

ROCK WETTABILITY EVALUATION BY IMMERSION CALORIMETRY

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ABSTRACT

In the present paper, we are discussing an approach for wettability evaluation by the measurement of enthalpy variation related to the immersion process. From calorimetry it is possible to get the variation of state functions like internal energy (at constant volume) or enthalpy (constant pressure experiments) related to the wetting process. They cannot be used directly to predict wetting properties while Gibbs free energy variations can be used for that. In the immersion process, the variation of the Gibbs energy is equal to the variation of the surface energies of the system.

In the calorimetry experiments, a core sample is immersed in a liquid or a liquid vapour and the associated small heat effect (immersion enthalpy) is measured with a calorimeter. Measurements of Gibbs free energy variation at immersion of a surface (i.e. a porous media like a rock) into water and oil phases allows one to determine wettability. Feasibility study of such approach has already been done. Comparison of specific surface area measured by the proposed calorimetry approach and well known Brunauer-Emmett-Taylor (BET) method was used for verification of the approach and published in our previous SCA papers [1]. The current paper is devoted to implementation and testing of the proposed technique for wettability evaluation. Performed test experiments with immersion of pure substances demonstrated encouraging results.

INTRODUCTION

Wettability is the major factor controlling the flow and distribution of fluids at different scales, from a single pore to oil reservoir. Wettability is determined by the physicochemical interactions of reservoir fluids with each other and with the heterogeneous surface of the formation. Due to the complexity of investigation of surface interactions no universal method for wettability determination exists up to date, which drives continuous research on this theme.

The wettability of strongly water-wet or strongly oil-wet reservoirs may in some cases be inferred from log analysis, while core analysis methods are implemented for a more accurate wettability characterization. Standard core analysis methods, such as US Bureau of Mines (USBM) and Amott-Harvey methods or a combination of them are considered as industry standards for wettability estimation in core analysis. Both of the methods simulate reservoir processes during oil recovery and are based on the measurements of

the displacement efficiency of oil by water and water by oil during spontaneous imbibition and/or forced fluid displacements in the centrifuge. As an outcome of these tests as a rule, just one number is obtained: between -1 and 1 for the Amott test and between $-\infty$ and $+\infty$ for the USBM test. These methods give only qualitative characteristic of wettability and have some limitation on permeability (more than 10 mD for the Amott test) and shape of the sample for analysis (cylinder made with consolidated rock).

We propose an approach for qualitative and quantitative wettability evaluation based on immersion calorimetry [1-5]. Immersion occurs whenever a solid surface is exposed to liquid or gas [6]. In the immersion calorimetry experiments, a core sample is immersed in a fluid and the associated small heat effect (immersion enthalpy) is measured with a calorimeter. The heat effect is related to the alteration of the surface energy of the rock surface during the immersion process. Depending on the choice of initial conditions of the rock surface, the associated heat effect is related either to interaction of an adsorbate molecule with the surface (i.e. wettability of the surface) or only to size of the surface, i.e. specific surface area (SSA) of the sample. As a result, two important petrophysical parameters can be measured by an accurate thermodynamic technique with calorimetry.

The total heat that evolves during an immersion experiment also known as the enthalpy of immersion ΔH is related to the variation of Gibbs free energy ΔG of the system by the following expression: $\Delta H = A(\Delta G - \frac{T\partial\Delta G}{\partial T})$, where A is the sample surface area and T is temperature. The variation of the Gibbs energy of the system is in fact equal to the variation of the surface energy of the system. If the solid is immersed from the vacuum conditions: $\Delta G = \gamma^S - \gamma^{SL}$, where γ^S is the free energy at the solid-vacuum interface (i.e. surface tension) and γ^{SL} is the solid-liquid interface surface tension.

It is well known that wetting deals with three materials: solid, liquid and gas or a second liquid. When we are interested in the interaction between two liquids near a surface, two independent immersion experiments should be performed with two liquids (brine and oil for example) at the same pressure and temperature. The initial state of the surface should also be the same for both experiments. Contact angle between two liquids $L1$ and $L2$ on a solid surface can be obtained from Young's equation [2]

$$\cos\theta = \frac{k^{L1}\Delta H_{imm}^{L1} - k^{L2}\Delta H_{imm}^{L2}}{A\gamma^{L1L2}},$$

where γ^{L1L2} is the liquid 1 to liquid 2 interface surface tension and

$$k = [\gamma^S - \gamma^{SL}] / [(\gamma^S - \gamma^{SL}) - \frac{T\partial(\gamma^S - \gamma^{SL})}{\partial T}] \approx \gamma^{LV} / (\gamma^{LV} - \frac{T\partial\gamma^{LV}}{\partial T}).$$

Coefficient k for each liquids can be obtained from the measurements of the liquid-vapour surface tensions γ^{LV} of the liquid at different temperatures, which are easily obtained from literature or measured with commercially available equipment. The surface area of the sample should be determined separately either by some other method, such as

e.g. BET method [7], or again, with the use of the differential scanning calorimetry (DSC) by the modified Harkins-Jura method [1, 8].

EXPERIMENT DESCRIPTION

Immersion calorimetry can be performed on a wide variety of core sample types: from high permeability to low and ultra-low permeability rock, core cuttings and crushed core and/or powders.

The solids used in this study were selected to have expected wettability ranging from water-wet to oil-wet. Solids used were powders: a variety of borosilicate glass (CPG) samples of varying size (pore \O : 50 – 300 nm), carbon powder (99% purity) and calcium carbonate (99% purity). The studied samples were dried before experiments, under vacuum at 90°C during 24 hours. The fluids used were HPLC grade ($\geq 99.9\%$): deionized water and cyclohexane.

Micro calorimeter [1-3] was used for measurement of the heat effect due to immersion of a rock internal surface into a liquid. For our experiments we used a specially designed cell [1] that provides: 1) a means for connecting the sample to the vacuum for pre-treating of the sample; 2) connection to a vapor source system to fill the sample with an sorptive fluid ; 3) that both the immersion liquid and the sample are in the same calorimetric cell during the experiment in order to exclude mass-heat transfer during immersion of the sample; 4) jointing of both volumes with the sample and the liquid with minimal and reproducible side heat effect (wetting of the cell itself, opening the valve, pressure drop etc.) for being systematically accounted. The cell was designed for cylindrical sample of $\sim 1 \text{ cm}^3$ volume.

The proposed workflow includes two independent immersion experiments with the two different liquids. Prior to the experiments, the studied sample should be dried and vacuumed to remove any liquid and adsorbate from pores. After finalization of the immersion experiment with the first fluid, and prior to experiment with the second fluid, the sample should be dried and vacuumed again.

An experiment is started from “zero” pressure condition. The preliminary evacuated cell containing the sample is filled with the wetting liquid to immerse the sample surface. Immersion heat effect due to wetting of the cell itself (dark curve in Figure 1) should be removed from the measured heat effect due to wetting of the sample into the cell (red curve in Figure 1) for deriving of heat effect due to wetting of the studied sample. The heat effect due to sample immersion is immersion energy and is used for surface wettability evaluation. The duration of the immersion experiments depends on porous media permeability. From our practice, it takes several hours, typically 1 to 2 hours for immersion in cyclohexane and up to 4 hours for water immersion.

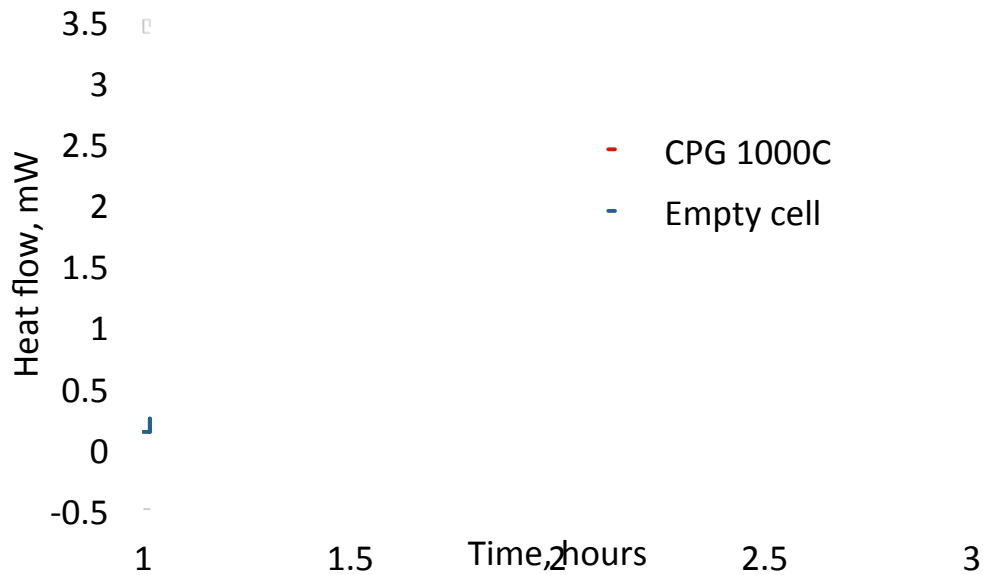


Figure 1. Typical immersion DSC heat flow curve measured with calorimeter on blank cell (dark curve) and cell with tested sample (red curve).

After completing the experiment with the first fluid (water in our case) prior to immersion into the second fluid the sample should be dried again. Drying during 24 hours at 105°C are enough if powders or core cuttings (without significant amount of clays) are used. To speed up the process, we split the sample into two portions for experiments with both fluids. The experiment with the second fluid should be performed at the same temperature and pressure.

RESULTS

Prior to wettability experiments, we tested calorimetry method for SSA measurement [1] with cyclohexane. The obtained SSA values were in rather good agreement with BET measurements (Table 1) especially for hydrophobic carbon powder and calcium carbonate that is intermediate wet. It means that the surface of studied sample was covered by at least a monolayer of the liquid during first step of adsorption-immersion experiment. Thus, immersion calorimetry can be used for SSA of both hydrophilic and hydrophobic samples. There is no need to cool the sample in liquid nitrogen that can destroy the sample [9]. This feature is one of the main advantages of calorimetry approach over the BET gas adsorption method.

After successful determination of SSA, we tested our workflow on the same pure and homogeneous powders of calcite, carbon, and controlled pore glasses (CPG) of different pore sizes. Test results are presented in the table below.

Table 1. Specific surface area and wettability of powders.

Sample	Surface Area by Nitrogen Adsorption, m ² /g	Surface Area by Water Adsorption, m ² /g		Surface Area by Cyclohexane Adsorption, m ² /g	Wettability $\cos\theta$ (θ)
	BET method	BET method	by immersion calorimetry	by immersion calorimetry	
CPG 500C (pore \emptyset : 50 nm), borosilicate glass	49.2 - 54.3	45.5	43.8	51.1 - 53.7	1.80 (0 ⁰) <i>Absolutely water-wet</i>
CPG 1000C (pore \emptyset : 100 nm), borosilicate glass	26.6 - 27.6		23.2		1.68 (0 ⁰) <i>Absolutely water-wet</i>
CPG 3000C (pore \emptyset : 300 nm), borosilicate glass	8.4 - 9.5		9.3	10.1	
Calcium Carbonate	3.8	1.59	1.2; 0.96	3.1	0.46 (62 ⁰)
Carbon	1.75 – 2.0	1.47	1.0	2.3	0.31 (71 ⁰)

As it can be seen from Table 1, derived cosine of the contact angle (θ) calculated by Young's equation for pure hydrophilic glass powder is greater than 1. In other words: $\gamma^{SL1} > \gamma^{SL2} + \gamma^{L1L2}$, where L1 is cyclohexane and L2 – water. It corresponds to complete wetting described by Anthanase Dupré and Paul Dupré [10, 11] with introducing the spreading parameter $S = \gamma^{SL1} - (\gamma^{SL2} + \gamma^{L1L2})$. When $S > 0$, the liquid wets the surface completely without forming a contact angle (complete wetting). When $S < 0$, partial wetting occurs and Young–Dupré equation has physical solutions for θ .

Derived contact angle of carbon is in range of intermediate wettability while we expected to obtain these values close to 95⁰ (oil-wet range) [12]. The same tendency is observed for calcite. It can be explained by such phenomena as roughness [13] as well as possible presence of a precursor film [13]. By the way, the immersion calorimetry method provides at least qualitative information on wettability that can be estimated for any shape of studied sample (including core cutting) and types of the rock (including low and ultra-low permeable rock).

CONCLUSION

Immersion calorimetry allows measurement of wettability of a core sample by two identical experiments with independent immersion into the two individual fluids. The main advantages of the proposed technique are possibility of evaluating wettability state of both core plugs and cuttings (including powders) with wide range of permeability: from conventional reservoir rock to micro Darcy tight rocks and nano-Darcy shales.

The technique was tested on artificial powders with known properties. Acceptable qualitative correspondence between the measured and reference contact angles was obtained for studied samples. Close values of contact angles measured on two controlled

pore glass samples with significantly different pores and SSA but the same surface properties prove the capability of the procedure.

The calorimetry technique should also be tested on a set of natural rock samples (core plugs) with wettability measured using existent commercial methods.

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