finally, the solid was dried under air at 25 °C.

Table 3
BET surface area (m^2/g)

	H_2O	N_2	$C_{10}H_{22}$
Calcite	1.83	3.94	1.23
Mica	8.96	8.3	8.44

3.2. Gas and vapor adsorption isotherms

The specific surface areas of the solids were determined by nitrogen adsorption at 77 K (Micromeritics ASAP 2010 apparatus) by applying the BET method with a molecular cross-sectional area of 16.2 $Å^2$ for nitrogen [15]. The results are presented in Table 3. The BET method was also applied to the water and *n*-decane adsorption isotherms, which were determined with a homemade apparatus based on a symmetrical commercial vacuum microbalance from Setaram [16]. The molecular cross-sectional areas were fixed to 10.5 [15] and 74.9 $Å^2$ [17] for water and *n*-decane, respectively.

Water and *n*-decane vapor adsorption experiments were performed for both unmodified and modified samples. The outgassing of solid samples was performed under vacuum (10^{-5} Torr) at 150 °C until a constant weight was reached. The