# ROCK SURFACE CHARACTERIZATION BY IMMERSION CALORIMETRY: WETTABILITY AND SPECIFIC SURFACE AREA

E. Dyshlyuk[1], D. Korobkov[2], V. Pletneva[2]
Schlumberger, [1-]Dahran Carbonate Research and [2-]Moscow Research Center

*This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in St. John's Newfoundland and Labrador, Canada, 16-21 August, 2015*

## ABSTRACT

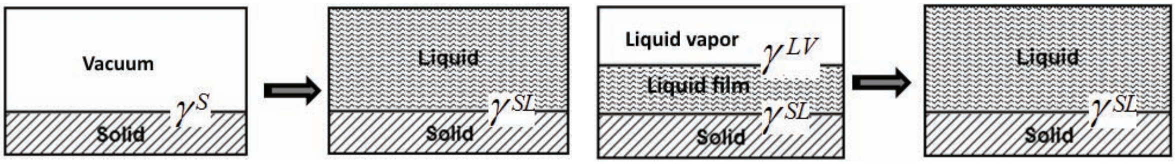
Petrophysical properties such as wettability and surface area control hydrocarbon storage and transport properties. In the work being reported in this paper, we present the theoretical aspects as well as experimental technique and results of testing and validating a proposed calorimetry technique for specific surface area and wettability characterization. Identical immersion calorimetry experiments with slightly different initial conditions of the sample are analyzed to obtain these two properties of a core sample. Validation of the experimental technique is an important step, which is performed in this work by comparing the surface areas of the samples obtained by the proposed technique with the surface area obtained by the well-known Brunauer-Emmett-Taylor (BET) gas-adsorption technique. Surface area measurements are performed on a set of core plugs and reference samples, including hydrophilic and hydrophobic powders of pure substances, minerals, and clays.

## INTRODUCTION

This paper is a continuation and enhancement of our previous studies on rock characterization by calorimetry [1, 2]. The differential scanning calorimetry (DSC) technique, which is used in the current study, allows one to measure transient differential heat flows between the two cells of a differential scanning calorimeter. Implementation of the DSC technique to laboratory core analysis can provide a significant amount of valuable information with unprecedented accuracy. In particular, the DSC technique can help to determine wettability heterogeneity of a core sample from adsorption calorimetry [2] pore size distribution from the thermoporometry method, as well as the surface area and average wettability state of a rock from immersion calorimetry [1].

In the immersion calorimetry experiments, a core sample is immersed in liquid 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. Immersion experiments are commonly conducted with the use of a sealed glass ampule containing the sample, which is broken inside the calorimeter cell filled with liquid. After the ampule is broken, liquid fills the surface of the sample; thus, changing the surface energy of the sample. Depending on the choice of initial conditions of the rock surface, the associated heat effect is related either to the wettability state of the surface or to the surface area 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, $\Delta H$, during an immersion experiment or the enthalpy of immersion is related to the variation of the Gibbs free energy ($\Delta G$) of the system by the following expression: $\Delta H = S\left(\Delta G - T\partial\Delta G/\partial T\right)$, where $S$ 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 a solid is immersed from vacuum conditions, then $\Delta G = \gamma^{S} - \gamma^{SL}$ , where $\gamma^{S}$ is the solid-vacuum interface surface tension and $\gamma^{SL}$ is the solid-liquid interface surface tension (Figure 1a). At the same time, if a liquid film is on the surface of the sample prior to immersion, the variation of the Gibbs energy is given by $\Delta G = \left(\gamma^{SL} + \gamma^{LV}\right) - \gamma^{SL} = \gamma^{LV}$ (Figure 1b), where $\gamma^{LV}$ is the liquid-vapor interfacial surface energy/surface tension.



$\Delta G = \gamma^{S} - \gamma^{SL}$

(a) Wettability characterization: $\cos\Theta$

$\Delta G = \left(\gamma^{SL} + \gamma^{LV}\right) - \gamma^{SL} = \gamma^{LV}$

(b) Surface area characterization: $S$

**Figure 1**. Illustration of the two immersion experiments—(a) immersion from vacuum for wettability characterization;(b) immersion after precoverage of the sample with a liquid film for surface area characterization.

The first experiment (solid is immersed from vacuum conditions) can be used to characterize the wettability of a sample [1, 3, 4]. Since the surface tension of a liquid, $\gamma^{LV}$, (e.g., water surface tension ~ 72 mN/m at 25°C) and its variation with temperature, $\partial\gamma^{LV}/\partial T$, can be measured or are known from the literature, the second experiment (also known as the modified Harkins-Jura procedure [5], which was developed after the original work [6]) can be used for sample surface area measurements as follows :

$$S = \Delta H \Big/ \left(\gamma^{LV} - T\partial\gamma^{LV}/\partial T\right). \tag{1}$$

Although the assessment of wettability of a core sample is the primary target of these experiments, it is quite difficult to perform any other quantitative experiments on wettability measurements to compare the results. Thus, standard core analysis methods such as USBM, Amott, or their modifications do not provide information on the contact angle, while the contact angle method is difficult to implement on porous media. Because the surface area measurement is much easier to quantify by other methods, we decided to validate this technique first by quantitative comparison of surface areas of different samples measured by the proposed method and the well-known BET gas adsorption technique [7]. The next step of our procedure would be to compare wettability obtained by this method with other known methods.

## EXPERIMENT DESCRIPTION AND RESULTS

Immersion experiments are commonly conducted with the use of a sealed glass ampoule containing the sample, which is broken inside the cell that contains the immersion liquid. Another variant of the cell is a membrane cell [8], which consists of two compartments divided by thin metal foil; the upper compartment contains liquid and the lower compartment contains the sample. During the experiment, the membrane is broken by a rod and the liquid wets the sample. For each of these configurations, it is necessary to take into account additional thermal effects appearing in the experiment due to breaking of the ampoule or rupture of the membrane. The disadvantage of using these cells for our future applications in the determination of wettability is that they are not capable of working in high-pressure environments, which is required for wettability experiments at reservoir conditions. To overcome this problem, a special calorimetry cell was developed [9].

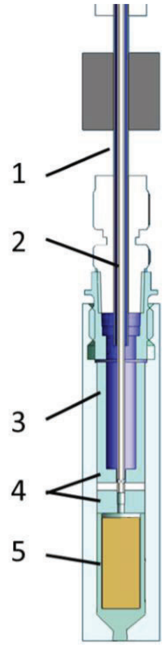


Figure 2. Experimental cell design: 1 external tube; 2 internal moveable tube; 3 wetting liquid compartment; 4 friction-less valve; 5 sample compartment.

The special calorimetry cell provides: 1) a means for connecting the sample to the vacuum/ vapor system for pretreatment the sample; i.e., vacuum the sample and/or adsorb the liquid film on the surface; 2) both the immersion liquid and the sample had to be in the same calorimetric cell during the experiment in order to exclude mass-heat transfer during immersion of the sample; 3) for the heat effect due to combining both volumes of the sample and the liquid so as to not influence the results and be reproducible and for being systematically accounted.

The designed cell (Figure 2) is equipped with two coaxially arranged tubes (1 and 2 in Figure 2) (1/16-in. tube into a 1/8-in. tube, respectively), independently connected to external volumes. The internal tube is used for evacuation of the sample and vapor adsorption, while the external tube is used for filing of the cell with the wetting liquid. The inner tube can move in the vertical direction; i.e., when it is in the bottom position, the sample is in a contact with a line for evacuation and vapor adsorption, but when it is lifted up vertically (with a special pneumatic device), the cell compartments are connected and the liquid fills the sample volume through the valve. The sample compartment is a 9-mm diameter, 20-mm tall cylinder.

Prior to the experiment, a sample in the lower compartment should be dried in a vacuum under a specific temperature ( typically 85°C) to remove any loosely adsorbed vapors from the surface. An experiment is initiated under a "zero" pressure condition. The preliminary evacuated cell containing the sample to be studied is filled with the wetting liquid vapor to create continuous film on the sample surface. The heat effect due to vapor adsorption can be used for surface wettability heterogeneity evaluation [2] (not described here). The immersion step is now completed, resulting in the second heat effect peak (Figure 3), which is used for surface area assessment in accordance with Eq. (1).

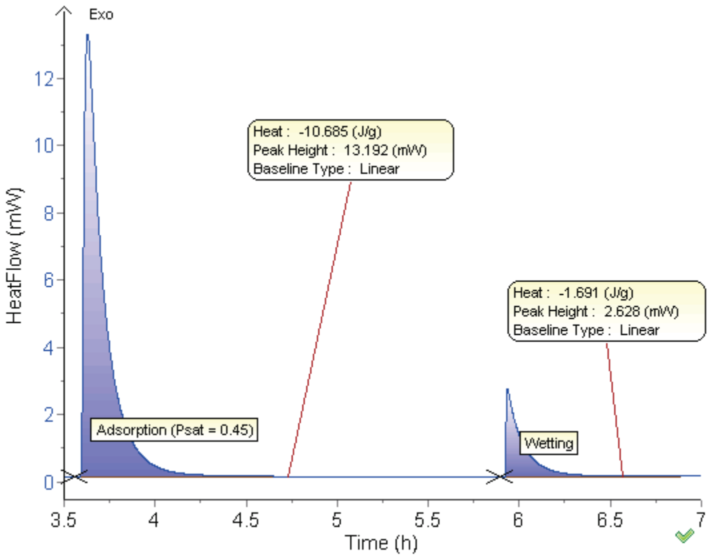


Figure 3. Adsorption-immersion heat flow curve

It is important with the proposed method that the absorbed liquid layer be sufficiently thick so that the liquid layer screens the surface from the other molecules. In this case, the variation of the Gibbs energy during the immersion step is equal to $\gamma^{LV}$ and the interpretation of the results of experiments with Eq. (1) is valid. This condition is fulfilled when the thickness of the adsorbed layer is equal to approximately 1.5 monolayers of adsorbed species [5]. When using water as a liquid, this condition is most often fulfilled for hydrophilic samples if the liquid layer is adsorbed with humidity of ~ 45 % [5]. At the same time, this condition might not hold with the hydrophobic samples or when the adsorption isotherm of a hydrophilic sample is starting very slowly during the first half of the adsorption isotherm, as for example probably the case with the carbonate samples [2]. All of the experiments performed in this work were with distilled water, and the liquid film is adsorbed from the 45% humidity atmosphere, which is created by an external water-filled and temperature-controlled tank.

Surface area measurements with calorimetry were performed on artificial and natural powders and carbonate rocks (Table 1). The measurement time at each step of ordinary adsorption-immersion experiment was approximately 2 hours. In the case of clays, we had to increase the experimental time (three to six times until the baseline stabilized) for both the adsorption and immersion step to measure complete adsorption and immersion heat effects accurately. The specific surface area of the porous samples was also measured by the BET method (some by two independent laboratories to evaluate the measurement precision).

As shown in Table 1, the correspondence between the measured specific surface areas is very good for a majority of the samples (including some mesoporous controlled pore glass CPG powders) except for those samples marked in gray. Poor correspondence in the surface areas is indicated with the bentonite powder, most likely due to the swelling of bentonite in water. Thus, the BET method is able to measure only the external surface of the bentonite, while the calorimetry method can also measure internal surface of the clay. From the opposite point of view, we see a good correspondence between the montmorillonite sample measurements. Montmorillonite is also a swelling clay (actually, the main constituent of bentonite) and one would expect (at least we did) it to behave similar to the bentonite behavior. Our present conclusion is that the montmorillonite powder sample could have gone through an irreversible change in its structure due to eventual water vapor adsorption/condensation. Now, the full surface, including internal one, is exposed to both of the methods.

As was explained previously, proposed method cannot be successfully implemented with hydrophobic samples (carbon) or with samples having a low adsorption of vapor during the first part of the adsorption isotherm (carbonate samples). It is difficult to reach some exact conclusions from the data of these carbonate core sample experiments because the specific surface areas of these samples are very small and consequently, the accuracy of both the BET and calorimetry experiments is not overly high. For now, we can observe that both techniques give the same order of magnitude values and show the same systematic variation; i.e., an increase in the surface area after extraction of the cores. The difference between the measurements with cores can be also explained by the presence of clays (about 5%) and halite (about 5%).

## CONCLUSION

Immersion calorimetry experiments allow measuring the surface area of a core sample and its wettability state by two identical experiments with slightly different initial conditions. A special calorimetry cell was developed to allow for determining core sample wettability at reservoir conditions in this experimental work and for future tests. Although understanding wettability is a primary goal of the ongoing study, in the present phase of this work, validation of the measurement technique was required. It is difficult to validate wettability measurements by independent tests; therefore, the current work focused on the validation of the technique by comparing the surface areas of different artificial and natural samples as well as actual core samples. The values for comparison were obtained by a well-known BET gas adsorption technique. Respectable correspondence between the measured surface areas was obtained for most hydrophilic samples, which proves the accuracy of the procedure. Hydrophobic samples and carbonate samples show a more complex behavior, which is anticipated from the theory of the method. Special care should be taken in the future tests during the measurements of samples that contain a considerable amount of swelling clays. Future tests will include analogous experiments with nonpolar hydrocarbons, which will hopefully allow us to overcome the mentioned hindrances when implementing the method for surface area measurements, followed by experiments on core sample wettability measurements.

## REFERENCES

1. E. Dyshlyuk, "Application of Differential Scanning Calorimetry to Core Analysis," in *Society of Core Analysts*, SCA2013-055, Napa Valley, California, USA, 2013.
2. E. Dyshlyuk, N. Bogdanovich, D. Korobkov and V. Pletneva, "The measurements of core sample surface wettability heterogeneity by adsorption calorimetry," in *Society of Core Analysts*, SCA2014-088, Avignon, France, 2014.
3. E. Dyshlyuk, "Method for Determining Wettability of a Surface". Russia Patent Claim # 2014109083, February 2015.
4. E. Dyshlyuk, "Method for Reservoir Wettability Properties Determination". Russia Patent 2497098, 2013.
5. S. Partyka, F. Rouquerol and J. Rouquerol, "Calorimetric determination of surface areas Possibilities of modified Harkins and Jura procedure," *Journal of Colloid and Interface Science*, vol. 68, pp. 21-32, January 1979.
6. W. Harkins and G. Jura, "An Absolute Method for the Determination of the Area of a Finaly Divided Crystalline Solid," *Am. Chem. Soc.*, vol. 66, pp. 1362-1366, 1944.
7. S. Brunauer, P. Emmett and E. Teller, "Adsorption of Gases in Multimolecular Layers," J. *Am. Chem. Soc*., vol. 60, p. 309, 1938.
8. P. Aukett, "A New Membrane Cell for the Determination of Heats of Immersion Using the Setaram C-80 Microcalorimeter," J. *Thermal Analysis*, vol.33, p.323, 1988.
9. E. Dyshlyuk and V. Baldygin, "Device for Measurement of Heats of Adsorption and Wetting". Russia Patent 2524414, 2014.

**Table 1**. Specific surface area of powders and core plugs obtained by different methods.

| Powder and core samples name, material | Surface area, from manufacture, $m^2/g$ | Surface area by immersion calorimetry, $m^2/g$ | Surface area by BET, $m^2/g$ |
|---|---|---|---|
| Reference samples (artificial and natural powders) | | | |
| CPG 3000C (pore Ø: 300 nm), borosilicate glass | 8.4 | 9.3 | 9.5 |
| CPG 1000C (pore Ø: 100 nm), borosilicate glass | 26.6 | 23 | 27 |
| CPG 500C (pore Ø: 50 nm), borosilicate glass | 49.5 | 43 | 54 |
| Corundum, $Al_20_3$ | 155 | 197 | 153 |
| Corundum, $Al_20_3$ | | 11.3 | 12.4 - 14.5* |
| Corundum, $Al_20_3$ | | 11.5 | 12.2 - 14.0* |
| Quartz, $SiO_2$ | | 6.0 | 6.9 - 8.3* |
| Kaolinite | | 10.3 | 10 |
| Montmorillonite | | 265 | 232 |
| Bentonite | | 250 | 15.6 |
| Calcium carbonate, $CaCO_3$ | | 1.2 | 3.8 |
| Carbon, C | | 1.0 | 1.75 |
| Core plugs, carbonate rock, before/after extraction (described in [2]) | | | |
| Sample 1 | | 0.20 / 0.54 | 0.04 / 0.27 |
| Sample 2 | | 0.07 / 0.40 | 0.00 / 0.30 |
| Sample 3 | | 0.57 / 0.62 | 0.18 / 0.33 |
| Sample 4 | | 0.63 / NA | 0.20 / 0.28 |
| Sample 5 | | NA / 0,63 | 0.12 / 0.24 |

* BET measurements by two independent laboratories