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Interfacial tension and contact angle of asphaltenic and resinous model oil in the presence of binary salts mixtures

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Using smart or low salinity waters known as green processes gained increasing attention due to their unique features and their positive impacts on the environment. In light of this fact and since there is limited knowledge about the effects of salts under engineered concentrations or binary mixtures and crude oil fractions on the interfacial tension (IFT) reduction and wettability alteration of the resinous (RSO) and asphaltenic synthetic oil (ASO), the current investigation is designed and performed for the first time. Moreover, the dynamic behavior of the IFT variation was carefully investigated and the relaxation time was obtained and modeled to see the impact of mono and divalent salts individually and in binary conditions. The relaxation times revealed that the lowest adsorption times were obtained for NaCl/CaCl₂ brine regardless of the examined oil types of ASO and RSO due to the high movement affinity of the polar functional groups toward the interface consequently reducing the required time for coverage and packing of active agents at the interface. Finally, the measured contact angle values revealed a significant effect of binary salts on the wettability alteration toward strongly water-wet conditions, especially for the RSO and ASO compared with crude oil.

Keywords Dynamic IFT, Asphaltene, Resin, Binary salt mixture, Relaxation time

According to the analysis, more than 60% of the original oil in place (OOIP) remained unrecovered after the primary production stage which uses the reservoir's natural pressure. In this way, enhanced oil recovery methods (EOR) were proposed and used to recover the trapped oil¹⁻³. In this way, several EOR methods, including gas injection, chemical injection, microbial injection, and smart water or low salinity water injection were examined through different oil reservoirs. According to the performed investigations, the interactions existed between the indigenous compounds of the reservoirs such as salts and ions concomitant with the rock and fluid properties is the priority to find the best method for higher oil production. Among the EOR methods, activating multiple mechanisms using ions adjustment generally known as the smart water injection process, is highly cost-effective and practical on the field scale, it seems highly beneficial to investigate the interactions between the different ions, especially in binary or ternary mixtures. Besides, the interfacial tension (IFT) reduction and wettability alteration are among the most crucial effective mechanisms since they can manipulate the water-oil movement, relative permeability and water-oil distribution as well as oil and water movement modification toward the rock surface leading to a higher oil production of the trapped oils⁴.

For example, the performed investigations revealed that among the different previously examined ions rendering the wettability towards more water-wet, Mg²⁺ has a higher impact⁵. Also, Gupta et al.⁶ reported that Ca²⁺ ion is so effective as it is individually being used under high concentration conditions, while Mg²⁺ does not have this capability based on the experimental studies performed on the calcite plates. Moreover, Zhang et al.⁷ found that the retarded contact of carboxylic compounds present in the crude oil has an undeniable impact on the wetness of the surface toward water-wet conditions.

Besides, Boumedjane et al.⁸ investigated the combined effect of Mg²⁺/SO₄²⁻ and Ca²⁺/SO₄²⁻ on the surface properties of the fluid/fluid and solid/fluid interfaces which revealed the better impact of these binary

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combinations on the wettability alteration toward desired conditions. Moreover, based on the study carried out by Lashkarbolooki et al.⁹, NaCl is the less effective salt on the IFT as the asphaltene and resin existed in the synthetic oil compared with the CaCl₂ and MgCl₂.

According to their findings, crude oil composition of resin, asphaltene, saturates, and aromatics is a crucial and effective parameter on the higher tertiary oil recovery that must be investigated in detail. Among these fractions, resin and asphaltene are the most active fractions which act as natural surfactants and react with the other chemicals that exist in the solution.

In the light of this fact, although a wide range of investigations were performed on the IFT of different aqueous solutions and crude oil, there is a limited number of investigations regarding the wettability using synthetic oils prepared by resin and asphaltene and different aqueous solutions.

In this way, the current investigation is designed and performed to complete our previous investigations regarding the effect of ions and their interactions with crude oil on the IFT reduction and wettability alteration. Several experiments were performed with single salt¹⁰, including NaCl, Na₂SO₄, KCl, CaCl₂, MgCl₂, and MgSO₄ and their binary mixtures with NaCl¹¹. Since it was found that the crude oil composition is a crucial parameter that directly affects the interactions between the salts and crude oil which appear as IFT reduction and wettability alteration¹¹, a new set of experiments using asphaltenic and resinous synthetic oil was performed with the aforementioned single brines¹². In other words, since crude oil regardless of its type (acidic, neutral or basic types) is a complex mixture of different chemicals, it is hard to extract generalized conclusions using the results obtained by crude oil. In this way, it seems that using specific fractions of crude oil which can act as natural surfactants, provides a better chance to find a generalized conclusion. Respecting the obtained results for IFT reduction using different types of crude oil and the existing limitations regarding the interactions between the binary solutions of salts and resin and asphaltene fractions on both IFT reduction and wettability alteration, the current investigation is systematically designed and performed. In more detail, the effect of asphaltene and resin fractions of crude oil and synergistic/antagonistic effect of NaCl salt and other salts in the seawater on the IFT and wettability alteration and spreading coefficient were investigated by measuring these parameters with the synthetic model oils and the binary salty mixture containing NaCl and results were compared with the previous publications (single salt and model oils)¹² and crude oil/single¹⁰ and binary¹¹ brine solutions.

Considering these facts, the current investigation is crucial since most of the previously performed investigations were focused on one salt. However, this investigation focused on the possible impact of binary salt solutions on the IFT and contact angle values of the oil/water systems. Besides, most of the previously performed investigations were focused on the application of crude oil leading to case-sensitive results. However, in this investigation resin and asphaltene fractions were used to prepare the synthetic oils for further studies. The point is that these two fractions are highly interactive with the salts and they also can act as natural surfactants. So, since there is a limited number of investigations regarding the impact of specific fractions of crude oil on the interaction of salts especially binary solutions on the IFT and contact angle, there is ample space in this field with a large number of ambiguities that must be clarified using similar studies. Moreover, using specific fractions of resin and asphaltene fractions provides the chance to obtain more generalized conclusions regarding the impact of crude oil type on the IFT and wettability alteration as the main EOR mechanism compared with the studies that used crude oil with thousands of compounds.

Experimental procedures

Dynamic IFT and contact angle measurement

In the current study, the pendant drop and sessile drop methods as an accurate and the mostly used methods for IFT and contact angle measurements were used. The pendant drop method is mainly comprised of different sections including forming the drop at the tip of the nozzle regardless of the drop orientation (rising or pendant position which is directly correlated to the density difference of the bulk and drop phases), image capturing system which comprised of a Charge-coupled device (CCD) camera and macro lens to provide a proper image from a small drop in the bulk phase and the on-line image processing software. The first section uses an automatic injection pump with a tunable injection rate equipped with a glass syringe and stainless steel needle. This direct installation of the needle to the syringe provides a smooth injection of fluid into the bulk phase without any time delay and provides a stable drop at the tip of the nozzle during the measurements. The second section provides suitable pictures with desired magnification and sharpness from the formed drop and then dispatches it to the online software. Finally, the software calculates the required properties of the image and then converts these measured properties to the corresponding IFT using the shape factor which is the main principle of the used software (Fanavari Atiyeh Pouyandegan Exir Co., Arak, Iran).

A detailed description of the used equipment and corresponding procedure is given elsewhere¹¹. Wettability is a determining factor in many areas of sciences from coatings to enhanced oil recovery and medical implants to pesticides. Due to a wide range of applications, the wettability measurements with several different methods especially sessile drop which is one of the most widely used and accurate methods, is highly investigated. Sessile drop is the most widely used contact angle measurement method which is mainly based on the optical tensiometer which ranges from manual instruments to completely automated systems. In the sessile drop method, the droplet, typically water, is placed on the solid sample, and the image of the drop is taken by a high-resolution camera which is then followed by automatic determination using online software.

Sessile drop measurement which gives a so-called static contact angle for the surface is mostly done with water. If the water contact angle is lower than 90°, the surface is said to be hydrophilic and if the contact angle is higher than 90°, the surface is hydrophobic. Hydrophilicity and hydrophobicity are important in many applications. Water contact angle measurement is often used for quality control purposes as it offers a quick and non-destructive way to check surface chemistry. Sessile drop is also often utilized for surface-free energy calculations

which detects contaminants and changes in surface chemistry that are generally only visible with sophisticated surface analysis techniques such as x-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF SIMS). This information is important because even very low levels of contaminations or small changes in the surface chemistry can impact adhesive bond strength.

In the current investigation, a specific type of sessile drop commonly known as the captive method was used to measure the contact angle of the oil drop in the presence of an aqueous bulk phase settled beneath the rock surface submerged in the aqueous phase. In detail, the required drop volume suspended at the tip of the nozzle and then the submerged thin section of the rock surface gently moved toward the suspended drop to grab the formed drop at the tip of the nozzle into the rock surface. At this time, the surface is moved upward to completely detach the suspended drop, and the measurement begins.

Materials

Since one of the most available water sources for secondary and tertiary oil recovery is the Persian Gulf water with a ionic strength of about 0.7 M, the current work is mainly focused on the application of aqueous binary solutions with the ionic strength of 0.7 for the IFT and contact angle measurements using six salts namely NaCl, KCl, Na₂SO₄, MgSO₄, MgCl₂, and CaCl₂ salts (purity better than 99% from Merck, Germany) dissolved in deionized water (DW) while the first salts is always NaCl (see Table 1). After that the quality of the prepared formation brine was analyzed using 930 Compact IC Flex from Metrohm (Switzerland) with 0.1% Accuracy and Precision.

In this study, the examined oil samples are asphaltenic and resinous synthetic oil samples isolated by American Society for Testing and Materials (ASTM (D2007-80)) method from a semi-heavy dead oil with 27 American Petroleum Institute (API°) with a total acid number of 0.2 mg KOH/g (one of the southern Iranian oil fields). In addition, the required silica gel with 35–70 mesh ASTM for column chromatography and resin isolation stage was supplied from Sigma-Aldrich, USA.

Asphaltene and resin extraction procedure

Since the main focus of the current investigation is examining the effect of binary solutions on the resinous synthetic oil (RSO) and asphaltenic synthetic oil (ASO) prepared by asphaltene and resin fractions, the ASTM (D2007-80) standard was used to isolate the required fractions for the rest of the experiments¹³. So, n-heptane was used for asphaltene precipitation in the preliminary stage by dissolving the oil sample in the n-heptane (ratio of 1 to 40)¹⁴ which was then filtered using filter paper. After that, soxhlet extraction was used to purify the extracted asphaltene through multiple washing sequences using n-heptane. Finally, the isolated asphaltene on the filter paper was dried and collected. In the next stage, resin extraction was performed using the deasphalted oil called maltene using the column chromatography method which was packed by silica gel^{13,15}. In detail, the required extractor solvent was poured over the top of the silica gel column to remove the soluble components. To extract saturated and aromatic compounds from the column, a binary solvent containing n-heptane and toluene with a volume ratio of 70:30 were used. After ensuring the complete extraction of aromatic and saturated fractions, resin fraction was extracted using a solvent solution prepared by mixing the acetone, toluene, and dichloromethane with 40:30:30 volume fraction. After that, the pasty resin can be achieved using further vaporization of the formed solution¹⁶. Finally, the synthetic oils with the concentration of 3 wt% were prepared by dissolving extracted asphaltene and resin in their common solvent, i.e. toluene^{15,17–19}.

Analysis

Elemental analysis

After extracting the resin and asphaltene fractions, it is highly required to elementally analyze these two fractions due to their diverse chemical formulas preventing the researcher to find the exact structures of these chemicals. In this way, instead of finding the exact structures of these fractions, it is possible to find some qualitative characteristics such as overall structure (aromaticity index which is directly correlated to the branched structure of these fractions) or to find the type of atoms that existed in these fractions especially the heteroatoms including nitrogen, oxygen, sulfur, etc. Although asphaltene and resin fractions may have a similar structure, they show different properties of physical appearance, aromaticity, size, and polarity^{19,20}. In general, it is reported that these molecules comprised of polyaromatic cores mainly include several fused rings and aliphatic chains containing heteroatoms such as nitrogen (N), sulfur (S), and oxygen (O)^{21,22}. The other point is that although the structure of

Ion	Binary salts				
	NaCl/KCl	NaCl/CaCl ₂	NaCl/MgCl ₂	NaCl/Na ₂ SO ₄	NaCl/MgSO ₄
Na ⁺	8046	10,725	10,725	13,794	9656
K ⁺	13,684	–	–	–	–
Ca ²⁺	–	3118	–	–	–
Mg ²⁺	–	–	1891	–	1701
Cl [–]	24,816	22,053	22,053	14,183	14,891
SO ₄ ^{2–}	–	–	–	9603	6722
Total	46,546	35,896	34,669	37,580	32,970

Table 1. The concentration (ppm) of specific ions in the studied binary brine solutions.

asphaltene and resin has not been well understood, it is believed that they contain aromatic compounds including some aliphatic chains^{23,24}. The core of aromatic compounds contains the number of heteroatoms that lead to the polarity of the hydrophilic part. Generally, the amphiphilic nature of surfactants meaning they contain both hydrophobic (tails) and hydrophilic (heads) groups which means they are both oil-soluble and water-soluble compounds²³. In this way, the elemental analysis (CHNSO) (Thermo Flash elemental analyzer (EA 1112 series)) was performed to obtain the weight percent of these polar atoms as well as hydrogen (H) and carbon (C) in the structure of the extracted asphaltene and resin fractions (see Table 2). The lower atomic H/C ratio of asphaltene compared to resin indicates the higher amount of aromatic compounds in the asphaltene structure. In addition, the major difference between extracted asphaltene and resin is the higher oxygen content in the resin structure (8.5 wt%) compared to that in the asphaltene structure (i.e. 5.6 wt%). In more detail, both fractions had similar weight percent of N atom in their structures (i.e. 1.8 wt%) while S atom in the asphaltene fraction (3.9 wt%) was slightly more than in the resin fraction (3.5 wt%).

Fourier transform infrared (FTIR) analysis

FTIR as an important means of identifying organic compounds (in combination with multivariate analysis) has been used to predict several parameters, such as crude oil properties and fractions (light and heavy virgin, naphtha, distillate, kerosene, vacuum gas oil, and residual in crude oil)²⁵, to discriminate and predict the crude oil source of different asphalt samples²⁶, to distinguish virgin olive oils according to geographic origin²⁷, and to differentiate ceramics having different provenance²⁸. The most routine aspect of this technique is that FTIR is useful for analyzing chemical composition. In this study, besides the elemental analysis, FTIR analysis was performed using Perkin-Elmer RXI, USA with a frequency range of 4000–400 cm^{-1} to find the functional groups of extracted asphaltene and resin fractions. The other important point which can be extracted via FTIR analysis is the determination of similar and dissimilar functional groups of the asphaltene and resin.

The analysis tabulated in Table 3 revealed that the following peaks at 739, 803, 856, 1025, and 1123 cm^{-1} appeared for the asphaltene FTIR spectra which were correlated to sp^2 C–H (aromatic and alkene), C–S–C, C–H alkenes and C–O and alkoxy C–O bands, respectively. The FTIR analysis also revealed the 730, 807, 859, 1031, and 1128 cm^{-1} peaks for resin fraction. The comparison between the FTIR for resin and asphaltene fractions revealed that the peak at 1278 cm^{-1} for resin cannot be observed for asphaltene which was correlated to alkyl C–O. On the other side, the observed peak at 1442 cm^{-1} for asphaltene and 1455 cm^{-1} for resin can be related to C–O (carboxyl) bond. Moreover, the peak at 1597 and 1600 cm^{-1} in asphaltene and resin structures is related to the C=C bond. The other main differences between the FTIR spectra of resin and asphaltene fractions are 1859,

Component	Asphaltene (wt%)	Resin (wt%)
C	81.8	77.0
H	6.9	9.4
S	3.9	3.4
N	1.8	1.8
O	5.6	8.5
Atomic H/C ratio	1.02	1.46

Table 2. Elemental analysis of extracted asphaltene and resin.

Functional groups	Observed peaks for asphaltene (cm^{-1})	Observed peaks for resin (cm^{-1})
sp^2 C–H (aromatic and alkene)	739	730
C–S–C	803	807
C–H alkenes	856	859
C–O	1025	1031
alkoxy C–O	1123	1128
alkyl C–O	–	1278
C–O (carboxyl)	1442	1455
C=C	1597	1600
C=O	–	1859
C–H _{ar}	–	1941
O=C–H	–	2728
O–H	3440	3420
N–H	3440	–
N–H ₂	–	3420
Alkyl and aromatic C–H	2852	3025

Table 3. Functional group of the extracted asphaltene and resin through XRD analysis.

1941, and 2728 cm^{-1} which related to the C=O, C-H_{ar}, and O=C-H bands, respectively, which only existed in the resin fraction. In addition, the O-H and N-H (i.e. heteroatoms bonded to H) stretching vibration can be seen at 3440 for the asphaltene sample while for resin a broader peak was observed compared to the asphaltene sample which can be attributed to O-H and N-H₂ stretching vibrations at 3420 cm^{-1} . Alkyl and aromatic C-H stretches were also observed for both samples in the range of 2852 cm^{-1} and 3025 cm^{-1} ^{129–32}.

Dynamic IFT modeling and spreading coefficient calculation

Asphaltene and resin molecules significantly affect the dynamic IFT behavior due to their polar features³³. Generally, the molecule attachment onto the interface is due to high adsorption activation energy barriers. In detail, if the diffusive part of the process is much larger than the kinetics part, it is expected that the diffusion controls the adsorption of active agents³⁴. In general, if the adsorption is limited by the activation energy barrier, the exponential decay model (Eq. 1) proposed by Lankveld and Lyklema³⁵ can be used to predict the IFT value as a function of time as well as the relaxation/adsorption time (τ)^{36,37}:

$$\gamma_t = \gamma_e + (\gamma_0 - \gamma_e)e^{-\frac{t}{\tau}} \quad (1)$$

where γ_0 , γ_t , and γ_e are the IFT at the beginning, each time (t), and equilibrium, respectively. It has been reported that this model is accurate to model dynamic IFT consisting of oleic phases^{37–40}. Comparing the dynamic IFT modeling including the mono-exponential decay model, dynamic adsorption model, and empirical equations revealed that the mono-exponential decay model is the most accurate method which also provides the opportunity to estimate the relaxation times of active components at the oil/aqueous solution interface^{37,40}.

Rocks

The used rock thin section from the outcrop was analyzed using Energy Dispersive Spectroscopy known as EDX analysis was used for the elemental analysis of the used rock thin sections. Besides, the aforementioned analysis, mapping image analysis was performed to find the dispersion of the elements and their concentrations in different areas of the thin sections (see Table 4).

According to the performed analysis, most of the used rock samples are made of oxygen, carbon, calcium, and magnesium which can be considered as an indication of a dolomite core sample. On the other hand, one can conclude using Field Emission Scanning Electron Microscope (FE-SEM) images that the rock surfaces are not smooth and homogenous which leads to uncertainties during the contact angle measurements. In this way, each contact angle measurement was performed at least four times to reduce the uncertainties of measurements respecting the surface roughness.

Preparation of thin section

The required thin sections, which were cut and polished, were settled in the RSO and ASO for a period of 2 months for complete restoration of the thin section wettability from the water (30° at the initial condition) to oil-wet conditions (160° due to adsorption of asphaltene and resin on the thin section surfaces). The point is that since the roughness of the surface is vital during the contact angle measurement, the current investigation is only focused on the apparent contact angle measure of the hysteresis which in the rest of this investigation is called “contact angle”.

Results and discussion

Effect of binary mixtures on the IFT of synthetic oils

In the first stage of this investigation, the dynamic IFT of synthetic model oils (3% wt of resin or asphaltenic fraction) in contact with different binary aqueous solutions with NaCl as the common salt of binary solutions was measured. After that, the impact of using binary solutions with NaCl as common salt was compared with the results reported by Hamidian et al.⁴¹ examined the sole effect of NaCl on the crude oil and synthetic oils IFT. In Fig. 1, the IFT of binary solutions of NaCl/KCl (with ionic strength of 0.7) in contact with ASO and RSO were compared with the IFT values reported by Hamidian et al.⁴¹ measured with only NaCl dissolved in the aqueous solution. Similar to the results reported by Hamidian et al.⁴¹ for NaCl, the results obtained for the mixture of NaCl and KCl revealed higher IFT reduction for the RSO than ASO. In detail, following the results depicted in Fig. 1

Element	wt%
C	13.15
O	44.75
Ca	25.44
Mg	11.23
N	2.19
Al	0.51
S	0.22
Si	2.51

Table 4. Elemental analysis of the used thin section obtained by EDX analysis.

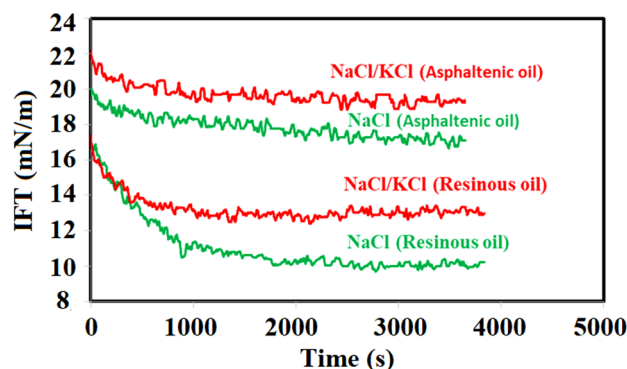


Figure 1. Evaluation of dynamic interfacial tension of asphaltic oil and resinous oil in the presence of monovalent cation and chloride anion.

revealed that IFT values reduce as a function of time for both ASO and RSO using KCl/NaCl solution while the IFT reduction was more obvious in the case of RSO. Besides, a closer look into the results depicted in Fig. 1 revealed that the dynamic behavior of the RSO system is higher than the ASO system although they rather reach an equilibrium value at the same time. The point is that the observed trend can be related to the different affinity of the ASO and RSO and the different interactions between their polar groups and ions at the interface. It would be obvious that the variation of equilibrium IFT values for the ASO sample in the presence of NaCl was lower than 2 mN/m coming from the lower interaction and affinity of asphaltene and ions while a larger reduction in IFT was observed for resinous model oil which is directly related to the higher surface activity of resin molecules.

The other point that can be extracted from Fig. 1 is that the existence of KCl is concomitant with the NaCl leading to an increase in the IFT compared with the solution that was individually prepared by NaCl. Considering these findings, it seems that the presence of potassium cation has impaired the performance of the sodium cation in the presence of the chloride anion for more IFT reduction due to a reduction in the activity of natural surfactants (asphaltene and resin) with an aqueous solution. A closer look into the results of Fig. 1 revealed that the presence of potassium cations directly affected the initial value of the ASO while the initial value for RSO remained constant. The reason behind this observed trend can be correlated to the resistive effect of RSO to dampen the fluctuations that may occur due to the presence of KCl salt. In other words, due to the surface activity of the resin molecules than the asphaltene molecules, RSO can digest the impact of KCl salt in the preliminary stage although its overall impact could not be eliminated. In other words, although the initial value for RSO remained constant for both NaCl and KCl/NaCl solutions, the equilibrium IFT values were significantly impacted. In detail, the individual presence of NaCl can reduce the IFT value from about 7 mN/m to 10 mN/m which is about 7 mN/m reduction in IFT while the concomitant presence of NaCl and KCl led to a reduction in IFT value from about 17 mN/m to 14 mN/m which is about 42% higher than the case was examined by Hamidian et al.⁴¹. However, the IFT variation for both NaCl and NaCl/KCl solutions using ASO was rather the same (about 2 mN/m) although the initial values were different. The other point that must be mentioned is that the presence of KCl salt leading to a significant impact on the IFT variation for RSO while the IFT variation trend was rather the same for ASO contacted with NaCl solution or NaCl/KCl. In detail, a glance into the results depicted in Fig. 1 revealed that using KCl/NaCl instead of NaCl in the solution led to a faster equilibrium due to the higher reduction in repulsive forces that existed between the two salts and resin molecules moved toward the interface.

In the second stage, the effects of CaCl_2 and MgCl_2 concomitant with the NaCl were investigated on the IFT reduction. In contrast to the results obtained for NaCl/KCl in the presence of asphaltene and resin fractions, the presence of CaCl_2 concomitant with NaCl has a considerable impact on the IFT reduction and dynamic IFT variation behavior of the studied systems especially for the RSO. In detail, in the case of using CaCl_2 for both ASO and RSO, not only the initial IFT value was changed for both RSO and ASO, but also the equilibrium IFT was reduced especially for the ASO. A glance into the results depicted in the Fig. 2 revealed that the presence of NaCl/ CaCl_2 can move the equilibrium IFT of ASO to about 13 mN/m compared with the equilibrium IFT of individual NaCl solution which was about 17 mN/m while the IFT variation from about 10 to 9 mN/m was observed for RSO. The other point is that although the impact of CaCl_2 on the IFT reduction of equilibrium IFT was more evident in the case of ASO, the presence of CaCl_2 led to a sharp reduction and change in the IFT pattern of aqueous solution/RSO. The point is that a closer look into the results revealed rather similar IFT variation trend for the solution including CaCl_2 and NaCl and the solution contains only NaCl.

A closer look into Fig. 2 revealed that although the presence of CaCl_2 led to IFT reduction for both synthetic oils, the presence of MgCl_2 led to a more complicated pattern for IFT variation. In detail, in contrast to the patterns observed for the effect of KCl and CaCl_2 presence concomitant with NaCl, the presence of MgCl_2 concomitant with NaCl led to IFT reduction for the synthetic oil prepared by asphaltene while this combination led to an increase in the IFT values for RSO. The reason behind this observed trend can be correlated to two different phenomena. The first one is that in the absence of affinity of active materials to the ions of aqueous solution (i.e. surface excess concentration of surface active materials unaffected by salinity), IFT increases as a function of salinity. But, there is a cage-like hydrogen-bonded structure of water molecules around the salt ions including Na^+ , Mg^{2+} , and Cl^- which can manipulate this general trend since the salts can be depleted near the interface in

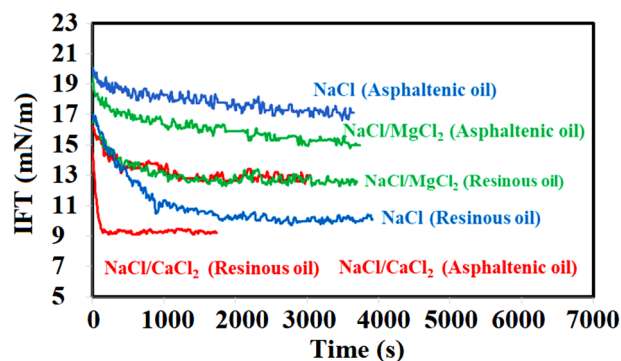


Figure 2. Evaluation of dynamic interfacial tension of asphaltenic oil and resinous oil contact with NaCl in the presence of divalent cation.

the shadow of a greater energy environment of the ions which disrupts due to the hydrogen bonding⁴². On the other side, it is possible to correlate the observed trend to the crystal radii of ions which directly affects the hydration numbers and hydrated radii of the system. In detail, it is well accepted that the ions with smaller crystal radii (here $Mg^{2+} < Ca^{2+}$) introduce higher hydration numbers and larger hydrated radii that affect the arrangement of ions into the interface. According to these facts, it seems that in the case of Ca^{2+} , both resin and asphaltene molecules can conquer the interactions that existed between water molecules and Ca^{2+} cations and force them to move toward the interface leading to IFT reduction while the situation was more complicated in the case of Mg^{2+} . So, it seems that in the case of RSO, the affinity of the Mg^{2+} ions to be remained dissolved in the water is higher than ASO which directly leads to higher IFT values for the $Mg^{2+}/NaCl/RSO$ than $Mg^{2+}/NaCl/ASO$.

The noteworthy point is that similar results were reported by Lashkarbolooki et al.⁹ regarding the IFT value of $NaCl/MgCl_2$ solution in contact with synthetic oil prepared by dissolution of 8 wt% of extracted asphaltene and resin in toluene (higher effect on the IFT reduction for asphaltenic oil compared with resinous oil). The higher IFT reduction of $NaCl/MgCl_2$ can be correlated to the higher affinity of Mg^{2+} toward oxygen as a heteroatom in asphaltene compared with resin. Investigation on the oxygen content of resin and asphaltene revealed a similar amount for the current study and the investigation performed by Lashkarbolooki et al.²¹. However, the IFT reduction for asphaltene was more differentiable which means the existence of another effective parameter such as aromaticity of the asphaltene and resin or functional groups. The other point is that the ratio of $NaCl$ to $MgCl_2$ was about 1.6 in the investigation performed by Lashkarbolooki et al.⁹ while this ratio is 3.6 for the current investigation. The point is that similar to the observed IFT trend for $NaCl/MgCl_2$ /asphaltenic oil, the IFT value of solution including $NaCl/CaCl_2$ and asphaltenic synthetic oil was decreased, while a reverse trend was observed for the effect of $CaCl_2$ salt compared with the $MgCl_2$ salt for the resinous oil.

In general, the IFT reduction for $NaCl/CaCl_2$ aqueous solution (especially for asphaltenic oil) was larger than the other studied system due to the more affinity of Ca^{2+} towards fluid/fluid interface in the presence of Na^+ and its proper interactions with asphaltene and resin components to produce complex ions compared to that occurred for Mg^{2+} . Generally, the most important reason for the different IFT behavior of oil samples in different brines can be associated with the different packing and orientations of asphaltene and resin molecules in different electrolytes. If complex ions form between the polar organic components of asphaltene and resin fractions and cations of brine, IFT experiences a reduction due to the enhancement of their affinity to the interface and their larger solubility in the aqueous phase. Complex ions are commonly known as a charged molecular aggregate consisting of metallic atoms or ions attached to one or more electron-donating molecules. Proper complex ions would be constructed if divalent calcium cations existed in the presence of monovalent sodium cations and a polar organic component, i.e. asphaltene and resin which donating their heteroatoms enhances the surface excess concentration of active agents leading to IFT reduction^{9,43}.

On the other hand, it is reported that the formation of metal/ligand complexation involving acetate with divalent metal ions can be occurred by the creation of bonding between metal ions and the carboxylate oxygen^{44–46}. Besides, it was reported that acetic acid in the presence of Ca^{2+} and Mg^{2+} exclusively forms the mononuclear complexes⁴⁴. Moreover, the resinous oil leads to higher initial and equilibrium IFT reduction than the synthetic oil prepared by asphaltene. The remarkable point about comparing crude oil and resinous oil is that the IFT variations for both are about the same, so it can be concluded that the IFT of crude oil in the presence of $NaCl/CaCl_2$ brine is a function of the resin, not the asphaltene. The other point that can be extracted is that the other existing fractions such as saturates and aromatics provide resistance to the salts and retard the effects of the ions on the IFT reduction.

In the last stage of IFT measurement, the impact of $NaCl/MgSO_4$ and $NaCl/Na_2SO_4$ pairs was investigated on the IFT variation of ASO and RSO. Investigating these two pairs is important and applicable since one of them has monovalent cations while the other one has divalent cations leading to different behaviors during IFT variation. According to the results given in Fig. 3, the results revealed that the addition of $MgSO_4$ and Na_2SO_4 has a positive impact on the IFT reduction of ASO compared with the solution comprised of only $NaCl$ although the impact of Na_2SO_4 is negligible. The point is that similar to the results observed for KCl , $MgCl_2$, and $CaCl_2$, the presence of ASO in the system leading to different and distinguished initial points for IFT while for the RSO

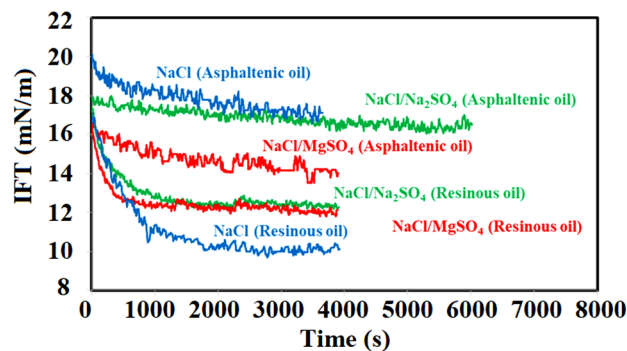


Figure 3. Evaluation of dynamic interfacial tension of asphaltenic oil and resinous oil contact with NaCl in the presence of sulfate anion.

system the initial points are rather the same regardless of the used salts. The reason behind this observed trend can be correlated to the stronger impact of asphaltene molecules on the ions solvation which rapidly grabs them from the bulk phase into the interface leading to rapid change in the IFT value while the RSO was not capable to introduce rapid interaction with the ions for the faster IFT change. Moreover, this observed trend can be correlated to the fact that the solvation energy of the ions in the water compared with the interactions that existed between asphaltene molecules and ions in the interface is weaker and consequently moving the ions toward the interface. However, the resin molecules are not capable to overcome the solvation energy of ions in the water to force the ions moving toward the interface. As a consequence of this weakness, the IFT for the RSO system is higher than the solution comprised of only NaCl while the situation is completely different for ASO.

The other possible reason behind the observed trend can be correlated to the higher aromaticity of the asphaltene fraction (i.e. 1.02) compared to the resin fraction (i.e. 1.46). As aforementioned, more polar heteroatoms in the resin structure and its higher H/C make it possible for more diffusion in water and adsorption at the interface between model oil and water, as a result, lower IFT value was observed for resinous model oil compared to the asphaltenic oil. Despite of high affinity of resin toward the water phase, the polar group of resin fraction shows no synergistic effect by the salts consisting of chloride and sulfate anions simultaneously. This low tendency can be correlated to the enhancement of intermolecular distance resulting in the decrease of the coverage fraction of the lateral chains of resin in the presence of SO_4^{2-} and Cl^- . Therefore, the trend of NaCl/ Na_2SO_4 and NaCl/ MgSO_4 salts is similar to the presence of MgCl_2 salt in NaCl salt (see Fig. 2), so the reasons explained for this salt in Fig. 3 can be applied to the simultaneous presence of Na_2SO_4 or MgSO_4 salts with NaCl.

Equilibrium IFT (EIFT) values for all the studied brines and both model oils at equilibrium state which are depicted in Fig. 3 revealed that the EIFT values depend on the kind of salts and natural surfactants. For both studied model oils, all of the brines revealed insignificant effects in the IFT reduction and even increasing effects in some cases although the lowest EIFT value was observed for NaCl/ CaCl_2 brine. The remarkable point is that the presence of different salts concomitant with NaCl, leads to different behaviors of the brine solutions in contact with the synthetic oil namely resinous or asphaltenic oil. For asphaltenic oil, except KCl, the presence of other salts in NaCl has a decreasing effect on IFT probably due to bonds between the divalent cations and chloride anion. In more detail, it seems that in the case of Mg^{2+} and sulfate anions, strong bonds due to the higher affinity of the polar functional groups to the interface and enhancement of coverage and packing at the interface lead to better reduction in IFT, while in the case of resinous oil in contact with different salts except for CaCl_2 , the presence of other salts in NaCl has an increasing effect on IFT.

In the next stage of this investigation, the obtained results were modeled using a mono-decay model with two different approaches of $x = e$ and $x = 10$ (see Figs. 4 and 5 and Tables 5 and 6). A closer look into Table 5 where the average absolute relative deviation percent (AARD %) as well as standard deviation of equilibrium IFT measurements were tabulated, revealed the acceptable level of accuracy of the used model besides its capability to evaluate the adsorption or relaxation time as a single adjustable parameter of the model. The point is that the mono-decay model was capable to well correlated the relaxation time with more accuracy using $x = e$ leading to $\tau = 600\text{s}$ while using $x = 10$ leading to underestimation of relaxation time with $\tau = 250\text{s}$ regardless of their accuracy to predict the IFT values which are the same. Besides the performed analysis using two different x values of e and 10 for the mono-decay model, the modeled IFT values versus $\log\left(\frac{\gamma_0 - \gamma_t}{\gamma_t - \gamma_e}\right)$ provide the chance of observing the different regions of induction time, rapid fall time, meso-equilibrium time, and equilibrium time. In the first stage, as it is obvious, the utilized mono-decay model was satisfactorily capable of not only predicting the IFT values but also differentiating the different regions as aforementioned and depicted in Fig. 4b. Moreover, the further analysis which their results depicted in Fig. 5 revealed that although using $x = e$ leading to more accurate prediction of different times regions, it is possible to correlate the relaxation time of using $x = e$ and $x = 10$ with a simple linear regression with an acceptable correlation coefficient of 0.9976. In other words, using the obtained linear correlation depicted in Fig. 5, one can easily convert the relaxation time of the mono-decay model with different powers to each other with an acceptable level of accuracy no matter what type of synthetic oil was used. In other words, the performed analysis revealed that the mono-decay model is well capable to predict the IFT values and the corresponding time zones of induction, rapid fall, etc. with high accuracy regardless of the used

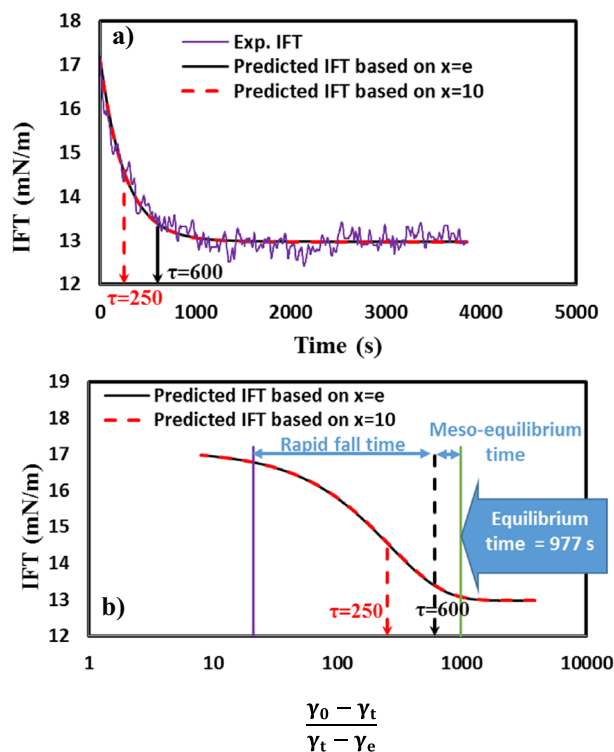


Figure 4. Capability of decay model to predict the dynamic interfacial tension, (a) IFT vs. time, and (b) IFT vs. different time steps.

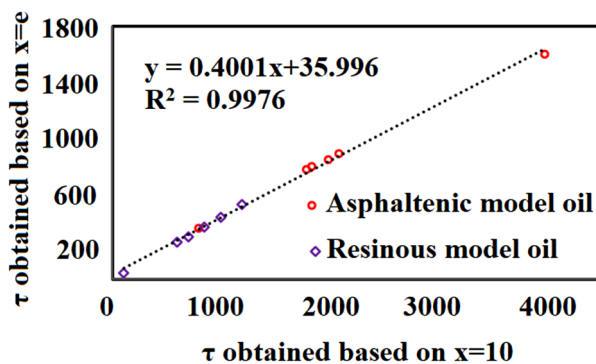


Figure 5. Capability of decay model to predict the dynamic interfacial tension using $x = 10$ and $x = e$.

	IFT (mNm)			
	ASO		RSO	
	EIFT (mN/m)	Standard deviation (SD)	EIFT (mN/m)	Standard deviation (SD)
NaCl	17.12	0.10	10.15	0.13
NaCl/KCl	19.98	0.27	12.97	0.08
NaCl/MgCl ₂	14.99	0.20	12.46	0.16
NaCl/CaCl ₂	12.97	0.29	9.73	0.18
NaCl/Na ₂ SO ₄	16.55	0.11	12.27	0.18
NaCl/MgSO ₄	13.98	0.26	12.02	0.26

Table 5. The standard deviation of EIFT and prediction error of mono-exponential decay model.

	Adsorption time (based on $x=e$)				Adsorption time (based on $x=10$)			
	Asphaltenic oil		Resinous oil		Asphaltenic oil		Resinous oil	
	τ (s)	AARD %	τ (s)	AARD %	τ (s)	AARD %	τ (s)	AARD %
NaCl	1000	1.46	550	1.69	1800	1.73	1200	1.75
NaCl/KCl	800	1.65	250	1.5	2100	1.61	600	1.49
NaCl/MgCl ₂	900	1.99	450	1.66	1850	2.26	1000	1.67
NaCl/CaCl ₂	350	2	50	3	800	2.03	105	3.12
NaCl/Na ₂ SO ₄	1500	1.6	350	1.7	4000	1.58	850	1.63
NaCl/MgSO ₄	1000	1.88	250	1.83	2000	1.99	700	1.86

Table 6. Comparison of the relaxation time of two considered models.

oil type. Respecting the accuracy of the proposed mono-decay model, the EIFT values of different solutions were calculated and tabulated in Table 5 along with the standard deviation of the calculated EIFT values.

The characteristic decay times (τ) of asphaltenic and resinous model oils for different aqueous solutions were shown in Fig. 4. A glance into this figure revealed that the adsorption times are extremely longer than with the adsorption time of the aqueous solution comprised of surfactants. In detail, the performed measurements by Bauget et al.¹⁷, Zhang et al.²² and Wang et al.¹⁸ for asphaltene/toluene mixture and water revealed an adsorption time of in a few seconds. It is also found that the adsorption time values were strongly dependent on the salt and oil types. In detail, the presence of salts in NaCl brine, for asphaltenic model oil, except for CaCl₂, led to an increase in adsorption time, while adsorption time values of resinous model oil, except for MgCl₂ experienced a reduction. One of the most important points of this figure is the high amount of NaCl/Na₂SO₄ adsorption time that can represent the slow rate of polar functional groups and ions interaction on the surface when this salt is in contact with asphaltenic oil. For both studied model oils, the obtained adsorption time was considerably lower in the presence of CaCl₂ since the higher affinity of the polar functional groups toward the interface reduces the required time for the coverage and packing of active agents at the interface.

Moreover, investigating the results tabulated in Table 6 revealed that the proposed model for calculating the adsorption time for different binary solutions is accurate since the average AARD% is below 2% except for the NaCl/CaCl₂ solution led to the lowest IFT values for both ASO and RSO. In other words, it seems that the proposed model for adsorption time prediction is highly sensitive to the IFT value and the adsorption behavior. In other words, this model loses its accuracy as the IFT value reduces since as the equilibrium IFT value reduces, the dynamic zone of IFT for the examined solutions narrows.

Wettability alteration

In the last stage of this investigation, the effects of different salts in binary conditions were examined on the wettability alteration of rock surfaces using the contact angle measurement (see Figs. 6 and 7). In this way, different thin sections were prepared using a rock sample which the majority was comprised of dolomite compounds based on the performed mapping image analysis which revealed the high content of silicon (Si), carbon, calcium, and magnesium. Since more than half of the world's hydrocarbon resources are stored in carbonate reservoirs, a large number of investigations were performed regarding the wettability alteration of carbonate rock surface toward the strongly water-wet conditions since the oil-wet nature of the carbonate rocks greatly hinders the oil production. In light of this fact and since a substantial proportion of the Earth's crust comprised of dolomite which is a carbonate mineral several academic researchers were centered on the precipitation and dissolution of the dolomite mineral known as the "dolomite problem" in the presence of different ions and chemicals^{47–49}. The research revealed that similar to the carbonate rocks, dolomite can be rendered oil-wet by carboxylates and that the oil-wetness can be reversed more effectively using different chemicals and ions^{50–55}. Unfortunately compared to the large number of performed investigations regarding the wettability alteration of carbonate rock surfaces using potential determining ions (PDIs), very limited systematic studies on the effect of PDIs on dolomite rock surfaces for wettability alteration have been reported^{56,57}.

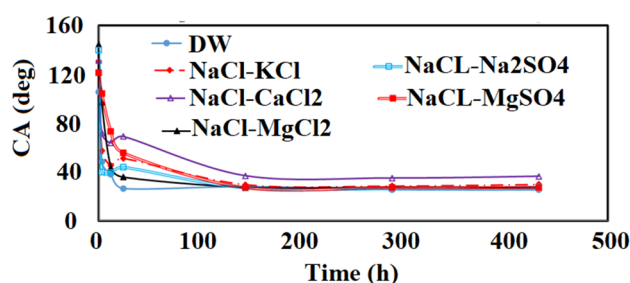


Figure 6. Wettability alteration of dolomite rock sample with aging in asphaltenic model oil.

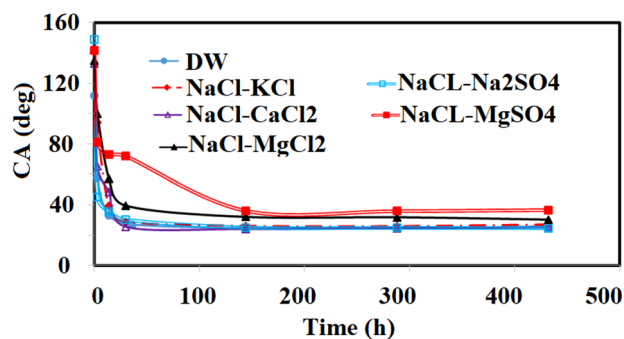


Figure 7. Wettability alteration of dolomite rock sample with aging in resinous model oil.

In this way, the current investigation is aimed to find the possible effect of different salts in binary solutions on the wettability alteration of dolomite rock surfaces. According to the performed measurements, the lowest contact angle value (the strongly water-wet condition) was observed for the system in which the distilled water was used as the aqueous solution. But, it is impossible to use the distilled water injection in the field scale due to economic issues (highly expensive) even if the distilled water injection leads to the highest oil recovery due to wettability alteration or IFT reduction. For a better understanding of the effect of the oleic phase, the equilibrium contact angle values using synthetic oil samples were measured and compared (see Fig. 8) with the values obtained using nonacidic crude oil with the same aqueous solutions (ionic strength of 0.7 including NaCl, Na₂SO₄, KCl, CaCl₂, MgCl₂, and MgSO₄)¹⁰. The results revealed the superiority of Na₂SO₄ and MgSO₄ for wettability alteration to strongly water-wet conditions while the other salts can change the wettability only toward neutral wet states. The phenomenon that is called the double layer is possible for any surface with charges to form a layer near the surface. In this layer, the consequence of ionization, ionic adsorption, and ionic dissolution can occur via particle attachment between the particles with opposite charges of their own (counter-ions) or escape from the particles that have charges similar to their own (co-ions)⁵⁸.

Comparing the results of binary mixtures obtained for resinous and asphaltenic oils, one can conclude that the presence of NaCl–MgSO₄ and NaCl–Na₂SO₄ has a similar effect as well as the application of crude oil while the application of NaCl–KCl, NaCl–CaCl₂, NaCl–MgCl₂ at the presence of resinous and asphaltenic oils leading to extremely better effects for wettability alteration toward strongly water-wet compared with the used crude oil (see Fig. 7).

Several mechanisms have been proposed for the effects of engineered brine solutions such as calcium ion can be substituted with the magnesium ion on the surface, and it is possible to expect to substitute magnesium ion with the calcium ion existing in the carboxylic compounds stick to the rock surface. Another point that should be considered and analyzed is the existence of SO₄²⁻ that can enhance the concentration of Mg²⁺ on the surface, which can substitute by Mg²⁺ on the surface and released in the solution⁷. In contrast, the concomitant existence of Mg²⁺ and Ca²⁺ while SO₄²⁻ exist may loosen the bonding between carboxylic compounds of crude oil and the carbonate rock surface that consequently leads to the unavoidable elimination of carboxylic compound from the rock surface rendering the surface towards the water-wet states.

So, it can be claimed that where the positive charge of carbonate surfaces adsorption of carboxylic groups to carbonate surface is unavoidable, and due to the injection of engineered brine solution that comprises of a high level of sulfate ion that can modify the surface. Furthermore, sulfate ion is a divalent ion and uses one of its capacities to react with the positive charge of the rock surface. While the other capacity utilizes to react with the carboxylic group that consequently leads to the release of oil droplets from the rock surface, even though it is possible to produce higher oil in the shadow of bonding between the oil droplet and the existing cations in the aqueous solution⁵⁹.

In detail, Boumedjane et al.⁸ reported that wettability alteration of calcite surface occurs due to the light electrostatic attraction existing between SO₄²⁻ ions and the mineral calcite surfaces which possess positive water-wet

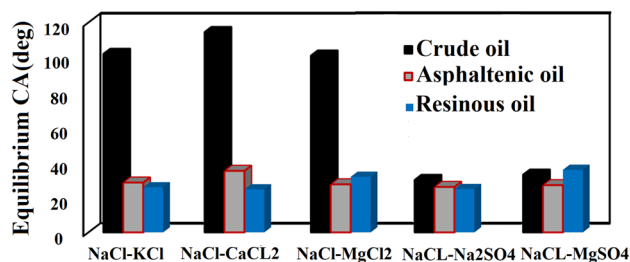


Figure 8. Comparison of equilibrium contact angle of this study obtained for asphaltenic and resinous model oil with its base crude oil (¹⁰).

sites. At this point, the sulfate ions could approach and enhance the negative charge of the rock surface, while on the other side, it may lead to a reduction in electrostatic repulsion between magnesium ions and the calcite surface making it easier for magnesium ions to reach the surface. At this point, they can easily interact with the organic compounds, or replace the calcium ions that are bonded to the carboxylate group in order to desorb them from the calcite surface. In this way, it can be concluded that the existence of sulfate ions can boost the wettability alteration effect of Mg^{2+} or Ca^{2+} with its catalytic role.

According to the results depicted in Fig. 8, it is revealed that the presence of saturates and aromatics in the crude oil act as a resistance to the dissolved salts which retards the wettability alteration. In detail, the measured contact angles for crude oil which is comprised of four different fractions of resin, asphaltene, saturates and aromatics revealed a slight effect of salts on the contact angle while using asphaltenic or resinous synthetic oils revealed a significant effect of salts for wettability alteration toward strongly water-wet conditions. In this way, it is obvious that two fractions of saturates and aromatics are two fractions that retard the effect of salts on the wettability alteration. The point is that the results reported by Saputra and his coworkers⁶⁰ revealed a similar trend regarding the effect of the aromatic fraction of the crude oil on the wettability alteration toward oil-wet condition while a contradicting trend regarding the effect of resin fraction was observed compared with the results obtained in the current investigation. They reported that higher contents of aromatic, resin, and asphaltene fractions lead to higher adsorption of crude oil components on the rock surface which can be directly explained by mutual solubility/polarity theory. In detail, as the first layer is formed by adsorption of the aforementioned fractions, the additional adsorption sites would be formed as a consequence of first layer formation leading to adsorption of the remainder of the oil components, i.e., the nonpolar saturates. So, the crude oil with a lower amount of aromatic, resin, and asphaltene and higher saturate contents faced with essential initial oil adsorption limitation on the rock surface leading to the more water-wet surface created on these crude oil samples.

Conclusions

In this study, the effect of binary solutions prepared with different salts of $CaCl_2$, KCl , $MgCl_2$, Na_2SO_4 , and $MgSO_4$ and $NaCl$ as the common salt was investigated on the IFT variation and wettability alteration. Besides, the influences of these solutions were examined in contact with the asphaltenic and resinous model oil instead of using crude oil which comprised of thousands of compounds. According to the performed measurements and analysis, the following conclusions can be extracted and categorized:

- KCl has a negative impact on the IFT reduction for the binary solutions regardless of the used oil (ASO or RSO).
- The substitution of the monovalent of KCl with $MgCl_2$, $CaCl_2$, $MgSO_4$, and Na_2SO_4 leading to better functionality of the ASO system for IFT reduction while the RSO system still faced the negative impact of different salts for IFT reduction except the solution prepared with the dissolution of $NaCl$ and $CaCl_2$ because of interactions between resin molecules' and $CaCl_2$ and better accumulation of ions in the interface.
- The reason for the better performance of ASO than RSO was correlated to the stronger binding between the ions and asphaltene molecules compared with the existing binding between the ions and water molecules.
- The lowest adsorption times were obtained for $NaCl/CaCl_2$ brine regardless of the examined oil type (synthetic asphaltenic or resinous oil type).
- Application of binary salts changed the wettability alteration toward strongly water-wet conditions especially for resinous and asphaltenic synthetic oils while saturates and aromatics fractions retards the wettability alteration toward desire condition.

Data availability

Dr. Mostafa Lashkarbolooki with contacting email of m.lashkarbolooki@nit.ac.ir would provide the data upon the request.

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Ramtin Hamidian: Experimentation, analysis and data curing, initial drafting Mostafa Lashkarbolooki: conceptualization, data analysis, design of the work, interpretation of data Ali Zeinolabedini Hezave: drafting, revising, and writing the manuscript, data acquisition, revising the analysis and interpretation of data All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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