



# Colloids and Surfaces A: Physicochemical and Engineering Aspects

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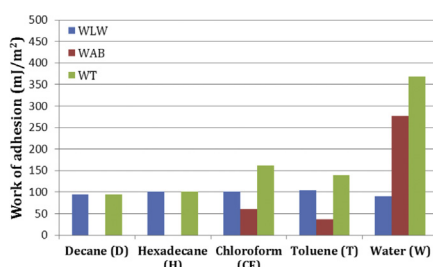
## Surface energy and wetting behavior of reservoir rocks

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### HIGHLIGHTS

- Investigated the surface energy of a reservoir rock using IGC.
- Examined the effect of moisture and temperature on their surface energetics.
- The surface interaction forces at the rock–fluid interface were quantified.
- Proposed a new approach for measuring the wettability index of a rock–fluid system.
- Wettability index scales from –1 (strongly oil-wet) to +1 (strongly water-wet).

### GRAPHICAL ABSTRACT



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### ABSTRACT

An accurate description of the surface chemistry of the reservoir rock–fluid system is essential to understand the attractive forces between the various phases (crudes, brines and the rock surface). These physico-chemical interactions determine the fundamental nature of the reservoir wettability and the wetting behavior of fluids on the reservoir rock surface. Inverse gas chromatography (IGC) is used to characterize the surface chemistry of a Saudi Arabian reservoir rock (henceforth referred to as ‘reservoir rock’) at different moisture coverage and temperatures. This information combined with the surface tension of the interacting reservoir fluids is utilized to develop a new method for quantifying wettability in terms of a wettability index. This index is based on the relative magnitude of the work of adhesion between the rock surface and the competing oleic/aqueous phase.

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## 1. Introduction

Since the early days of the petroleum industry, attempts have been made to understand the spreading behavior of reservoir fluids on the rock surface and use this knowledge to improve the oil

recovery from the reservoir. This led to the concept of wettability, which describes the tendency of a fluid to spread on a rock surface in the presence of another immiscible fluid. Therefore the reservoirs were usually classified as oil-wet, water-wet or intermediate-wet based on the affinity of the rock surface toward oil or water phase. Wettability assumes significance since it determines fluid distribution in the reservoir and the capillary forces holding them and thus affecting reservoir production, waterflood recovery and the performance of enhanced oil recovery (EOR) processes [1–7]. However

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attempts to describe or generalize the concept of wettability have largely remained unsuccessful [8].

Currently wettability is estimated in the laboratory by restoring the in situ wettability of core samples by aging them at elevated temperatures for long periods of time. There are two standard analyses adopted by the industry for wettability estimation: Amott test and USBM method [2]. Both analyses are rather time consuming and expensive. Thus the ensuing paper is an attempt to develop a fast and reliable alternative technique for wettability estimation utilizing our knowledge of interfacial interactions between the various phases.

It has been commonly agreed, that the two major factors affecting wettability are surface morphology and the intermolecular surface forces between the 3 phases (rock–oil–brine) [1,8,9]. Regardless of the morphology, the wettability of the system is determined by the relative magnitude of the forces of interaction between the two liquid phases and the rock surface [8,9]. These fundamental interactions (or surface energies) are usually classified into two classes: Lifshitz–van der Waals interactions (non-polar) and acid–base interactions (polar) [10].

Surface free energy (also called surface energy) is an important thermodynamic characteristic of a solid and is defined as the energy required to form (or increase) the surface by a unit surface under reversible conditions. There are two indirect methods commonly used to assess the surface energy of solids: vapor adsorption measurements using probe vapors and wetting (contact angle) measurements using probe liquids. Contact angle measurement is generally limited in its application to low energy smooth surfaces where finite contact angles can be formed using appropriate probe liquids. In case of irregular particulate materials, wicking measurements are used to infer contact angles. Since many high energy surfaces of interest such as minerals are wet by most liquids, the ‘two-liquid’ approach is used to obtain finite contact angles for the solid–liquid interface. In contrast the vapor adsorption measurements using inverse gas chromatography (IGC) at infinite dilution involves studying the individual interaction of the probe molecules with the surface sites. This approach enables an accurate description of the surface at different temperatures and other physical conditions by taking into account surface heterogeneity and the interaction forces responsible for the adsorption. A brief review of the technique and application of IGC has been can be found in the literature [11,12].

Thus the focus of our study is to quantify and understand the nature of these interactions by using inverse gas chromatography and use this knowledge to determine the wettability of the rock surface. The authors have successfully demonstrated the technique to quantify these fundamental interactions by characterizing the surface energetics of some sandstone and carbonate rocks using inverse gas chromatography [13,14]. Here we extend this technique to a carbonate rock obtained from a Saudi Arabian reservoir. This information is used it to demonstrate a new approach to quantify the wettability of a reservoir rock by relating it to a wettability index. The method for calculating the wettability index of the reservoir rock is based on measuring the difference between the work of adhesion between the two liquid phases and the rock surface using the van Oss–Chaudhury–Good approach. The ensuing paper will illustrate the mechanics of this process right from performing the surface energetic analysis of the reservoir rocks to calculating their respective wettability indices.

## 2. Theory

The principle and technique behind IGC measurements has been extensively discussed in the literature [13,14]. In this section, we will describe the process for determining the wettability index for

a reservoir rock, in contact with a brine phase and an oil phase. This step utilizes the knowledge of the surface energies of the three interacting phases (rock, oil and brine) in terms of their Lifshitz–van der Waals components and polar components.

The work of adhesion ( $W^A$ ) is a thermodynamic property and is defined as the work required for separating two different surfaces (denoted by 1 and 2) from each other. In other words, the work of adhesion between any two surfaces determines how strongly the surfaces are attracted to one another.

$$W^A = \gamma_1 + \gamma_2 - \gamma_{12} \quad (1)$$

where  $\gamma_{12}$  is the interfacial tension between the two surfaces 1 and 2,  $\gamma_1$  is the surface tension of the surface 1 and  $\gamma_2$  is the surface tension of the surface 2.

Building on the work of Good and Girifalco [15] and Fowkes [10], the van–Oss–Chaudhury–Good model [16,17] expresses the work of adhesion ( $W_{12}^A$ ) between two surfaces (1 and 2) as follows:

$$W_{12}^A = 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} + 2\sqrt{\gamma_1^-\gamma_2^+} + 2\sqrt{\gamma_1^+\gamma_2^-} \quad (2)$$

where  $\gamma_1^{LW}$  is the Lifshitz–van der Waals component of surface energy of surface 1,  $\gamma_1^-$  is the basic component of surface energy of surface 1 and  $\gamma_1^+$  is the acidic component of surface energy of surface 1. Similarly  $\gamma_2^{LW}$ ,  $\gamma_2^-$  and  $\gamma_2^+$  represent the Lifshitz–van der Waals component, basic component and acidic component of surface energy of surface 2 respectively.

Knowing the surface energy and its components for all the three phases: rock (S), brine (W) and oil (O), we can calculate the work of adhesion ( $W_{WS}^A$ ) between brine and the rock surface using Eq. (2) as follows:

$$W_{WS}^A = 2\sqrt{\gamma_W^{LW}\gamma_S^{LW}} + 2\sqrt{\gamma_W^-\gamma_S^+} + 2\sqrt{\gamma_W^+\gamma_S^-} \quad (3)$$

where  $\gamma_S^{LW}$  is the Lifshitz–van der Waals component of surface energy of reservoir rock surface,  $\gamma_S^-$  is the basic component of surface energy of reservoir rock surface and  $\gamma_S^+$  is the acidic component of surface energy of reservoir rock surface. Similarly  $\gamma_W^{LW}$ ,  $\gamma_W^-$  and  $\gamma_W^+$  represent the Lifshitz–van der Waals component, basic component and acidic component of surface tension of brine respectively.

Similarly the work of adhesion ( $W_{OS}^A$ ) between the oil and the rock surface can be calculated as follows:

$$W_{OS}^A = 2\sqrt{\gamma_O^{LW}\gamma_S^{LW}} + 2\sqrt{\gamma_O^-\gamma_S^+} + 2\sqrt{\gamma_O^+\gamma_S^-} \quad (4)$$

where  $\gamma_O^{LW}$ ,  $\gamma_O^-$  and  $\gamma_O^+$  represent the Lifshitz–van der Waals component, basic component and acidic component of surface tension of oil respectively.

Based on our hypothesis stated at the beginning, the wettability of the system is determined by the relative magnitude of the forces of interaction between the two liquid phases and the rock surface. The relative wetting property ( $\Delta_W$ ) is defined as follows:

$$\Delta_W = W_{WS}^A - W_{OS}^A \quad (5)$$

If  $\Delta_W$  is positive, this implies water preferentially wets the rock surface, whereas if  $\Delta_W$  is negative, this implies oil preferentially wets the rock surface. A value of zero for  $\Delta_W$  indicates that there is no preferential interaction between the rock surface to either the oil phase or the brine phase. Thus the rock surface behaves like an intermediate wet surface if  $\Delta_W = 0$ .

Based on this approach, we propose a wettability index (WI) by normalizing the relative wetting property ( $\Delta_W$ ) as follows:

$$WI = \frac{W_{WS}^A - W_{OS}^A}{W_{WS}^A + W_{OS}^A} \quad (6)$$

Thus for a water-wet rock, the value of WI scales from 0 (intermediate wet) to 1 (strongly water-wet), whereas for an oil-wet

rock, the value of WI scales from 0 (intermediate wet) to  $-1$  (strongly oil-wet). Therefore we have formulated a simple and accurate scale for mapping the wettability index between 1 and  $-1$ .

### 3. Materials and apparatus

The reservoir rock samples were ground using mortar and pestle and were subsequently sieved to obtain 100 mesh sieve fraction. The HPLC grade polar (dichloromethane and ethyl acetate) and non-polar ( $C_5$ – $C_9$  n-alkanes) solvents used for chromatographic injection were obtained from Acros Organics.

### 4. Experimental procedure

#### 4.1. Characterization of surface energy of the reservoir rock with increasing moisture coverage

The inverse gas chromatograph used in our study was built by Surface Measurement Systems Ltd (iGC-2000 model). The setup utilizes a series of mass flow controllers to prepare mixtures of helium carrier gas and probe solvents (non-polar and polar solvents). An automated injection valve injects 250  $\mu$ L of the elution mixture into the carrier gas flowing through the column into the detectors. A thermal conductivity detector (TCD) and flame ionization detector (FID) are coupled together at the end of the column for the sensitive analysis of the probe molecules. The chromatographic column used for holding the powdered mineral sample is housed in a separate column oven to maintain it at a constant temperature. Silanized glass wool (Aldrich) is used to pack the powdered rock samples in place. The silanized glass columns measured 30 cm in length and had the following dimensions (6 mm o.d and 4 mm i.d).

The sieved rock sample was washed with ethanol and dried in the oven at 150 °C for nearly 30 min. The cleaned sample was packed in a column and flushed with nitrogen gas at 150 °C for over 5 h to minimize any further moisture contamination. Before injecting the probe solvents, the column is further conditioned with helium gas at the test temperature and relative humidity for 2 h each. Moisture was deposited on the rock surface by controlling the relative humidity of the carrier gas. For studying a dry surface, the carrier gas had zero relative humidity. First moment method was employed to deduce the retention times from the elution curves generated by the detectors.

### 5. Results and discussion

#### 5.1. Characterization of surface energy of the reservoir rock with increasing moisture coverage

##### 5.1.1. Water adsorption isotherms

The water adsorption isotherms for the reservoir rock at 30 and 50 °C have been plotted in Fig. 1. Using  $N_2$  BET adsorption analysis, the specific surface area of the reservoir rock was measured to be 0.5584  $m^2/g$ . The water adsorption isotherm displays a strong type II isotherm behavior (Fig. 1). This indicates the formation of multilayers at higher RH. The calculated monolayer coverage is achieved at 20% RH and beyond 70% RH, moisture is deposited on the surface in a multilayered fashion. For a type II mechanism, the heat of adsorption is much higher than the heat of condensation i.e. the molecules would rather interact with the surface than with each other.

##### 5.1.2. Surface interactions or components of surface energy

The total surface free energy of a reservoir rock comprises of Lifshitz–van der Waals, acidic and basic components. As the water

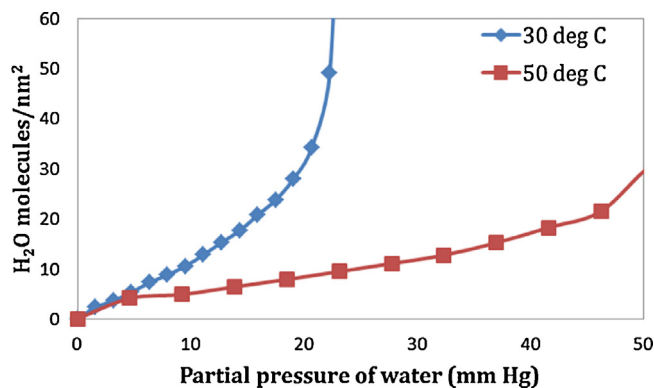


Fig. 1. Water adsorption isotherms for the reservoir rock at 30 and 50 °C.

adsorption isotherms for the reservoir rock (Fig. 1) have indicated, we observe increasing water surface coverage with increase in the relative humidity of the carrier gas stream. This results in a corresponding reduction in the surface energy of the reservoir rock with increase in moisture deposition onto the surface. The mineral surfaces are usually strongly heterogeneous and have a high surface free energy. The adsorbed water layer stabilizes the surface by presenting a lower energy homogeneous surface to the probe molecules to interact [18]. Thus the total surface energy of the reservoir rock decreases sharply as moisture content is slowly increased and eventually attains a plateau at higher relative humidity (Fig. 2). The slight increase in total surface energy at greater relative humidity at 50 °C is indicative of the effect exerted by the solubility of the probe molecules in the adsorbed water layers, which will be discussed in the coming paragraphs.

The Lifshitz–van der Waals component of surface energy comprises of the following interactions: Keesom (dipole–dipole interactions), Debye (dipole–induced–dipole interactions) and London dispersion forces (induced dipole–induced dipole interactions). Similar to the behavior of the total surface energy, we observe with increase in moisture coverage, the Lifshitz–van der Waals component of surface energy decreases rapidly and at high relative humidity will attain a plateau as shown in Fig. 3. This decrease is most rapid at low water coverage since the adsorbate molecules will prefer to occupy the most energetic sites on the reservoir rock. Thus the heat of adsorption of the first layer is dependent on the water coverage. For the second and subsequent layers, this is not expected to be significant as they are occurring on a layer of adsorbed water molecules. Thus at greater water coverage, the decrease of the Lifshitz–van der Waals component of surface energy begins to plateau.

Ideally at higher RH, it is expected that the Lifshitz–van der Waals component of surface energy of the moisture covered rock

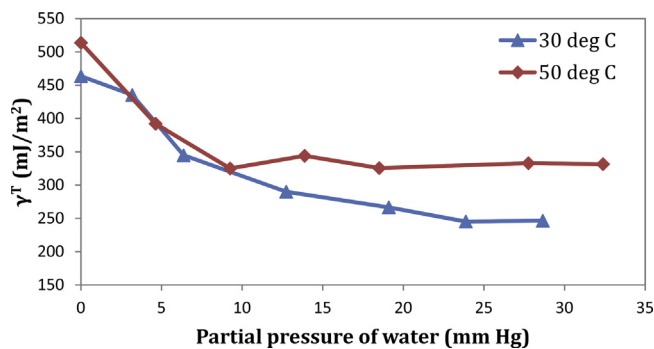


Fig. 2. Effect of water coverage on the total component of surface energy for the reservoir rock at 30 and 50 °C.

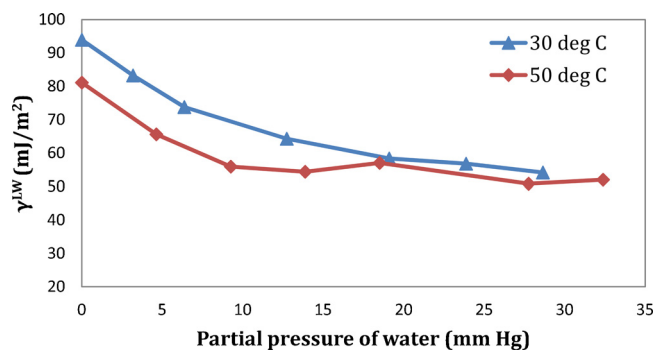


Fig. 3. Effect of water coverage on Lifshitz–van der Waals component of surface energy for the reservoir rock at 30 and 50 °C.

surface should tend toward the Lifshitz–van der Waals component of surface tension of bulk water. However the higher plateau of the Lifshitz–van der Waals component of surface energy at high moisture coverage indicates non-uniform distribution of water layers, leaving bare mineral surfaces to interact with the probe solvents [19]. This non-uniformity in the water coverage of the surface sites may be induced because of imperfections on the surface [20], which may be created when the mineral sample is ground.

The behavior of acid–base components of surface energy of the reservoir rock can be better understood in the light of the following reactions that take place on account of physisorption and chemisorption of water on the surface. At any given point, the surface of a mineral is covered with both physisorbed and chemisorbed water as soon as it comes in contact with moisture. Since the reservoir rock is a carbonate rock, the surface is usually populated by calcium, magnesium and carbonate groups. During physisorption (associative adsorption), the  $O^{2\delta-}$  atom associated with water covers the stronger acidic surface sites ( $Ca^{2+}$ ,  $Mg^{2+}$ ), while exposing the weakly polar  $H^{\delta+}$  of the water molecule on the exterior. Similarly the stronger basic surface site ( $CO_3^{2-}$ ) is covered by the  $H^{\delta+}$  of the water molecule while exposing the weakly polar  $O^{2\delta-}$  site on the exterior. In this way, the stronger polar sites due to the reservoir rock surface are replaced by the weaker polar sites of the water layer. This leads to a decrease in acidic and basic components of surface energy with increasing relative humidity (Figs. 4 and 5). Chemisorption (dissociative adsorption) is preceded by the decomposition of  $CaCO_3$  to  $CaO$ , which reacts with water to result in the formation of isolated hydroxyl groups at the  $Ca^{2+}$  sites and surface bicarbonate anions. In our study, we assume chemisorption is always present even in a dry test rock surface.

In a remarkable observation, we see that there is a sudden increase in the plateau of the acidic and basic components of surface energy (Figs. 4 and 5) at greater water coverage at 50 °C. This can be explained due to increased solubility of the polar solvents in the

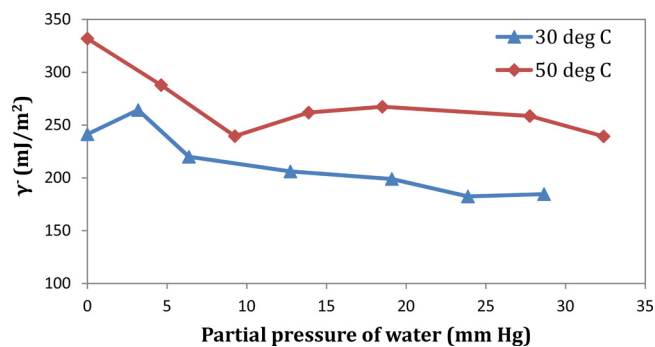


Fig. 4. Effect of water coverage on the basic component of surface energy for the reservoir rock at 30 and 50 °C.

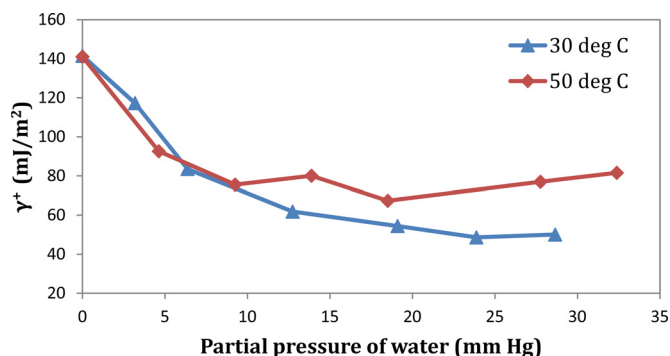


Fig. 5. Effect of water coverage on the acidic component of surface energy for the reservoir rock at 30 and 50 °C.

water multilayers deposited on the surface of the mineral at high relative humidity. This causes an artificial increase in the retention times of the probe solvents which distorts surface energy measurements. In comparison, no such similar effect is observed in case of the Lifshitz–van der Waals component of surface energy because of the insoluble nature of the non-polar solvents in water.

Since we observe appreciably large acidic and basic components of surface energy, we conclude that the reservoir rock surface is amphoteric in nature. This implies that the dynamic wetting properties are determined by both the reservoir surface and reservoir fluid chemistry. The reservoir fluids are usually a diverse mixture of crude oils and brines. Consequently, both crude oil and brine exhibit different polar and non-polar components of surface energy/tension. In line with our hypothesis, it is the relative strength of the interactions (measured by work of adhesion) between the crude oil–rock surface and brine–rock surface that would determine whether the rock behaves as an oil-wet or water-wet rock.

## 5.2. Work of adhesion and the wetting behavior of different polar and non-polar liquids

Since we know the surface tension data for some common polar and non-polar liquids, we will study their wetting behavior with respect to the reservoir rock and water phase. It is commonly assumed that reservoir oils are non-polar in nature and thus interact only by Lifshitz–van der Waals interactions. In the absence of surface tension data with their polar components for reservoir oils, we approximated the surface tension data for pure species (decane, hexadecane, chloroform, and toluene) from the literature [11] to be that of paraffinic oil, slightly acidic oil and slightly basic oil. The wetting behavior of these pure species will give us an idea as to how these types of oil will behave on the reservoir rock surface.

Using the surface tension data provided in Table 1 into Eq. (3) and (4), we calculated the work of adhesion between the different liquid phases and reservoir rock surface. These calculated works of adhesion are depicted pictorially in Fig. 6. Using this information, we also computed the relative wetting parameters and wettability indices for the reservoir rock with respect to the two liquid phases. This has been displayed in Table 2.

Table 1  
Surface tension and its components at 20 °C [11].

| Liquid          | Nature         | $\gamma^{LW}$ | $\gamma^-$ | $\gamma^+$ | $\gamma^T$ |
|-----------------|----------------|---------------|------------|------------|------------|
| Decane (D)      | Paraffinic oil | 23.83         | 0          | 0          | 23.83      |
| Hexadecane (H)  | Paraffinic oil | 27.47         | 0          | 0          | 27.47      |
| Chloroform (CF) | Acidic oil     | 27.2          | 0          | 3.8        | 27.2       |
| Toluene (T)     | Basic oil      | 28.5          | 2.3        | 0          | 28.5       |
| Water (W)       | Brine          | 21.8          | 25.5       | 25.5       | 71.8       |

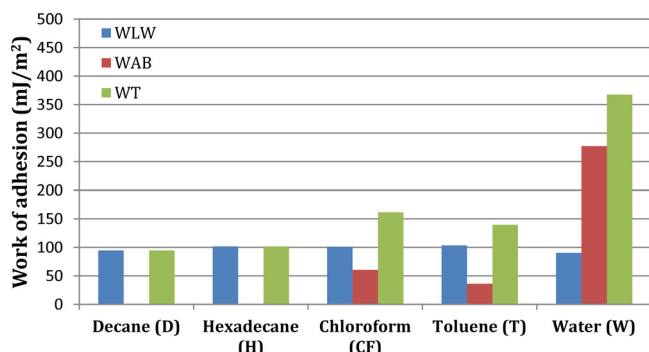


Fig. 6. Work of adhesion for the different wetting fluids on the reservoir rock.

Table 2

Relative wetting parameter and wettability index for the reservoir rock with respect to different fluid combinations.

| Phase 1         | Phase 2   | $\Delta_w$ | WI   |
|-----------------|-----------|------------|------|
| Decane (D)      | Water (W) | 272.918    | 0.59 |
| Hexadecane (H)  | Water (W) | 265.947    | 0.57 |
| Chloroform (CF) | Water (W) | 205.881    | 0.39 |
| Toluene (T)     | Water (W) | 227.977    | 0.45 |

In case of paraffinic oils such as decane and hexadecane, the work of adhesion with the reservoir surface is only due to Lifshitz–van der Waals interactions. On the contrary, water due to its polar nature shows very high work of adhesion. Thus water wets the reservoir rock surface quite significantly in comparison to the paraffinic fluids which is confirmed by the higher WI (0.59 and 0.57) in Table 2.

Chloroform and Toluene show slightly higher works on adhesion due to their slightly monopolar nature. In comparison, water again shows significantly higher works of adhesion causing the rock surface to act as a water-wet surface. Thus due to increased interaction of the oleic phase (chloroform and toluene, due to their monopolar character) with respect to the water phase, the wettability indices scale back in the 0–1 water wetness scale (0.39 and 0.45).

### 5.3. Bitumen–reservoir rock interactions and the wettability index

Let us consider the interactions of a typical mixture of oil such as bitumen with the reservoir rock surface, for which the surface energy was determined using inverse gas chromatography [21]. The surface energy and its components for bitumen and water are listed in Table 3. We observe that bitumen displays mostly Lifshitz–van der Waals component of surface energy and very small polarity compared to the reservoir rock surface.

Using the approach outlined in Section 2, the work of adhesion between the two liquid phases with the reservoir rock surface is calculated and tabulated in Table 4. The work of adhesion between bitumen and the reservoir rock surface is dominated by Lifshitz–van der Waals interactions. Similar to what we observed in Section 5.2, the polar nature of water causes a stronger interaction between the water phase and the reservoir rock surface. Thus water preferentially wets the reservoir rock surface in comparison to bitumen as indicated by the positive  $\Delta_w$  and WI

Table 3

Surface tension and its components for bitumen and water at 30°C [11,21].

| Liquid      | $\gamma^{LW}$ | $\gamma^-$ | $\gamma^+$ | $\gamma^T$ |
|-------------|---------------|------------|------------|------------|
| Bitumen (B) | 48.3          | 0.4        | 0.8        | 50.4       |
| Water (W)   | 21.8          | 25.5       | 25.5       | 71.8       |

Table 4

Work of adhesion between the liquid (bitumen–water) and the reservoir rock surface.

|          | Bitumen (B) | Water (W) |
|----------|-------------|-----------|
| $W^{LW}$ | 134.73      | 90.52     |
| $W^{AB}$ | 42.84       | 277.04    |
| $W^T$    | 177.57      | 367.55    |

Table 5

Relative wetting parameter and wettability index for the reservoir rock.

|                | Relative wetting, $\Delta_w$ | Wettability index, WI |
|----------------|------------------------------|-----------------------|
| Reservoir rock | 189.99                       | 0.35                  |

(0.35) for the reservoir rock surface as displayed in Table 5. Similarly one notices, the reservoir rock in the bitumen–reservoir rock–water system (WI=0.35) behaves as a less water-wet surface when compared to the paraffinic oil–reservoir rock–water system (WI=0.57–0.59). Thereby also indicating the role of surface properties of the fluids on the wetting behavior of the rock surface.

Based on the scale we developed, +1 corresponds to very strongly water-wet rock while –1 corresponds to very strongly oil-wet rock. Thus the reservoir rock surface studied in comparison to their adhesion strength with bitumen and water phase indicates that they are fairly water-wet due to a positive WI value lying in the range of 0–1.

## 6. Conclusion

In this study, we have introduced the technique of inverse gas chromatography to characterize the surface energetics of a reservoir rock at varying moisture coverage and at 30 and 50 °C. Using this approach, the polar and non-polar components of the surface energy for the reservoir rock were mapped and quantified at varying surface conditions. The Lifshitz–van der Waals and acid base component of surface energy showed a decreasing trend with increase in moisture coverage due to water (low energy surface in comparison to the rock) preferentially clustering around the high energy sites. The surface chemistry of the reservoir rock was further characterized using water adsorption isotherms.

The surface energies for the reservoir rock and various polar and non-polar fluids were used to demonstrate a new approach to quantify the wettability of a reservoir rock by relating it to a wettability index. The method for calculating the wettability index of the reservoir rock was based on the hypothesis that the wettability of the system is determined by the relative magnitude of the forces of interaction between the two competing liquid phases and the reservoir rock surface. The work of adhesion and the wetting behavior of various pure fluids (decane, hexadecane, chloroform, toluene and water) against the reservoir rock surface were calculated using the van Oss–Chaudhury–Good approach. The wetting behavior of these fluids was treated as approximations of the wetting behavior paraffinic–acidic–basic oils on the reservoir rock surface. Based on the relative wetting behavior of the two competing phases against the reservoir surface, the wettability index for the mineral surface was proposed and calculated. The scale ranges from –1 to +1, with –1 referring to very strongly oil-wet rock while +1 refers to very strongly water rock.

Finally this approach was validated against the reservoir conditions by treating bitumen and water as the two competing fluid phases and computing the wettability index for the reservoir rock surface. The wettability index of 0.35 indicated that reservoir rock shows a predominantly water-wet behavior in relation to bitumen and the water phase.

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