

CHARACTERIZATION OF FLUID-ROCK INTERACTION BY ADSORPTION CALORIMETRY

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ABSTRACT

We continue our study on rock characterization by calorimetry [1, 2]. In this study, differential scanning calorimetry (DSC) technique and gas sorption technique were used to characterize fluid/rock interaction, which is related to the wettability state of the surface of the formation. The paper presents an approach for surface characterization by measuring the change in enthalpy associated with adsorption process. Using calorimetry, it is possible to obtain the variation of state function-enthalpy, due to interaction between molecules of a fluid and a surface. DSC adsorption enthalpy measurements were used in a combination with gas sorption technique, which allows one to measure the amount of adsorbed media. Comparison of the adsorption isotherms for different fluids (for example water and hydrocarbons) can provide valuable information on wettability of powder, cuttings, conventional and tight rocks, that cannot be obtained by any other existent methods. For conventional rocks, it can be used for characterization of the wetting state (i.e., for evaluation of contact angle).

In the paper we discuss the approach and results of tests that have been conducted using an artificial porous media and powders with predefined composition, surface state, and size of pores.

INTRODUCTION

Porous media properties, that primarily define and control the processes of hydrocarbon storage and recovery are: pore size distribution, specific surface area and energy of fluid-surface interaction [1, 2]. Specific surface area determines storage capacity of the rock while fluid-surface interaction energy affect such things as how fluids adsorb and be recovered from the rock.

All sorption processes are accompanied with certain heat effects, which can be accurately measured with calorimetry. Thus, knowledge of specific surface and measurements of the sorption heat effect allow obtaining wetting properties of pores with high accuracy.

Immersion experiments can be considered as a particular case of adsorption. In the immersion calorimetry experiments, a core sample is immersed in a liquid and the associated 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 initial conditions of the rock surface in the experiment, the associated heat effect is related to either 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 calorimetry technique [3, 4]. In particular, immersion calorimetry was implemented for contact angle measurements of different powders [4]. However, it was later found that the method has a significant drawback: in some cases it is impossible to ensure complete wetting of the surface. So, the measured heat effect does not correspond to expected wetting area. In contrast with immersion, adsorption process can be free of this drawback and adsorption calorimetry can be used for characterization of any surface (from hydrophilic to hydrophobic) even in nanopores.

Adsorption and wetting processes can be described through a change of enthalpy. The total heat ΔH that evolves during adsorption experiment, or the enthalpy of adsorption, is related to the variation of the Gibbs free energy per unit area (ΔG) of the system by the following expression: $\Delta H = S(\Delta G - \frac{T\partial\Delta G}{\partial T})$, 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 an adsorption occurs from vacuum, then $\Delta G = \gamma^S - (\gamma^{SL} + \gamma^{LV})$, where γ^S is the solid-vacuum interface surface tension (free surface energy), γ^{SL} is the solid-liquid interface surface tension and γ^{LV} is the liquid-vapor interface surface tension (Fig. 1).

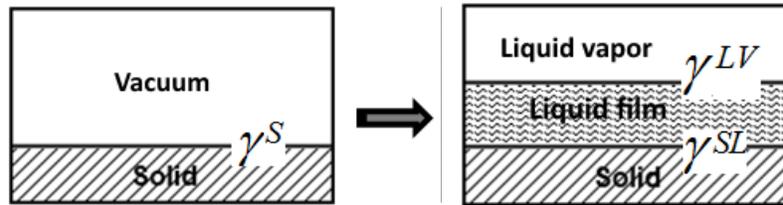


Fig. 1. Illustration of adsorption experiments

Two independent adsorption experiments with two required liquid vapour interfaces should be performed for evaluation of contact angle between these liquids in proximity to the studied surface. The initial state of the surface should 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 [5]:

$$\cos\theta = \frac{\gamma^{SL1} - \gamma^{SL2}}{\gamma^{L1L2}} = \frac{S \cdot \gamma^{L1V1} - k^{L1} \cdot \Delta H_{ads}^{L1} - S \cdot \gamma^{L2V2} + k^{L2} \cdot \Delta H_{ads}^{L2}}{S \gamma^{L1L2}}, \quad (1)$$

where γ^{L1L2} is the liquid 1 to liquid 2 interface surface tension. Coefficient k is a ratio of the variation of Gibbs energy to the Enthalpy:

$$k = \Delta G / \Delta H \approx \gamma^{LV} / (\gamma^{LV} - \frac{T\partial\gamma^{LV}}{\partial T}).$$

Coefficient k is a simplification based on experimental observation made by Briant J. and Cuiec [6] for many solids and liquids. The coefficient for each liquid can be obtained

from the measurements of the liquid-vapour surface tension γ^{LV} and its variation with temperature. These values could be easily obtained from literature or measured with commercially available equipment. The surface area of the sample S should be determined separately by some other method, such as the Brunauer–Emmett–Teller (BET) method [7].

EXPERIMENT DESCRIPTION

Thermodynamic characterization of solid-liquid interaction has been performed using a calorimeter equipped with a vapour dosing system described in [2]. A new calorimetry cell was designed and manufactured for adsorption experiments. It provides connection of the sample in the calorimeter with external vapour supply and degassing systems. The cell and both systems should be leakproof and ensure leakage no more than 0.05 mbar per hour.

We tested the proposed approach on artificial samples. Adsorption and desorption heat isotherms were measured for available powders of controlled porous glasses (CPG), calcite and carbon black that was used for immersion calorimetry [4]. An example of measured heat flow in/out the cell due to adsorption and desorption is demonstrated in Fig. 2. Adsorption heat effect at each pressure step was calculated by integration of the heat flow. Good precision ($\pm 5\%$) was established by the results of repeated measurements of the heat effect. Conventional adsorption isotherms were also measured for the studied sample by the static volumetric gas adsorption technique for evaluation of specific surface by low temperature nitrogen adsorption (BET) and vapour (water and hexane) adsorption capacity (Fig. 3).

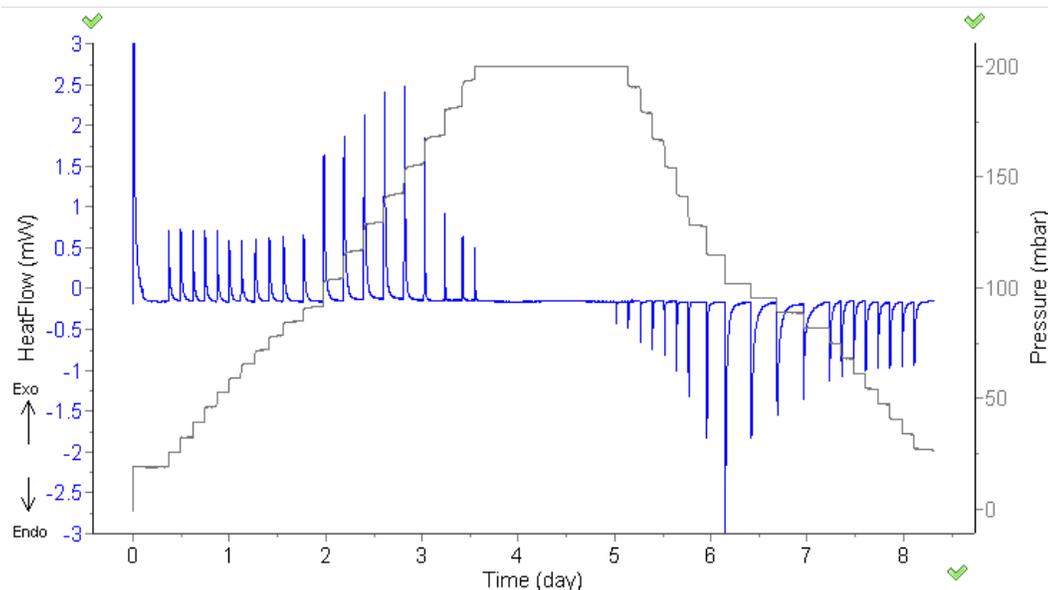


Fig. 2. Measured heat flow at adsorption and desorption of hexane on a CPG sample.

While dealing with adsorption (especially with water vapor) on a surface of porous and solid materials, it is extremely important to remove a sorbate. Otherwise, a thin film of residual sorbate, (that usually sorbs from the air) drastically changes the amount of studied sorbate and heat of adsorption while forming its first monolayers on the surface. For removing residual sorbate from the surface we use routine surface cleaning that includes two steps: (1) removing of fluid from the pore volume by solvent extraction followed by drying in a vacuum or conventional oven at 60-105°C (typical for rock samples) at a heating rate ~ 0.5 °C/min; (2) cleaning of the surface from any sorbate and degassing, which is mandatory prior any adsorption experiment. A typical procedure for routine degassing of different solids and powders without water in composition (like quartz, feldspar, carbonate, carbon, glass, silica alumina etc.) consists of overnight degassing while heating at temperature 150 °C. Removing sorbate from the surface is extremely important since even thin monolayer film of residual sorbate can drastically alter adsorption of the target sorbate. Thus, an organic from air can adsorb on a glass surface and reduce water vapour adsorption on it.

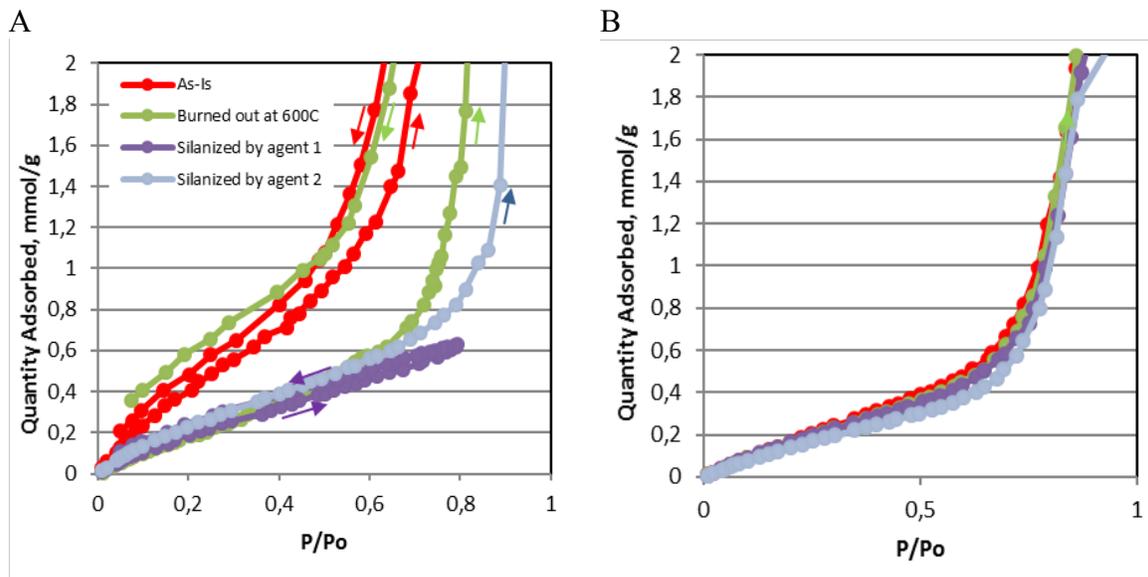


Fig. 3. Adsorption of water (A) and hexane (B) vapour on porous glass surface.

There are two common ways for removing residual sorbate: washing by solvents and burning-out. Applying a burnout procedure for removing organics from porous glass has been recommended by some powder manufacturers. We have tested surface cleaning procedures for water and hexane adsorption on porous glasses (Fig. 3). We have observed that solvents (benzene, alcohol) and oxidizer (H_2O_2) do not alter the surface of porous glass: the obtained adsorption isotherms on the samples before and after the treatment coincide within the measurement error. In contrary, heating of glass samples at temperature higher than 250°C modify the fluid-surface interactivity drastically. After burn-out of CPG samples at 600°C the surface became hydrophobic (Fig. 3). Even more, its adsorption capacity decreased to a value corresponding to measured value on the same CPG powders modified by silane [8]. Modification of CPG's surface has been done by trichloromethylsilane (Agent 1 in Fig. 3) and trimethoxypropylsilane (Agent 2 in Fig. 3) to study of fluid-surface interaction at the same surface having different wettability (hydrophobic and hydrophilic) but the same structure. Numerous measurements of

hexane adsorption have shown that hexane adsorption does not depend neither on burn-out nor hydrophobization by silane (Fig. 3, B).

RESULTS

The analysis of adsorption isotherm, that was measured by the static volumetric gas adsorption technique, showed that the wettability can be estimated by comparing water vapor and hexane adsorption isotherms (Fig. 3). Molar adsorption capacities of the hydrophobic (modified with silanes or a temperature treating) glass surface are almost equal for both studied liquids — water and hexane. Taking into account high surface tension of water (72 mN/m) and the low for hexane (19 mN/m) one can suppose that in presence of both fluids the surface is wetted predominantly with hexane and the water molecules are merged in droplets due to the cohesion forces. On the contrary, the hydrophilic untreated glass surface has a higher adhesion forces that increase the quantity of adsorbed water.

The specific heat effect isotherms (normalized to specific surface) of water vapour adsorption on the surface of the CPG (pore diameters of 50, 100 and 300 nm) do not depend on the pore size. The measurements on the nonporous powders with different chemical compositions demonstrated significant influence of the surface composition on the measured heat effect (Fig.4).

In general, we made the following observations (Fig. 4): the first part of the adsorption process was accompanied by essential heat effect that depends on the surface. The following process reflects the surface heterogeneity and then the surface roughness and the mineral composition. Fig.4A shows that the heat of water vapor adsorption on the hydrophilic surface of the porous glass is much higher than that for the hexane and depends on quality of surface cleaning. The 300-nm pore size CPG sample was a brand-new powder while the 50-nm pore size sample was stored for a few months after opening its container.

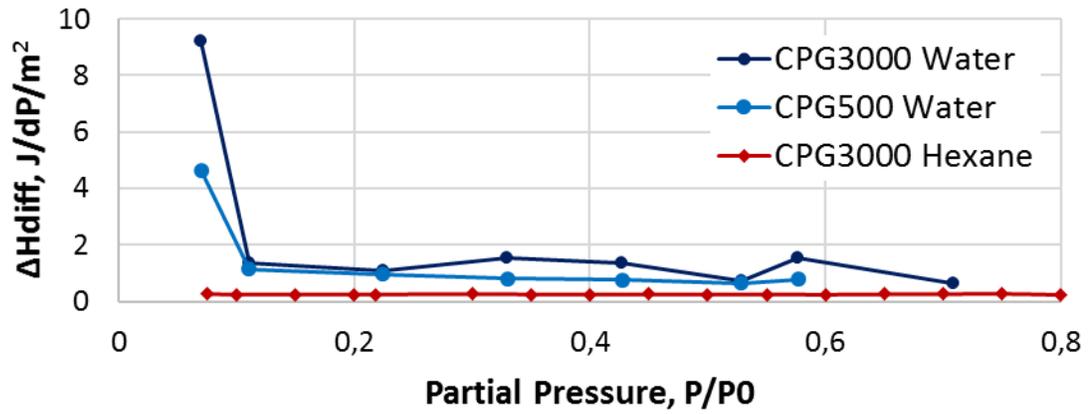
The heat of water adsorption on the surface of carbon black (Fig. 4B) was 3.8 times higher than that for hexane adsorption at every studied pressure range. This value is close to the ratio of the surface tensions of the both liquids (72 mN/m and 19 mN/m). This fact allowed us to conclude that there is an almost equal wetting of the surface i.e. higher interaction (in contrast with hexane) of the water with the surface (adhesion) was compensated by the high cohesion forces. This conclusion is in a good agreement with the literature data on contact angle between water and hexane on fused quartz surface, which is about 95° [9].

The adsorption of the water and the hexane vapors on the surface of calcite (Fig. 4C) was more complex due to the surface heterogeneity and a possible chemisorption.

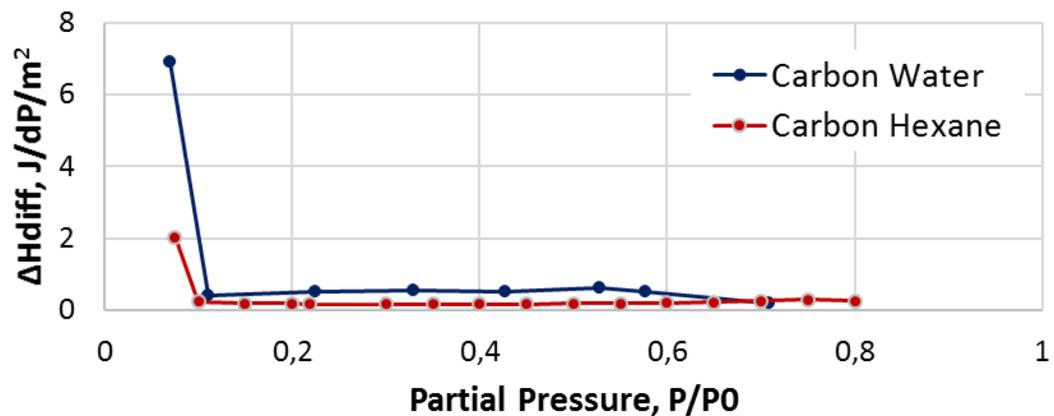
Mutual analysis of the static volumetric adsorption technique with the calorimetry allowed evaluating of the molar heat of adsorption as well as the surface coverage (Fig. 5) for porous glasses. Hexane adsorption on the glass surface resulted in a heat effect of the same order as the enthalpy of hexane condensation (the red line in Fig. 5), even

though the first-layer molecules interact with the surface with a higher energy (up to 2 times). A small

A



B



C

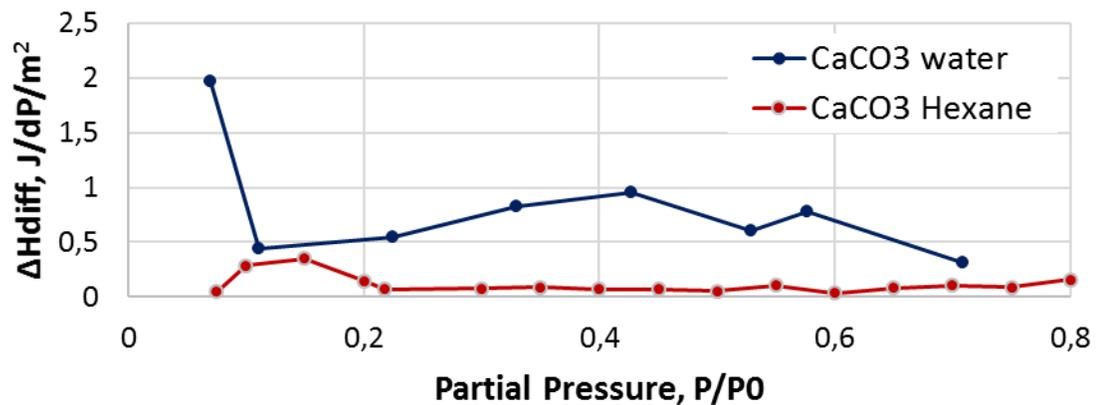


Fig. 4. Differential heat effect due to water and hexane vapor adsorption on a porous glass (A), a carbon black (B) and calcite (C). Heat effect is normalized to the values of specific surface and

pressure. The legend indices show pore diameter in angstroms.

radius of pores, which is close to the thickness of two monolayers, resulted in the higher quantities of adsorbed hexane on the nanoporous glass with 4-nm pore size. Here, we observed a capillary condensation effect just after the forming of a monolayer.

This study showed that separated calorimetry and porosimetry measurements of water adsorption did not produce reliable data on molar heat of adsorption. The main reason could be the different means of vapor pressure supply, and thus different amounts of adsorbed fluid in both experiments. A quantitative interpretation of the measured heat effects without considering the number of adsorbed molecules using Eq. 1 demonstrates a higher value of adsorption heat effect than expected (cosine of contact angle > 1). The most probable reason is an action of cohesion forces, i.e. the heat effect generated due to the interaction between sorbate molecules while forming a multilayer surface film. Use of the above method requires simultaneous measurements of adsorbed liquid and heat effect. Since there was a significant discrepancy in the volumes of sorbate in both water adsorption experiments, only qualitative wettability evaluation can currently be performed.

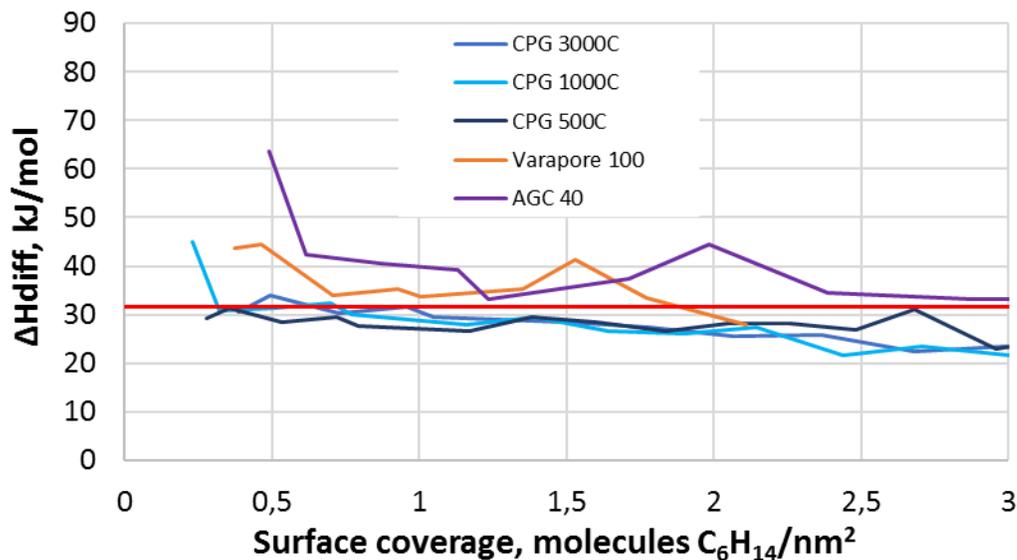


Fig. 5. Molar heat of Hexane adsorption in mesoporous glasses. Red line is enthalpy of Hexane condensation. Indices in sample names show pore diameter in angstroms.

CONCLUSION

Adsorption calorimetry has great potential for characterizing fluid-rock interaction. We have shown high sensitivity of the method to state and composition of the surface. Rock

wettability can be evaluated by two identical experiments with independent vapour adsorption of each fluid. Further development requires combining calorimetry and static volumetric gas adsorption systems for evaluation of the molar heat effect of adsorption.

Experiments were conducted for evaluation of sample preparation procedure for silica glass. Preparation is crucial for adsorption experiments and necessary for restoring the initial state of the sample surface after tests or removal of organic contamination. A burnout procedure was shown to result in strong surface alteration (hydrophobization).

The results for water vapour adsorption experiments confirmed the significant influence of surface composition on heat effect. Expected nanoconfinement effect has not been observed for CPG samples having 50 nm or greater pore sizes. Results for water and hexane vapors showed that, in general, the first step of adsorption reflects a heat effect depending on sample composition, and further steps reflect mostly specific surface area. Surface preparation prior to testing is extremely important. For water vapour, the heat of adsorption on hydrophilic porous glass was significantly greater than for hexane, while for the neutral surface of carbon black the response was proportional to surface tension values.

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, D. Korobkov, V. Pletneva, "Rock Surface Characterization by Immersion Calorimetry: Wettability and Specific Surface Area," in *Society of Core Analysts*, SCA2015-059, St. John's Newfoundland and Labrador, Canada, 2015
4. D. Korobkov, V. Pletneva, E. Dyshlyuk, "Rock wettability evaluation by immersion calorimetry," in *Society of Core Analysts*, SCA2016-021, Snow Mass, Colorado, USA, 2016.
5. Rouquerol, F., Rouquerol, J. and Sing, K. Adsorption by Powders and Porous Solids. s.l. : Academic Press, 2009.
6. J. Briant, L. Cuiec. Comptes-rendus du 4eme colloque ARTEP, rueil-malmaison, 7-9 June, 1971. Ed. Technip, Paris.
7. S. Brunauer, P. Emmett and E. Teller, "Adsorption of Gases in Multimolecular Layers," *J. Am. Chem. Soc.*, vol. 60, p. 309, 1938.
8. B. Seed, "Silanizing Glassware," *Current Protocols in Cell Biology*, John Wiley & Sons Inc, 2000, A.3E.1-A.3E.2.
9. W.A. Zisman. "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution." *Advances in Chemistry*; American Chemical Society: Washington, DC, 1964. 1-51.