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Consequences of Asphaltene Adsorption on Flow Phenomena in Porous Media

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النتائج المترتبة من امتزاز الاسفلتين على ظاهرة الانسياب في الوسط الصخري

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يمكن لأغلب معادن المكمن المبتلة بالماء أن تتغير بامتزاز المركبات القطبية أو نتيجة لترسبات عوامل عضوية أو أشياء أخرى موجودة أصلا بالنفط الخام.

ومن بين هذه العوامل العضوية النشطة من تألف الماء أو تطرده. وتمتز النهايات التي تألف الماء على السطح تاركة النهايات الطاردة للماء مكونة السلوك المبتل بالزيت.

وحيث أن قابلية الابتلال تعرف على أنها قابلية الأسطح للبلل بواسطة أحد الموائع المكونة للسوائل المكمنية، وعلى هذا الأساس تؤخذ قابلية الابتلال للصخور على أنها من أهم العوامل التي تساهم في تغيير الخواص البتروفيزيائية لصخور المكمن، حيث أنها تؤثر على سبيل المثال، على الضغط الناتج من الخاصية الشعرية ونسبة نفاذية الماء النسبية على نفاذية الزيت النسبية وتوزيع الموائع في الوسط الصخري وخواص النفاذية النسبية، ويترتب على هذا المستهدف من الإنتاج النفطي بطرق تطوير المسترد النفطي.

تهدف هذه الدراسة إلى وصف قابلية الابتلال لصخور حقل الشرارة وتطوير مركب كيميائي مبتكر لحماية وصيانة المكامن. تمت اختبارات تشبع ديناميكية بواسطة عمود زجاجي مجوف استخدم فيه صخر مفتت مأخوذ من حقل القوي المجري وذلك لاستقصاء عملية امتزاز الأسفلتين الذي تم فصلة من زيت ليبي خفيف جدا، وزيتان خفيف ومتوسط من حقل مجري. كما تمت دراسة تأثر قابلية امتزاز الصخر للاسفلتين. أظهرت النتائج الأولية عدم وجود اختلاف ملحوظ في امتزاز الاسفلتينيات التي تم استخدامها، كما تم الحصول على علاقة خطية واضحة تربط بين التركيب المعدني للصخور وفاقد الامتزاز النوعي عندما تمت معالجة الصخر بواسطة الكلسايت (كربونات الكلسيوم البلورية) والطين.

استقرارية الطبقة الرقيقة المجهرية للماء المنتشر في مسام السطح الصخري كانت من النتائج المتحصل عليها التي أظهرت علاقة خطية تشرح تأثير نسبة إشباع الصخر بالماء المتخلف مع امتزاز الاسفلتين.

تأثر امتزاز الأسفلتين على قابلية الابتلال الصخري أظهر نظام طارد للماء فعال على العينات التي تم استخدامها.

نتائج البرنامج البحثي تقترح أن المحاليل الاسفلتية وقطفات المنتجات الثقيلة وأيضا الزيت الخام التي تحتوي على نسبة عالية من الاسفلتين يمكن أن تستخدم كوسطٍ معالج لطرد الماء في الوسط المسامي.

Abstract: *The original water wetting of most reservoir minerals can be altered by adsorption of polar compounds or deposition of organic agents or matter originally present in the crude oil. These organic active agents include both a polar (hydrophillic) and non-polar (hydrophobic) ends. The hydrophillic ends are adsorbed on the surface, exposing the hydrophobic ends leading to oil-wet behavior.*

Since wettability is defined as the tendency of surfaces to preferentially wet by one fluid

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phase; Altering the wettability is, therefore, considered to be a key factor in shifting the petrophysical properties of the reservoir rock (e.g. Pc, and krw/kro), the distribution of fluids within the porous medium, relative permeability characteristics, and consequently, the target of oil production by any improved oil recovery (IOR) process.

Primary aims of the present investigations were the wettability characterization of the Sharara field and development of an innovative chemical for protection and maintenance of reservoirs.

Column saturation dynamic tests were performed to investigate the adsorption of asphaltenes separated from light Libyan oil, medium and heavy Hungarian oils onto a crushed formation rock obtained from Algyö field. The effect of asphaltenes adsorption on wettability was also studied. Initial results revealed that there is no significant difference in the adsorption of different asphaltenes. A well-defined correlation was found between the mineral composition of the adsorbent and the specific adsorption loss when the rock was treated with a particular percentage of calcite and clay. Stability of microscopically thin layers of water distributed along the surfaces of the pores was also investigated. A correlation showing the effect of residual water saturation on asphaltene adsorption processes was presented.

The effect of asphaltene adsorption on wettability has shown an effective hydrophobization on all rock samples. The final conclusion of the research program suggests that a solution of asphaltenes, distillation heavy cuts and even crude oils with high asphaltene contents can, equally be used as a treating media for hydrophobization of porous media.

INTRODUCTION

Understanding the role of asphaltene in wettability reversal will help in planning more efficient oil recovery processes. In this context, this work has two objectives:

- The wettability characterization of the Sharara field (located in Libya)
- Development of an innovative chemical for protection and improvement of the recovery at the field scale.

The wettability characterization of the Sharara field was performed using water contact angle measurements as a function of time on carbonate rock having homogenous and heterogeneous surface. The reservoir wettability characteristics are often attributed to adsorption of asphaltenes onto the mineral surface of reservoir rock[1]. Therefore, the effect of asphaltene adsorption on wettability was evaluated by treating the rock plates with asphaltenes-toluene solution, stock tank oil-toluene solution and just stock tank oil. For comparable conditions, three asphaltenes were precipitated from three different oils: light (Sharara), Medium (Algyö) and heavy (Nagylegyel).

Dynamic tests served for determination of specific adsorption of asphaltenes from the three types of oils were conducted. Reservoir rocks and natural adsorbents having different mineral compositions were used to compare the adsorbed amount under a fixed flow conditions.

An asphaltene adsorption study was started on asphaltene/rock system. This system consists of adsorbent as a toluene suspension packed in a glass column and a fixed stock asphaltene solution of 0.5g/l concentration was flowed continuously onto adsorbent.

All cumulative curves showed a definite maximum. The value of the maximum and the corresponding injected volume depend on both the asphaltene and the adsorbent type. Asphaltene/rock/water system was then investigated. Water is added in this system to account for the effect of residual water saturation on asphaltene adsorption processes.

The flow measurements were focused on the effect of asphaltene adsorption on absolute, effective, relative and normalized relative permeability of natural formation cores in gas/water system. Similarly, the impact of asphaltene treatment on capillary pressure curves and J functions were determined by centrifugal method using the same formation (sandstone) cores.

Literature Survey

Even though the main cause of asphaltene deposition has not been well understood yet, and this topic is far from being concluded[3], many research papers agreed on the fact that the efficiency of recovery processes was affected by the amount of asphaltene adsorption onto rock surface and asphaltene deposition onto the production facilities.

Many factors like: the change in flow conditions, temperature, pressure, composition of crude oil, brine chemistry, viscosity, capillary pressure, characteristics of reservoir rock and, the wetting degree of the rock, etc. were considered important in wettability alteration due to the presence of crude oils, consequently, the asphaltene adsorption on the rock surface. For instance, it had been proved that one of the main problems in miscible flooding processes was the asphaltene precipitation accrued due to the change of flow behaviour, phase equilibrium and rock characteristics during the injection of miscible gas. It is well known that a rich variety of wetting behaviours can be induced in rocks by treatment with crude oils. As with reservoir wettability, these changes are commonly ascribed to adsorption of asphaltenes[4]. It has also been confirmed that the physical adsorption of polar compounds/organic materials that were initially present in the reservoir crude oils has a great effect on shifting the wet conditions from a water-wet to oil-wet and vice versa. In this direction, Morrow *et al.*[5] screened several polar compounds present in the crude oil that may be responsible for the change in wettability. Ali *et al.*[6] studied the effect of asphaltene precipitation on carbonate rock permeability. That had been done when the effluent asphaltene concentration was compared to that at the inlet, asphaltene deposition was noted in the pore channels. They thought that two distinct mechanisms were identified, deposition and adsorption. Deposition could be explained in terms of trapping and mechanical plugging. They concluded also that most of the asphaltene deposition is likely to take place near the well bore.

The deposition was found to be a function of permeability, flow rate and concentration. On the other hand, experimental results showed that asphaltene deposition has an impact on reservoir permeability and end-point saturations. That was concluded by Kamath *et al.*[7] when a series of dynamic displacement tests were conducted to evaluate the effect of asphaltene deposition on water flooding in both consolidated and unconsolidated sand pack.

Glampietro *et al.*[8] accomplished a series of adsorption tests to determine the isotherms of asphaltene on sandstone rock. They noted that the asphaltene adsorption is a continuous phenomenon and does not reach saturation similar to conventional surface-active materials. Collins *et al.*[9], used in their work, an asphaltene sample recovered from a deposit on the tubing string of a producing well in Alberta, Canada, light oil reservoir to study the adsorption of asphaltenes and water on reservoir rock minerals. One of their conclusions was that adsorption of asphaltenes was reduced but not eliminated by the presence of water.

Dubey and Waxman[10] studied the asphaltene adsorption and desorption on clay minerals, silica and carbonates. The effect of adsorbed asphaltenes on water-wet sandstone rock resulted in a partially water-wet or neutral water-wet system. That was illustrated by the United States Bureau of Mines Method (USBM) wettability indices and oil saturation vs. capillary number curves.

The asphaltene fractions of oil generally consist of condensed aromatic and naphthenic molecules with molecular weight in the range of several hundred to several thousand grams per mole. "Heteroatoms in asphaltene such as nitrogen, sulfur and oxygen indicate the presence of polar groups. Such a molecular structure has properties similar to that of surfactant"[11]. Surfactant injections are considered to be one of the effective IOR methods.

Kim *et al.*[11] concluded that the role of asphaltenes seems to be substantial in altering the interfacial properties of water and oil systems. They also added that the instability of interfacial tension (IFT) is due to asphaltene characteristic of asphaltene particles.

Yu Liu and Buckley[12] conducted an experimental work in which they stated that adsorption of crude oil components on prewetted surface was strongly time dependent and followed a two stage pattern: initial fast adsorption followed by low rearrangement of adsorbate. They also concluded that desorption of crude oil components depends on both brine composition and temperature.

Buckley *et al.*[13] summarised that the extent to which wetting is altered in crude oil/brine/rock (COBR) systems by adsorption of crude oil asphaltic material, was affected by changes in oil solvent properties, even in a mixture in which the asphaltenes are stable with respect to precipitation.

Wettability of reservoir rock can cover a broad spectrum of wetting conditions that range from very strong water-wet (VSWW) to very strong oil-wet (VSOW). Within this range, complex mixed wettability conditions, given by combination of preferentially water wet and oil wet surface, have been identified. Consequently, wettability is considered to be a significant issue in multiphase flow problems ranging from oil migration from source rocks to enhanced oil recovery processes as alkaline flooding or alternate injection of CO_2 and water[2].

Laboratory displacement tests were used to evaluate the effect of wettability on oil recovery. Wettability of COBR systems is usually determined by the Amott test or the USBM methods. Results for (VSWW) conditions are commonly used as a reference state. Reported changes in recovery as systems become less water-wet range from being much lower to being much higher than those given by the originally VSWW conditions. Accordingly, the goal of wettability studies was to provide consistent explanation of these apparent inconsistencies and to identify most favourable conditions for oil recovery.

Chang *et al.*[14] studied the impact of wettability and core heterogeneities on relative permeability. Their numerical simulation runs on separately characterized lithologies to describe the flow mechanism in mixed-wet porous media showed that an increase in oil wettability increases the water relative permeability and decreases the oil relative permeability. They also concluded that a decrease of initial water saturation, produced an increase in relative permeability hysteresis. Baldwin[15] stated that the magnitude of the fluid surface interaction, as measured by wettability affects the movement of ultimate production of oil. He found that relative permeability vary with the surface permeability, and confirmed that relative oil permeability decreases as the strength of oil interactions with the rock surface (oil wettability) increased.

It is worth mentioning that relative permeability is not only a single function of fluid saturation and wettability of rock surface, but it is dependant on saturation history as well. The saturation history hysteresis is an outcome of the redistribution of two or more immiscible phase saturation during drainage and imbibition processes. That was confirmed by Jun-Zhi and Lile[16] in their study of the influence of wettability and saturation sequence on relative permeability hysteresis in unconsolidated porous media.

Desbrandes and Bassiouni[17] have conducted an experimental study to investigate the effect of wettability on formation pressure profile recorded at the oil water contact with residual oil present in the water zone. They observed that in a water-wet sand pack, the pressure gradient changes quickly from oil to water gradient at the movable oil level. This change was located above the free water level. However, in the oil-wet sand pack, the gradient also changes quickly at the movable water level, and this change was located below the free water level. Using the J-function concept, they related the contact angle to the water rise in the water-wet model or the oil fall in the oil-wet model. Dixit *et al.*[18] have developed a three dimensional (3D) network model to derive the capillary pressure curves from a non uniform, mixed and fractionally wet systems. Results indicated that oil recovery via water imbibition in weakly water-wet cores can often exceed that obtained from strongly water-wet samples. McDougall and Sorbie[19] used network modelling to examine the sensitivities of a given process to a variety of phenomena. They investigated the very important role played by wettability at the pore scale in both fractionally and mixed wet media in order to explain how wettability influences the resulting capillary pressure, relative permeability and water flood recovery efficiency. They found out that the simulated capillary pressure data have demonstrated that standard wettability tests (*e.g.*, Amott-Harvey and free imbibition) may give misleading results when the sample is fractionally wet in nature.

Basu and Sharma[20] used the Atomic Force Microscopic to record the force required to rupture thin brine films on quartz surfaces in order to follow the change in wetting properties of the reservoir rock. They concluded that the film breaks when the magnitude of capillary pressure exceeds the repulsive surface force in the thin film. These thin film forces are related in a complicated way to the brine chemistry, oil composition and surface morphology. They added that low values of critical capillary pressure imply that large section of reservoir rocks may be rendered mixed-wet as the brine film are unstable. On the other hand, high critical pressure values imply water-wet reservoir.

ADSORPTION STUDIES

In a recent paper[3], a detailed comparative study of asphaltenes adsorption on reservoir rocks was reported. The laboratory measurements were extended to different n-pentane asphaltenes precipitated from Hungarian and Libyan crude oils (Table 1). A crushed reservoir rock (Algyõ field, Hungary) in its original form and enriched then by

Table 1. Asphaltene content and viscosity of the tested crude oils.

Oil	Asphaltene content, %	Viscosity, mPa s (30 °C)
NL-119 (Hungarian)	19.04	380.00
Alg-541 (Hungarian)	2.21	4.27
A27 (Libyan)	0.56	3.14

montmorillonite and calcite were used as basic adsorbents. The adsorption tests were performed under static (batch type) and dynamic (column elution) conditions.

The amount of asphaltene adsorbed by the formation rock was calculated by the following equation:

$$\Gamma = (C_i - C_e)\frac{V}{W}$$

Where:

Γ = the adsorption (mg/g of adsorbent).
C_i = the initial concentration (mg/l).
C_e = the effluent concentration (mg/l).
V = volume of solution (ml).
W = weight of adsorbent (g of dry core).

In the static tests, the dependence of the adsorption loss on concentration was described by the Tóth's isotherm:

$$n^S = \frac{n^S_\infty \cdot c_e}{\left[1/k + c_e^t\right]^{1/t}}$$

$$n^S = n^S_\infty \ \text{if} \ 1/k << c_e^t$$

Where:

n^s = Calculated adsorbed amount mg/g.
C_e = Concentration of asphaltene mg/cm^3.
t = Interaction parameter.
K = Constant.

It was concluded that there was no significant differences in the adsorption of n-pentane asphaltenes, but a well-defined correlation was found between the mineral composition of the adsorbent and the specific adsorption (retention) loss (Figs. 1 and 2).

The outermost layer of molecules dominates the wetting properties of a solid. The water thin film formed on the solid surface as result of spreading the water was investigated experimentally (column elution as well) to determine its effect on asphaltene adsorption. That was done when different volumes (0.1-1.0 ml.) of distillate water were added into the dry formation rock. The VIS spectrophotometry reading showed that there were no asphaltene adsorbed when the sand pack was fully saturated with water. The relation between the volumes of water utilized to saturate the adsorbent and the specific adsorption (retention) loss produced another well-defined correlation (Fig. 3).

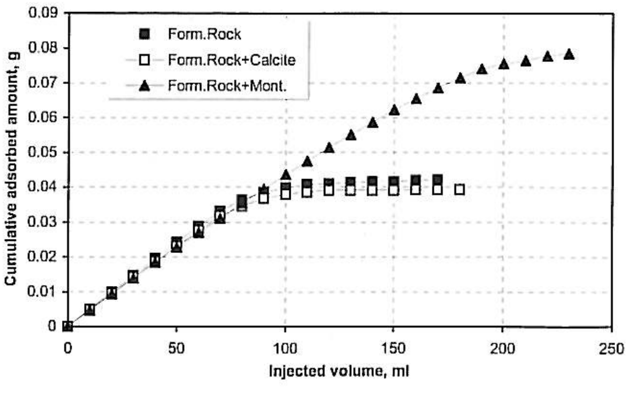

Fig. 1. Dynamic adsorption of A-27 asphaltene solution.

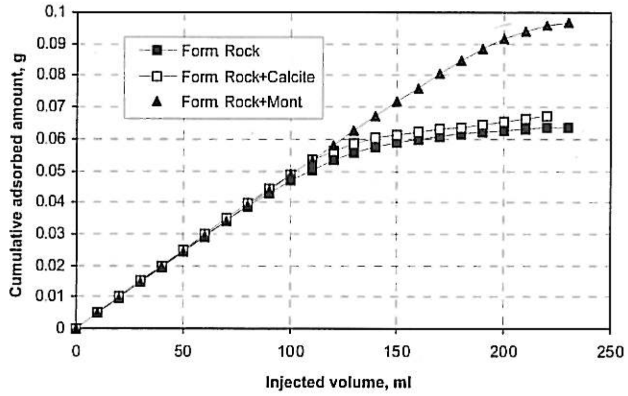

Fig. 2. Dynamic adsorption of NI-119 asphaltene solution.

WETTABILITY STUDIES

The wettability of a smooth carbonate rock having homogeneous and heterogeneous surface were used as a model material for evaluation of the asphaltene treatments. First, the contact angle of water on carefully cleaned rock plates was determined as a function of time. After this step, the same plates were immersed into asphaltene toluene solution for 24 hrs. The treated rock plates were then rinsed with solvent and dried at 80° C in vacuum oven. In a parallel test, the treatment was carried out with a solution that contained not asphaltene, but the original oil in the same concentration. In another test, the treatment was carried out with the original oil only. Equilibrium

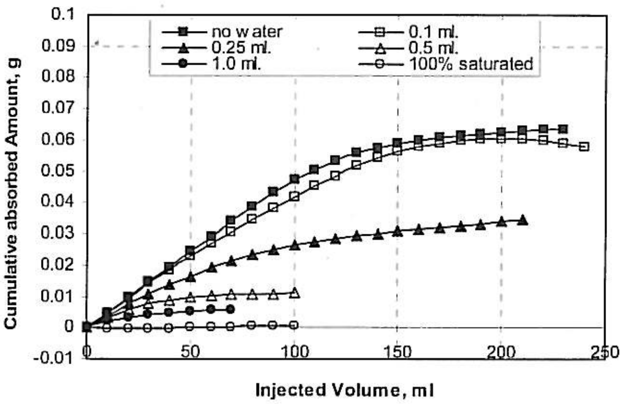

Fig. 3. Effect of water added on asphaltene adsorption.

contact angle was set after 10 min. in all the cases. Results of the wettability tests are shown in (Table 2). in which the contact angles measured on untreated surface serve as a basis of comparison. The presented results confirmed that the contact angle on homogeneous surfaces was always higher than those measured on heterogeneous surfaces, except in the case of treating with just original A-27 oil, the contact angles were almost equal. The results showed also that the asphaltenes from heavy and light oils were equally effective in wettability alteration. When the oil solution was used as a treating agent, only the heavy oil proved to be effective. The Libyan oil was also effective when it has been used alone as a treating agent.

Table 2. Effect of asphaltene on wettability (contact angle).

Treatment	Homogenous	Heterogeneous
No-treatment	85	54
NL-119 asphaltene in toluene	124	115
A-27 asphaltene in toluene	121	120
NL-119 oil in toluene	120	110
A-27 oil in toluene	77	54
A-27 oil	107	113

EFFECT OF ASPHALTENE ADSORPTION ON FLOW PROPERTIES

Asphaltene Solution and Reservoir Rock

Standard procedure was used to precipitate the asphaltene by n-pentane. First, the light cut of the oils was removed by atmospheric distillation up to 210°C. The solvent-residue ratio was 10:1, namely 15 ml of the light cut-free oil was mixed with 150 ml solvent. After 24 hours, the mixture was filtered; the solid asphaltene washed carefully and dried in vacuum at 70°C. Diluted asphaltene solutions were used. First, a stock solution with 0.5 g/l concentration was prepared using toluene as a solvent. All tests were performed with this stock solution. The analytical (calibration) curve was practically linear in the mentioned concentration range. The RSD of the measurements was better than ±5 %. The formation rock sample was obtained from the Algyõ field (S-Hungary). The data of the mineralogical composition of the rock determined by X-ray diffraction were listed in recent paper[21]. Prior to flow studies, the cores were characterized by He and Hg porosimetry. The geometry and porosity of these cores before and after treatment with asphaltene solution are summarized in Tables 3 and 4. It can be seen that the effect of asphaltene treatment on porosity is negligible.

Table 3. Geometry, pore volume and porosity of formation cores.

Symbol	Length, cm	Cross-section, cm^2	Vp, cm^3	$\Phi_{He\text{-}b}$, -	$\Phi_{w\text{-}b}$, -
SB-1	6.961	4.691	6.422	0.2154	0.1956
SB-2	7.092	4.711	6.669	0.2147	0.1996
SB-3	7.137	4.707	7.286	0.2169	0.2046
SB-4	7.112	4.714	7.517	0.2242	0.2075

Table 4. Effect of asphaltene treatment on porosity of cores.

Symbol	$\Phi_{He\text{-}a}$, -	$\Phi_{w\text{-}a}$, -	$\Phi_{He\text{-}b}/\Phi_{He\text{-}a}$, -	$\Phi_{w\text{-}b}/\Phi_{w\text{-}a}$, -
SB-1	0.2212	0.1830	0.9738	1.0686
SB-2	0.2181	0.1909	0.9844	1.0454
SB-3	0.2201	0.1704	0.9855	1.0454
SB-4	0.2292	0.1777	0.9782	1.0454

Permeability Measurements and Water Saturation

The absolute, effective, relative and normalized relative permeability of cores were determined with the aim at characterizing the flow properties of water and gas in the original and the asphaltene treated cores. In the literature, numerous methods have been proposed for the determination of the relative permeability curves. The so-called "displacement" type procedure developed by Tóth *et al.*[22,23] was applied in this study. Four relatively similar cores were selected for this study. Absolute and effective permeability before treatment are listed in Table 5.

Table 5. Absolute and effective permeability of cores before asphaltene treatment.

Symbol	$k_{a\text{-}b}$, mD	b_b^*, -	$k_{w\text{-}b}$, mD
SB-1	37.36	0.2837	n.d.
SB-2	44.97	0.0731	25.34
SB-3	33.82	0.4312	19.08
SB-4	45.30	0.2128	25.12

b_b^* = Klinkenberg constant before treatment

The absolute permeability of cores was determined by nitrogen using the Klinkenberg's technique. The protocol and sequence of relative permeability measurements in gas/water system was described in detail in a previous paper[3]. Results of the permeability measurements are summarized in Table 6 and (Figs 4-7). The normalized curves are also presented in these figures. It can be seen that the absolute gas permeability of cores decreased after asphaltene treatments. Parallel with this change, the

Table 6. Absolute and effective permeability of cores after asphaltene treatment.

Symbol	k_{a-a}, mD	b_a^*, -	k_{w-a}, mD
SB-1	27.56	0.9591	23.28
SB-2	38.33	0.6493	29.66
SB-3	30.10	0.8452	16.01
SB-4	39.51	0.5677	36.64

b_a^* = Klinkenberg constant after treatment

Klinkenberg constant multiplied and became more uniform among the treated cores. On the basis of these experimental findings, it may be concluded that the smallest pores and capillaries were really blocked, and as a result, the tortuosity and the free flow cross-section decreased after asphaltene treatment. With regards to the effective water permeability, the impact of the asphaltene treatment was controversial and the number of experiments is not enough to draw statistically correct conclusion and unfortunately the data for core SB-1 was missing. Evaluation of water saturation data obtained before and after asphaltene treatments clearly indicated a hydrophobization effect in all cores (Table 7). In general, the residual saturation measured after gas injection decreased by 4-6 %, except in the case of core SB-4, the change is roughly 50 %. On the other hand, the residual gas saturation or maximal water saturation at the end of water injection increased a little. Thus, the asphaltene treatment may have both positive and negative effect

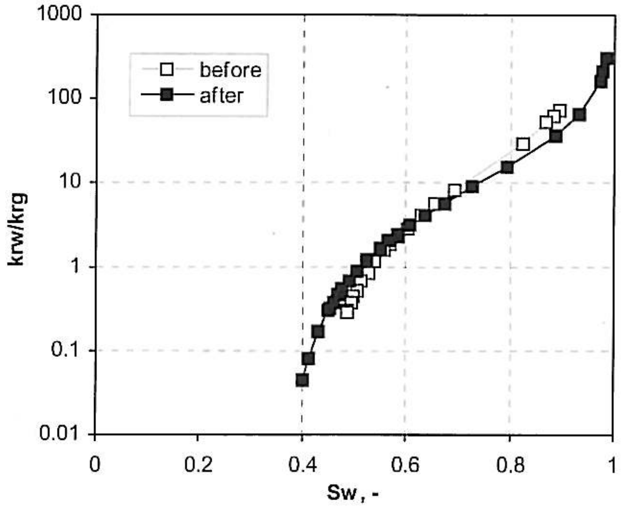

Fig. 4. Effect of asphaltene treatment on relative relative permeability (SB-1 core, drainage direction).

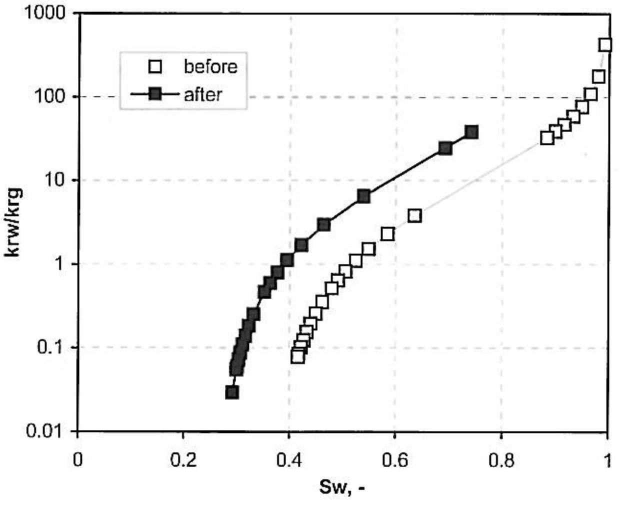

Fig. 5. Effect of asphaltene treatment on relative permeability (SB-2) core, drainage direction).

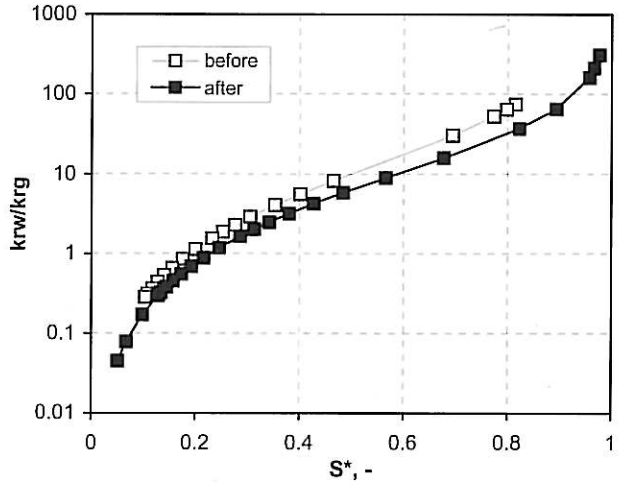

Fig. 6. Effect of asphaltene treatment on normalized relative permeability (SB-1 core, drainage direction).

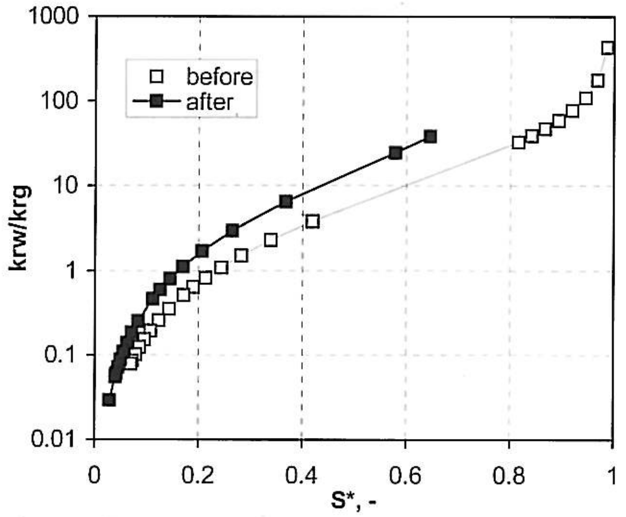

Fig. 7. Effect of asphaltene treatment on normalized relative permeability (SB-2 core, drainage direction).

Table 7. Effect of asphaltene treatment on water saturation of cores.

Symbol	Before treatment		After treatment	
	S_{wmin-b}, -	S_{wmax-b}, -	S_{wmin-a}, -	S_{wmax-a}, -
SB-1	0.4252	0.9730	0.3676	0.9710
SB-2	0.3723	0.9830	0.3357	0.9857
SB-3	0.2121	0.9128	0.1797	0.9383
SB-4	0.2012	0.8973	0.1038	0.9134

on relative gas permeability depending on the core structure and fluid saturation. That can be seen in the relative permeability curves shown in Figures 4 and 5. The normalized relative permeability curves shown in (Figs. 6 and 7) proved a similar behavior as the original ones did. It has been noted that the curves were not coinciding, that is to say, that the actual flow path of gas and water in cores are different in the original and the treated cores. Once again, the reasons must be searched in the hydrophobization and its consequences in porosity, tortuosity, capillary forces, *etc.*

Capillary Pressure Measurements

Experimentally, both the diaphragm and the centrifugal methods were routinely used. Two of the serial measurements will be presented here which well demonstrate the effect of asphaltene treatment on capillary pressure curves. Basically, two methods are used for fitting of laboratory data to reservoir conditions. The so-called J-function uses the physical properties of rock and fluid as a correcting term and is expressed as:

$$J(S_w) = \frac{P_c}{\sigma}\left(\frac{k}{\Phi}\right)^{1/2}$$

Another proposed formula in literature is:

$$J(S_w) = \frac{P_c}{\sigma\cos\Theta}\left(\frac{k}{\Phi}\right)^{1/2}$$

$$W = \frac{J(S_w)_a}{J(S_w)_b}$$

Where:

σ = Interfacial tension (dyane/cm).
Pc = Capillary pressure (dyne/cm^2).
K = Permeability (cm^2).
Φ = porosity (%).
Θ = Contact angle (æ%).

Supposing that the hydrophobization slightly affects k, Φ and σ, the W value gives an indirect information for wettability alteration at constant P_c. Therefore, the second procedure was used in this research program. The primary obtained capillary pressure curves and the normalized J-functions as a function of water saturation are shown in Figures 8 to 11. Meanwhile the data for water saturation and threshold pressure are listed in Table 8.

Results reflected that both the normal and the normalized J-function curves run below the original ones after asphaltene treatment (Figs. 10-11). At low water saturation, the curves may intersect each other, however, they practically approach the same limiting residual values. Effective hydrophobization could not be predicted by the residual water saturation (Table 8) and this fact apparently contradicts to the conclusions, which might be drawn by the modification of capillary and threshold pressure data. The phenomena are explained by the small size and end effect of cores and the native properties of the centrifugal technique. After asphaltene treatment, the threshold pressure considerably decreased. These experimental results definitely indicate a strong

Table 8. Effect of asphaltene treatment on residual water saturation and threshold-pressure (P_c data).

Symbol	Before treatment		After treatment	
	$S_{wmin\text{-}b}$, -	$P_{t\text{-}b}$, bar	$S_{wmin\text{-}a}$, -	$P_{t\text{-}a}$, bar
SB-6	0.2352	0.1402	0.2491	0.1304
SB-6 (normalized)	-	0.0885	-	0.0673
SB-10	0.2395	0.1168	0.2414	0.0985
SB-10	-	0.1077	-	0.0763

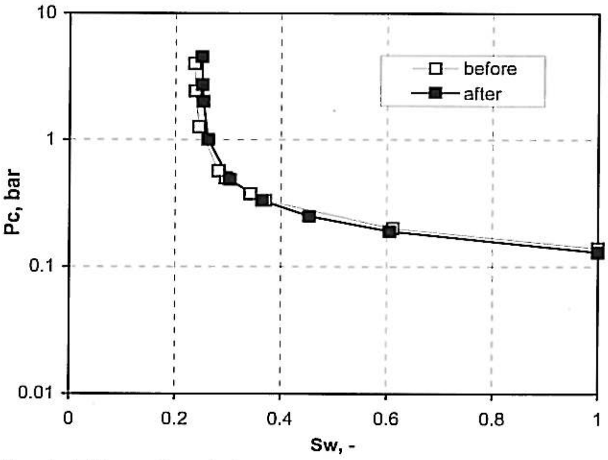

Fig. 8. Effect of asphaltene treatment on capillary pressure curve (SB-6 core, centrifugal technique).

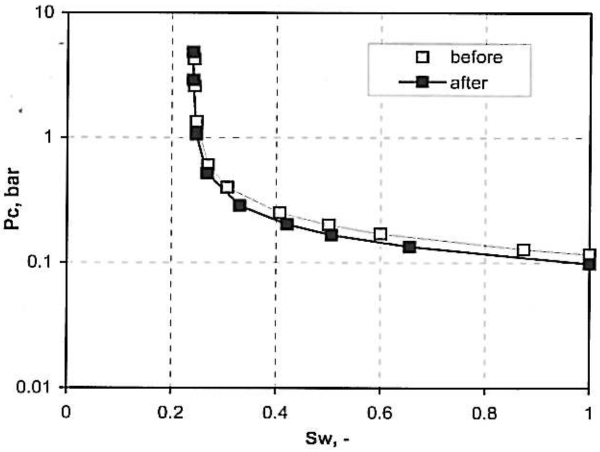

Fig. 9. Effect of asphaltene treatment on capillary pressure curve (SB-10 core, centrifugal technique).

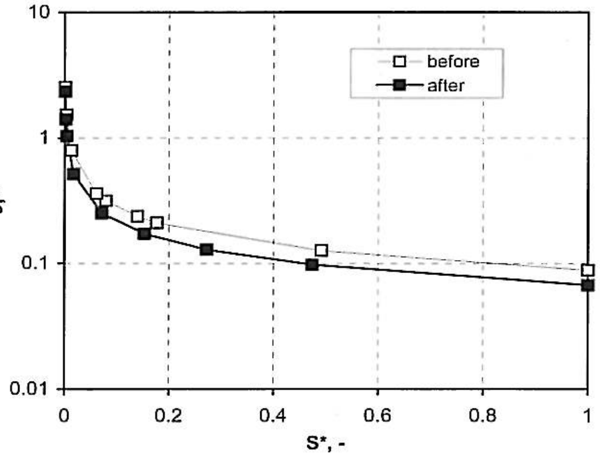

Fig. 10. Effect of asphaltene treatment on normalized capillary pressure curve (SB-6 core, centrifugal technique).

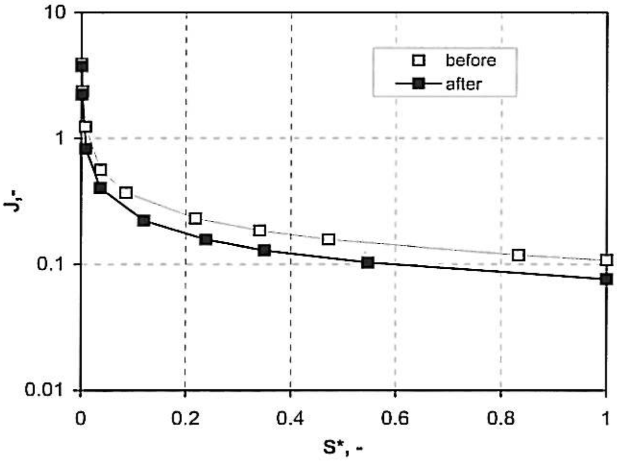

Fig. 11. Effect of asphaltene treatment on normalized capillary pressure curve (SB-10 core, centrifugal technique).

hydrophobization after treatment not only in the initial period of water drainage by gas, but through almost the whole process (down to 30 % water saturation which is close to the residual value). Although the curves in (Figs. 8-11) fall very close to each other, the difference of water saturation belonging to constant capillary pressure and J values are remarkable. As shown in Figures 12 and 13, that difference rapidly decreases with the capillary pressure and reaches zero as the drainage gets to the final stage. Anyhow, the asphaltene adsorption resulted in an accelerated water displacement in both cores, or in other words, identical water saturation could be obtained at lower capillary pressure after asphaltene treatment.

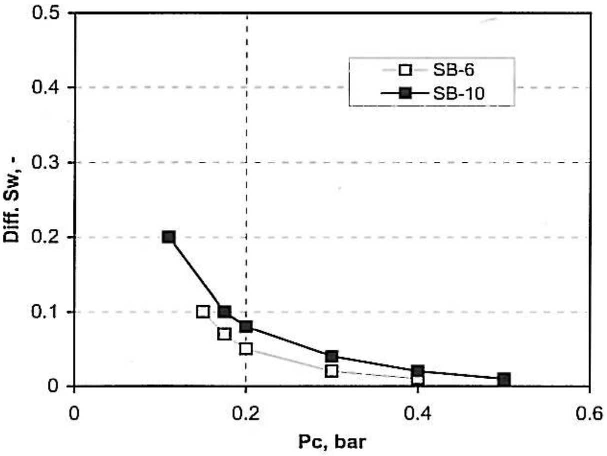

Fig. 12. Difference of water saturation at constant capillary pressure caused by asphaltene treatment.

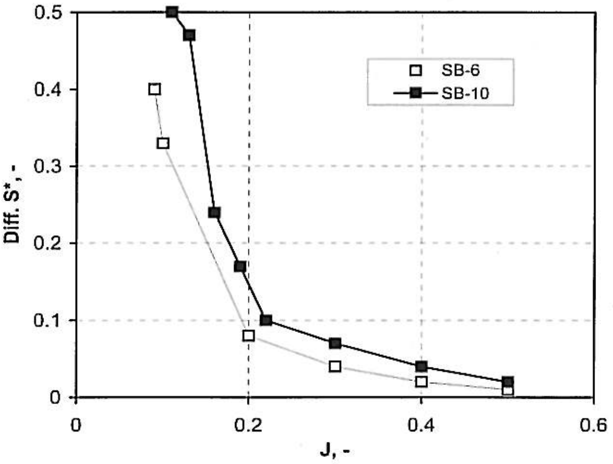

Fig. 13. Difference of normalized water saturation at constant J function caused by asphaltene treatment.

CONCLUSION

1. Langmuir and the Tóth isotherm were used to describe the static (batch or equilibrium type) adsorption tests. However, in high asphaltene concentration, particularly in clay rich system, these formulas cannot be applied for description of the sorption phenomena.

2. The measured and calculated adsorbed amounts of the static tests were in good agreement with the dynamic adsorption loss determined by the maximal values.

3. All asphaltenes (light, medium and heavy) significantly influenced the wettability of carbonate type formation rocks.

4. The Libyan oil, in its original form, caused nearly the same wettability alteration on carbonate rock surface as its asphaltenes in toluene solution did. This result suggests that the sandstone Sharara field, probably remained water-wet or intermediate after contact with oil, but the native wettability of the consolidating mineral components (carbonates, dolomites) was substantially modified and became oil-wet during the accumulation and entrapment process.

5. The effect of asphaltene adsorption on wettability influencing the accessible pore volume,

residual water saturation, threshold pressure, *etc.*, clearly shows an effective hydrophobization on all formation core samples.

6. Modification of the relative permeability and capillary pressure curves suggests that the spontaneous water imbibition might be drastically restricted by asphaltene treatment.

REFERENCES

[1] Anderson, W.G., 1986 (Oct.) Wettability literature survey-part 1: rock/oil/brine nteractions and the effects handling on wettability . Paper *SPE* 13932,JPT,1125-1144.

[2] Morrow, N.R.,1990 (Dec.). Wettability and its effect on oil recovery. Paper *SPE* 21621, JPT.

[3] Rays, B.H., Lakatos, I., Pernyesz, T., and Janos, T., 2003 (June). Adsorption of asphaltenes on formation rocks and its effect on wettability. *SPE* Paper 81470, presented at the 13th *SPE* Middle East Oil Show and Conference Bahrain.

[4] Yan, J., Plancher, H., and Morrow, N., 2001 (Feb.). Wettability changes induced by adsorption of asphaltenes. Paper *SPE* 37232, Presented at the *SPE* International Symposium on Oilfield Chemistry held in Houston, Texas.

[5] Morrow, N.R., Gram, P.J., and McCaffery, F.G., 1973 (Aug.). Displacement studies in dolomite with wettability control by octanic acid *Soc. Pet. Eng.J.*, 221-232.

[6] Ali, M.A. and Islam, M.R., 1997 (Oct.). The effect of asphaltene precipitation on carbonate rock permeability. Paper *SPE* 38856, presented at *SPE* Annual Technical Conference and Exhibition held in San Antonio, Texas, USA.

[7] Kamath, V.A., Yang, J., and Sharma, G.D., 1993 (May). Effect of asphaltene adsorption on dynamic displacement of oil by water, Paper *SPE* 26046, proc. *SPE* Western Regional Meeting, Anchorage, Alaska.

[8] Glampietro, P., Canonico, L.B., Galbariggi, G., Bertero, L. and Camianl, C., 1996 (Aug.). Asphaltene adsorption onto formation rock: an approach to asphaltene formation damage prevention *SPE* Production and Facilities, 156-160.

[9] Collins, S.H. and Melrose, J.C., 1983 (June). Adsorption of asphaltene and water on reservoir rock minerals. Paper *SPE* 11800, presented at the International Symposium on Oilfield and Geothermal Chemistry held in Denver, CO. USA.

[10] Dubey, S.T. and Waxman, M.J., 1991 (Aug.). Asphaltene adsorption and desorption from mineral surfaces. Paper *SPE* 18462, *SPE Reservoir Engineering*, 389-395.

[11] Kim, S.T., Boudh-Hir, M.E., and Mansoori, G.A., 1990 (Sep.). The role of asphalene in wettability reversal. Paper *SPE* 20700 presented at the 65th Annual Technical Conference and Exhibition of the SPE held in New Orleans, LA.

[12] LIU, Y. and Buckley, S., 1997 (March). Evolution of wetting alteration by adsorption from crude oil. Paper *SPE* 28970, *SPE Formation Evaluation*, 5-11.

[13] Buckley, S., Liu, Y., Xie, and Morrow, N., 1997 (June). Asphaltenes and crude oil wetting- The effect of oil composition. Paper *SPE* 35366, *SPE Journal*, 107-119.

[14] Chang, Y.C., Mohanty, K.K., Huang, D.D., and Honarpour, M.M., 1997. The impact of wettability and core-scale heterogeneities on relative permeability. *J. of Pet. Sc. and Eng.I*, **18**,1-19.

[15] Baldwin, B.A., 1988 (March). Water imbibition and characterization of North Sea chalk reservoir surface. Paper *SPE* 14108. SPE Formation Evaluation, 125-130.

[16] Jun-Zhi Wei and Ole B. Lile., 1992 (May). Influnce of Wettability and saturation sequence on relative permeability hysteresis in nconsolidated porous media. Paper *SPE* 25282.

[17] Desbrandes, R.,and Bassiouni, Z., 1990 (Oct.). In situ formation wettability determination in depleted zone. Paper *SPE* 21182, Presented at the SPE Latin American Petroleum Engineering Conference held in Rio de Janeiro.

[18] Dixit, A.B., McDougall, S.R., Sorbie,K.S., and Buckley, J.S., 1996 (April). Pore scale modelling of wettability effects and their influence on oil recovery. Paper SPE/DOE 35451, Presented at the 1996 *SPE/DOE* Tenth Symposium on Improved Oil Recovery held in Tulsa, OK.

[19] McDougall, S.R., and Sorbie,K.S., 1995 (Aug). The impact of wettability on water flooding: Pore-scale simulation. Paper *SPE* 25271, SPE Reservoir Engineering.

[20] Subhayu Basu and Mukul M. Sharma, 1996 (Oct.). Defining the wettability state of mixed wet reservoirs: measurement of critical capillary pressure for crude oils. Paper *SPE* 36679, Presented at the SPE 71st Annual Technical Conference and Exhibition held in Denver, Colorado, U.S.A.

[21] Rayes, B.H., Pernyeszi, T., Lakatos, I., Tóth, J. 2003 (Feb.). Comparative study of asphaltene adsorption on formation rocks under static and dynamic conditions. Paper *SPE* 80265, presented at the SPE International Symposium on Oilfield Chemistry held in Houston, TX, U.S.A.

[22] Tóth, J., Bódi, T., Szûcs, P. and Civan, F. 2000. Analytical Techniques for determination of relative permeability from displacement experiments. in lakatos, I. *Novelties in Enhanced Oil and Gas Recovery*, Progress in Mining and Oilfield Chemsity, 2:91, Akadémiai Kiadó Ltd., Budapest .

[23] Tóth, J., Bódi, T., Szucs, P. and Civan, F. 2002. Convenient formulae for determination of relative permeability from unsteady-state fluid displacement in core plugs. *J. Petroleum Geoscience and Engineering*, 35:33 .