



Chemical Engineering Thermodynamics

Experimental and modeling investigation of dynamic interfacial tension of asphaltenic–acidic crude oil/aqueous phase containing different ions

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ABSTRACT

In this way, after experimental measurement of interfacial tension, different models including mono-exponential decay, dynamic adsorption models and empirical equation are used to correlate this time-dependent behavior of interfacial tension (IFT). During the modeling approach, the induction, adsorption, equilibrium, and meso-equilibrium times as well as diffusivity of surface active components known as natural surfactant including asphaltene and resin from crude oil to the interface are obtained. In addition, the surface excess concentration of surface active components at the interface and Gibbs adsorption isotherm are utilized to analyze the measured dynamic IFTs. Finally, the mechanisms of crude oil/aqueous solution IFT including (a) the activity of surface-active components and (b) surface excess concentration of them at fluid/fluid interface are proposed and discussed in details.

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1. Introduction

The capillary forces acting in the interface region between crude oil and water entrap the oil ganglia in a complex network of underground capillary pathways keep the oil unrecovered in the reservoir [1,2]. The magnitude of capillary force is directly proportional to the interfacial tension (IFT) of fluids which means that lower interfacial tension value, higher capillary number means. In addition, since the IFT is directly related to the capillary force, more oil recovery is possible as the IFT reaches to a specific level [3,4].

Although using aqueous solutions only containing ions is not able to achieve this ultra low IFT value, the IFT of aqueous solution containing different ions and crude oil have received increasing consideration over the recent years. Nevertheless, aqueous solution containing ions with different concentration can be used as smart water and low salinity water flooding as an EOR method beside as a transfer fluid of EOR agents. Therefore, investigation of the IFT of aqueous solutions/crude oil is an important parameter. Generally, there are several methods to reduce the IFT including using surface active agents, addition of salts to the aqueous solution, etc. Among these possible options, addition of salts into the aqueous solution has gained an increasingly attention during the past decades due to unique advantages on the reduction of IFT [5]. In the light of these advantages, although, several investigations have been performed to formulate the effect of salinity on the IFT, no

one can address this issue in general. The existence of several contradicting results and mechanisms [5–13] is the sign of this claim. But the clear point is that there is not a straightforward relation between the composition and type of crude oil and saline water quality and IFT variation. In the light of this fact, the influences of aqueous ions including NaCl, KCl, CaCl₂, and MgCl₂ on the equilibrium IFT of an asphaltenic crude oil with high acidic compounds were previously investigated by coauthors [14] for concentrations ranged between 0 and 45,000 mg·kg^{−1} and ambient conditions.

The results obtained by the coauthors revealed similar trends for the IFT at different salt concentrations with homolog systems including NaCl/KCl, and MgCl₂/CaCl₂ [14]. Besides, another investigation performed by the coauthors demonstrated that the effects of resin and asphaltene presented in the crude oil on the IFT of acidic crude oil/aqueous phase [15,16]. The results showed that there are three dominant parameters which affect the IFT, including (a) the presence of surface active agents in the oleic phase, (b) the type of salts, and (c) salt concentration. According to the findings, it was concluded that the presence of resins and asphaltenes has a dual effect in the presence of divalent salt concentrations. In more details, for the case of low divalent salt concentrations, the asphaltene content leads to a greater decrease in the IFT compared with the resins, while for the elevated salt concentration solutions, the effect of resin for IFT reduction is dominant [15]. In addition, the results demonstrated that the lowest equilibrium IFT values were obtained if the concentration of all the used ions reaches to about 15,000 mg·kg^{−1} [14,15]. The noteworthy point is that investigation on the dynamic behavior of IFT has been largely ignored despite the

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dynamic behavior (raised from adsorption kinetics of surface active molecules at the liquid interfaces) being more important than static behavior in enhanced oil recovery applications [17]. The reason behind this adsorption kinetic is controlled by transport processes in the bulk and the transfer of molecules from a solution state into an adsorbed state or *vice versa* [5,11].

The short-time approximation equation (Eq. (1)) was used to calculate the diffusivity of surface active components from bulk to the crude oil/brine interface [18,19]:

$$\gamma_t = \gamma_0 - 2RT\Gamma\sqrt{\frac{3Dt}{7\pi}} \quad (1)$$

where R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is temperature (K), D is diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$), t is time (s), Γ is surface active agents (natural surfactant) concentration ($\text{mol} \cdot \text{m}^{-3}$), γ_t is the IFT of the system at surface age (time), γ_0 is the clean interfacial tension at time $t = 0$, and Γ is surface excess concentration ($\text{mol} \cdot \text{m}^{-2}$).

In general, the surface excess concentration is defined as the concentration of a species in the interfacial region which is in excess of the concentration of that species in the bulk [5]. The crude oils are composed of four main components known as: saturates, aromatics, resins and asphaltenes [20]. Resins and asphaltenes are important compounds in the crude oils which are in close relation to high molecular weight polycyclic hydrocarbons [14,15]. On the other hand, asphaltenes and resins are natural surfactants making them interesting compounds for many researchers. The N, S and O elements existed in asphaltene structure distinguishing it from the hydrocarbons. In other meaning, being polar in nature, asphaltenes are surface-active substances which are able to significantly modify the properties of interfaces by adsorption [15,21].

At the last part of the adsorption process, as the adsorption has nearly attained its equilibrium value and the subsurface concentration varies little with time following equation is used [5,11,22]:

$$\gamma_t = \gamma_e + \frac{RT\Gamma_{eq}^2}{C} \sqrt{\frac{7\pi}{12Dt}} \quad (2)$$

where γ_e and Γ_{eq} are the equilibrium IFT and the equilibrium surface excess concentration, respectively. The γ_0 (Eq. (1)) and γ_e (Eq. (2)) are obtained by the intercept of the IFT *versus* $t^{1/2}$ and $t^{-1/2}$ plots, respectively.

Therefore, at the start of the adsorption process, the short-time approximation would be used while at the end of the process the long-time approximation model is replaced. The short-time approximation is expected to become worse with increasing times and the long-time approximation with decreasing times [23].

The simplest way to evaluate the diffusion relaxation time, τ , is to use the mono-exponential decay model [5,24]:

$$\gamma_t = \gamma_e + (\gamma_0 - \gamma_e) e^{-\frac{t}{\tau}} \quad (3)$$

Based on this equation, as the affinity and concentration of the active material increase, the adsorption time and reaching of the meso-equilibrium region reduce (when the change in dynamic IFT is reduced as a function of time).

In addition, the results reported in different literature demonstrated the high capability of the empirical equation to describe the IFT behavior [25,26]:

$$\frac{(\gamma_0 - \gamma_t)}{(\gamma_t - \gamma_e)} = \left(\frac{t}{t^*}\right)^n \quad (4)$$

where n and t^* are constants whose values depend upon the nature of surfactant. The values of t^* and n can be calculated by transforming Eq. (4) to its linear form:

$$\lg \frac{(\gamma_0 - \gamma_t)}{(\gamma_t - \gamma_e)} = n \lg t - n \lg t^* \quad (5)$$

The measured dynamic interfacial tension (DIFT) can be divided into four different regions including induction region, fast fall region, meso-equilibrium region, γ_m , (where γ_t shows only a small change with time), and equilibrium region [26] when the DIFT was plotted *versus* $\lg \frac{(\gamma_0 - \gamma_t)}{(\gamma_t - \gamma_e)}$.

In general, most of the previous published literature measured a single IFT value by assuming the equilibrium status of two fluids while the time-dependent IFT (DIFT) of crude oil/brine solutions which is a crucial parameter remains largely unexplored.

Due to the aforementioned facts, in the current investigation a series of systematic experiments are conducted to draw a complete picture about the interfacial properties of asphaltenic-acidic crude oil followed by modeling.

Since the optimal salinity is a crucial parameter in EOR processes, the first objective of this study is to experimentally measure the crude oil-aqueous ions dynamic IFT for aqueous ions including NaCl, KCl, MgCl_2 , and CaCl_2 at $15,000 \text{ mg} \cdot \text{kg}^{-1}$ (optimum concentration for equilibrium IFT) and pressure of 500, 1000, 2000, and 4000 psi (1 psi = 6.895 kPa) while the temperature held constant at 30°C . Finally, measured dynamic IFT of all systems is modeled using three different models namely diffusion-controlled, mono-exponential decay models, and empirical equation. With the assist of these models, induction, rapid fall (relaxation or adsorption), meso-equilibrium and equilibrium times, the diffusivity of surface active agents in the crude oil to the crude oil/aqueous phase surface and the surface excess concentration of surface active agents of de-ionized water (DW) systems are compared to brine solution systems.

2. Experimental

2.1. Experimental apparatus

The IFT between two fluid phases is defined as an enhancement in the Gibbs energy per unit increase in interfacial surface area while the pressure, temperature and number of mole are kept constant [27]. Throughout the years, different IFT measurement methods have been proposed by different researchers for immiscible fluids [28,29]. A monograph by Rusanov and Prokhorov [30] provided a broad review of the technical literature on the IFT techniques with detailed discussion of the theoretical bases and instrumentations. In general, the purpose and experimental environment are two parameters which dictate what kind of IFT measurement technique must be used.

Pendant drop tensiometry has been shown to be a useful tool for the experimental measurement of the relaxation in IFT due to the adsorption of surfactant at a fluid interface [31]. Since in the current investigation the IFT range is between 1 and $50 \text{ mN} \cdot \text{m}^{-1}$, the pendant drop method is utilized due to its good unique capabilities. For example, it is possible to perform this measurement at the elevated temperature and pressure. In the light of these advantages and considering its accuracy and suitability [11], the pendant drop which is based on the equilibrium of static force is the preeminent method suited for the current investigation [32,33]. Measurement of dynamic IFT using the pendant drop method is based on the reality that the drop changes its shape as a result of interface relaxation [19]. In brief, pendant oil drop is injected into a high pressure/high temperature view cell that is already filled with brine at desired condition.

The visual cell is equipped with three heating elements, a PT100 thermocouple, a PID controller with an accuracy of 0.1 K and a pressure transmitter with a full scale accuracy of 0.25%. To eliminate the heat loss, the visual cell is equipped with a jacket. After a period of time which

introduced into the system to be assure about the stabilization of pressure and temperature, the crude oil was gradually discharged into the visual cell chamber [34]. As soon as the produced drop at the tip of the nozzle reaches the maximum volume which could stabilize for sufficient time, the crude oil injection was stopped.

Once the proper drop at the tip of the nozzle generated the system is isolated during the video recording stage. At this point, the fully automated software (Axisymmetric Drop Shape Analysis) was started to monitor the drop and analyze it each 2 s at least for 1 h. In brief, the tendency of an interface between two immiscible phases to create the smallest surface area, gives rise to a pressure difference between the two fluids on either side of a curved interface:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (6)$$

where ΔP is the capillary pressure, γ is the interfacial tension and R_1 and R_2 are the principal radii of curvature.

If the drop is assumed to be axisymmetric about its vertical axis, then ΔP at any given point on the interface curve can be written with reference to the apex point where $R_1 = R_2 = R_0$ [35]:

$$\Delta P = \frac{2\gamma}{R_0} + \Delta \rho g z = \gamma \left(\frac{1}{R_1} + \frac{\sin \varphi}{x} \right) \quad (7)$$

where R_0 is the radius of curvature at the origin of the x - z coordinate (apex point), $\Delta \rho$ is the difference in the densities of the two phases, g is the gravitational acceleration, z is the vertical height measured from the datum plane and φ is the turning angle measured between the datum plane and the tangent to the interface at the point (x, z) . R_1 is defined as the inverse of the rate of change of the turning angle, φ , with respect to the arc-length parameter, s .

In this way, the shape of the pendant drop has to be analyzed and the fluid densities have to be known in order to determine the IFT. A vibrating tube densitometer (Anton-Paar, Austria) worked at high pressure and temperature was used to measure the density of the fluids. A detailed description of the employed experimental setups is illustrated elsewhere [10,33].

2.2. Crude oil and salt properties

The properties of the used crude oil supplied from one of the Iranian oil reservoirs are presented in Table 1. The results of comprehensive chemical analysis of the crude oil including gas chromatography (GC) analysis, infrared (IR) spectroscopy (PerkinElmer Spectrum RX1) and total acid number measurement (ASTM D 664-1989 [36]) are presented elsewhere [14,15]. In brief, the used crude oil had a high acid fraction ($\text{TAN} = 1.46 \text{ mg KOH} \cdot (\text{g oil})^{-1}$) and high asphaltene (11 wt%) and resin contents (13 wt%) consist of sulfoxide, sulfone, and carbonyl functions as well as small amounts of phenolic, amine, and amide functionalities. It is noticed that the crude oil is considered as an acidic crude oil if the TAN number of an oleic phase is higher than $0.5 \text{ mg KOH} \cdot \text{g}^{-1}$

[37]. All of the salts including NaCl, KCl, MgCl_2 and CaCl_2 were supplied from Merck, Germany and the properties of them are listed in Table 2.

Table 2
Salt properties

Salt	Chemical formula	MW/g·mol ⁻¹	Density of 15,000 mg·kg ⁻¹ of salt/g·cm ⁻³	Purity/%
Sodium chloride	NaCl	58.44	1.0081	>99.5
Potassium chloride	KCl	74.55	1.0121	>99.5
Magnesium chloride, hexahydrate	$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	203.30	1.0098	>99
Calcium chloride	CaCl_2	110.98	1.0074	>99

3. Results and Discussion

The repeatability of the measurement for the used oil and two aqueous solutions is shown in Fig. 1. The results of these measurements revealed an average deviation of 1.3% and 2.9% for KCl and MgCl_2 aqueous solutions, respectively, for dynamic IFT measurements. The obtained results showed that repeatability of dynamic IFT measurements was satisfactory despite the slight change of volume of crude oil drop. The relation between ions and distribution of surface active components of oil phase into the crude oil/aqueous phase interface are examined using dynamic IFT measurement. Fig. 2 showed that dynamic IFT of 15,000 mg·kg⁻¹ of KCl/crude oil as a function of pressure had a similar trend if they were plotted *versus* time. As can be seen, the IFT decreases as a function of time, because of the adsorption of polar components such as asphaltene and resin at the crude oil/aqueous phase interface. This observed trend strengthens the hypothesis of natural surfactant activation at the fluid/fluid interface. Besides, a close examination of the obtained results revealed that although no significant effect is introduced by pressure into the dynamic behavior of IFT, it is able to slightly increase the value of IFT.

In addition, the results illustrated that KCl aqueous phase introduces a similar electrostatic behavior as a function of pressure. In order to obtain the induction, adsorption, equilibrium and meso-equilibrium times, mono-exponential decay model and empirical equation were utilized.

In addition, Fig. 3 shows the dynamic IFT of crude oil/15000 mg·kg⁻¹ of KCl aqueous solution at a pressure of 4000 psi (1 psi = 6.895 kPa) as a function of $\frac{(\gamma_0 - \gamma_t)}{(\gamma_t - \gamma_e)}$ using a semi-logarithmic scale. Induction, adsorption and equilibrium times are also depicted in Fig. 3. As can be seen, the measured DIFT was divided into four different regions including induction region (I), fast fall region (II), meso-equilibrium region (III), and equilibrium region (IV). Due to low induction time, the fast fall region could be considered equal to adsorption time. The point that should be mentioned is that it is possible to calculate the meso-equilibrium time by subtracting the adsorption time from equilibrium time.

For the sake of a better comparison, standard deviation (SD) of measured equilibrium IFT of DW and monovalent salts as well as the employed constant parameters of models with AARD of predicted IFT to the experimental IFT are tabulated in Table 3. Comparing the AARD of the mono-exponential decay model with empirical equation (see Table 3) shows that mono-exponential decay model prediction is better than empirical equation for DW, NaCl and KCl in the entire range of studied pressure. Since the effect of the pressure on the DIFT is the same for all of the examined pressures, only one set of fitting parameters was used for all the examinations at constant temperature. In other words, the fitting parameters are obtained using regression method using the minimum error for a constant temperature and four constant pressures as an objective function. In general, although a slight deviation in the result of modeling is observed, a good capability of the empirical equation was recorded. This result showed that dynamic IFT is satisfactory decay based on the exponential function.

Table 1
Crude oil properties

Specification	Result	Test method
Specific gravity @ 20 °C	0.9224	ASTM D-40452
API	21.49	ASTM D-40452
Density of C_{12} fraction/g·cm ⁻³	0.9917	ASTM D-40452
Average molecular weight/g·mol ⁻¹	310	IP-86
Molecular weight of residue C_{12} /g·mol ⁻¹	529.5	IP-86
Water content/vol%	1.5	ASTM D-95
Sulfur content/wt%	3.62	ASTM D-2622
Wax content/wt%	3.25	BP-237
Kinematic viscosity @ 20 °C/m ² ·s ⁻¹	215.8×10^{-6}	ASTM D-445

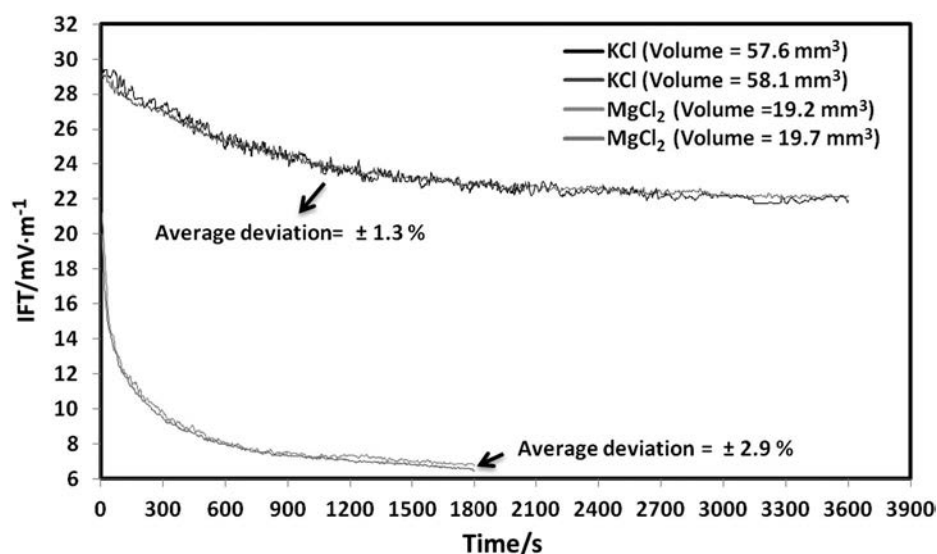


Fig. 1. Dynamic IFT repeatability of the used crude oil and KCl and MgCl_2 at $15000 \text{ mg} \cdot \text{kg}^{-1}$ and 1000 psi (1 psi = 6.895 kPa).

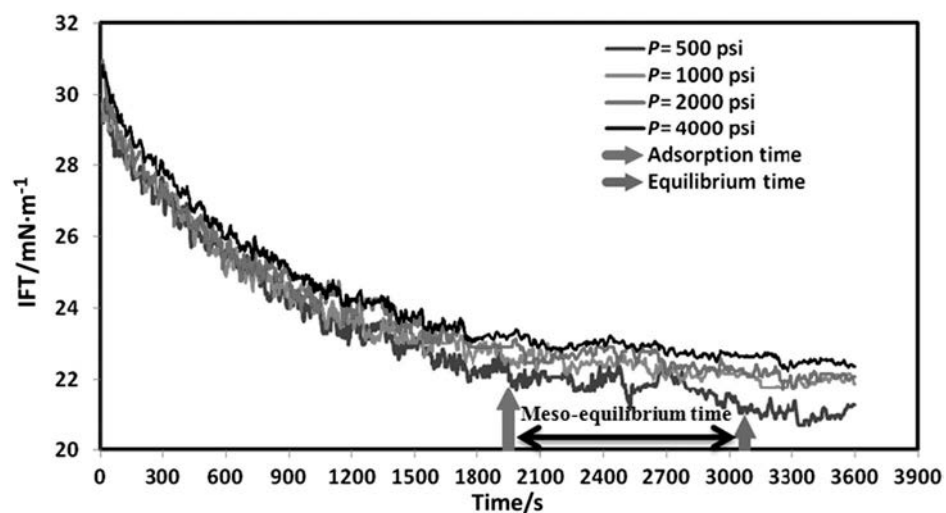


Fig. 2. Time-dependent behavior of IFT at different pressure for $15000 \text{ mg} \cdot \text{kg}^{-1}$ of KCl aqueous solutions (1 psi = 6.895 kPa).

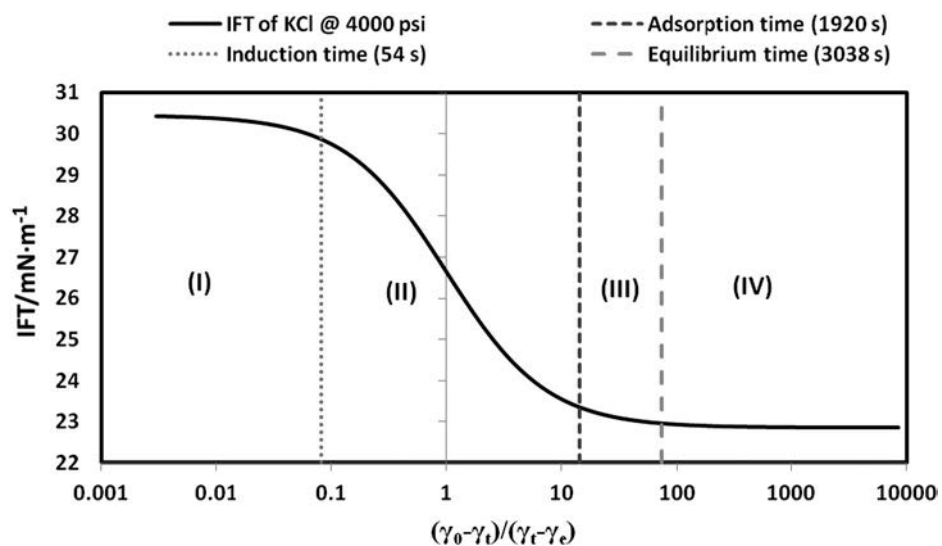


Fig. 3. Generalized dynamic IFT versus $\lg \frac{(\gamma_0 - \gamma_e)}{(\gamma_t - \gamma_e)}$ based on empirical equation for crude oil/ $15000 \text{ mg} \cdot \text{kg}^{-1}$ of KCl aqueous solution at $T = 30^\circ \text{C}$ and $P = 4000 \text{ psi}$ (1 psi = 6.895 kPa).

Table 3
Errors of equilibrium IFT measurement and the used models for prediction of dynamic IFT of monovalent salts (1 psi = 6.859 kPa)

Model	<i>P</i> /psi	DW				NaCl				KCl			
		500	1000	2000	4000	500	1000	2000	4000	500	1000	2000	4000
IFT	EIFT/mN·m ⁻¹	21.91	21.92	21.70	21.80	20.49	20.80	21.10	21.04	21.08	22.05	22.05	22.42
	SD	0.39	0.30	0.48	0.24	0.09	0.12	0.14	0.08	0.18	0.18	1.10	0.11
Exponential decay model	τ /s	2480	2530	2510	2540	2320	2300	2340	2340	1970	1950	1940	1920
	AARD/%	1.4	2.0	1.5	1.6	1.3	0.9	2.3	1.1	1.6	1.6	1.8	0.9
Empirical equation	<i>n</i>	1.435	1.435	1.435	1.435	1.221	1.221	1.221	1.221	1.322	1.322	1.322	1.322
	<i>t</i> [*]	625.6	625.6	625.6	625.6	642.4	642.4	642.4	642.4	410.9	410.9	410.9	410.9
DAM	STA	AARD/%	1.9	2.6	2.1	2.1	2.6	2.4	2.6	2.5	2.2	1.7	1.4
		Slope	0.169	0.162	0.165	0.158	0.216	0.226	0.219	0.229	0.188	0.186	0.187
		γ_0 /mN·m ⁻¹	30.98	31.25	31.20	30.52	31.82	32.49	32.89	32.81	30.11	30.21	30.46
		AARD/%	< τ	1.3	1.4	1.3	0.9	1.4	1.0	0.8	1.3	1.5	1.7
		Total	1.8	1.4	1.6	1.7	2.1	2.1	2.0	2.4	2.8	3.4	2.9
	LTA	Slope	240.2	247.0	241.6	247.8	199.3	189.2	199.3	188.1	176.6	149.9	147.8
		γ_0 /mN·m ⁻¹	17.95	18.10	17.82	17.91	17.75	17.92	18.75	18.86	18.23	19.32	19.64
		AARD/%	> τ	1.3	1.3	1.2	1.1	2.1	1.4	2.8	3.1	1.5	1.1
		Total	5.8	6.3	5.9	6.7	4.6	5.0	5.1	4.7	4.5	3.8	4.0
													3.6

A closer examination in Figs. 4 and 5, one can observe that the dynamic IFTs of 15,000 mg·kg⁻¹ of divalent salts including CaCl₂ and MgCl₂ solutions nearly increase as the pressure increases. Besides, these figures demonstrate that the dynamic IFTs of both systems are considerably independent of pressure. Also, it can be seen that the IFTs of

brine + crude oil systems were reduced to ~6.6 and ~16.7 mN·m⁻¹ for MgCl₂ and CaCl₂, respectively. The depicted results demonstrated that the IFT of divalent ions (i.e. CaCl₂ and MgCl₂) experienced a sharp reduction in the early stage of measurements. For the sake of comparison, adsorption, equilibrium, and meso-equilibrium times of used crude oil/

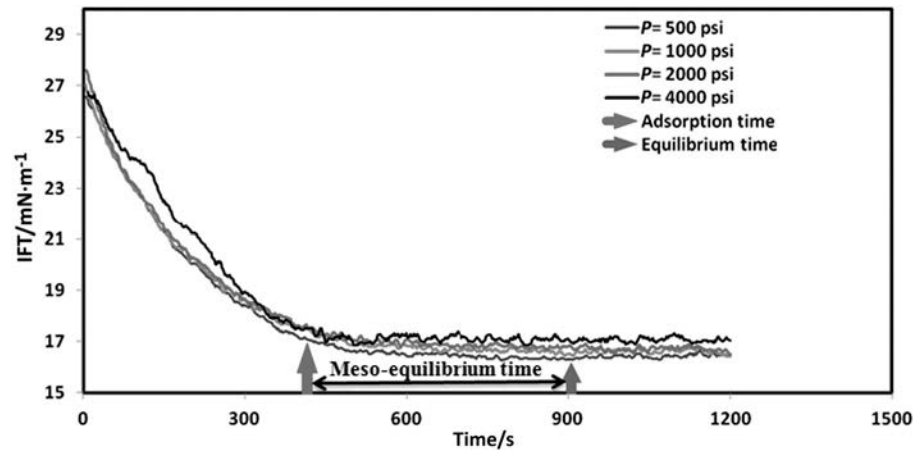


Fig. 4. Time-dependent behavior of IFT at different pressure for 15,000 mg·kg⁻¹ of CaCl₂ aqueous solutions (1 psi = 6.895 kPa).

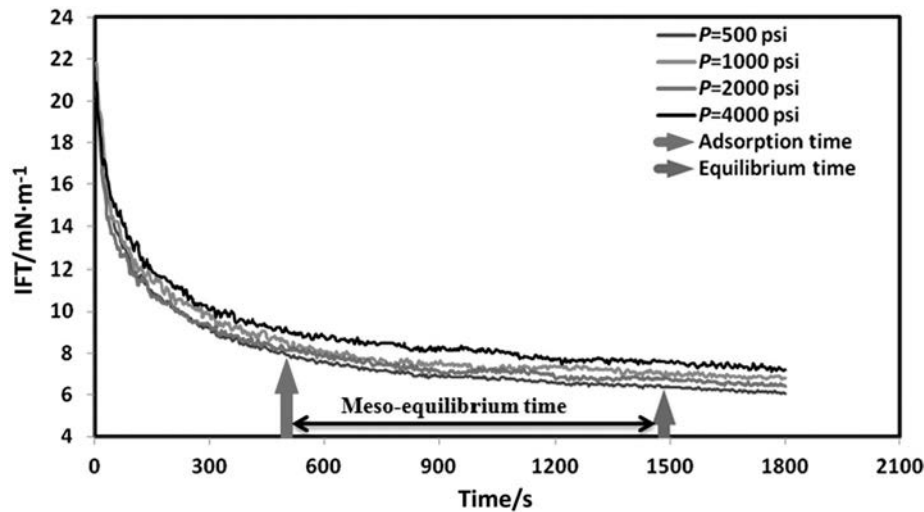


Fig. 5. Time-dependent behavior of IFT at different pressure for 15,000 mg·kg⁻¹ of MgCl₂ aqueous solutions (1 psi = 6.895 kPa).

different aqueous solutions as a function of pressure are shown in Fig. 6(a), (b), and (c), respectively. As can be seen in Fig. 6(a), addition of 15000 $\text{mg} \cdot \text{kg}^{-1}$ of monovalent salt reduces adsorption time (~ 1950 and ~ 2330 for KCl and NaCl, respectively) compared with DW

(~ 2500 s). It should be noticed that the lower adsorption time is needed if the rate of movement of the surface active agents towards the interface is higher. In more details, the concentration of the surface active agents at the interface approaches maximum affinity to the interface in the lower

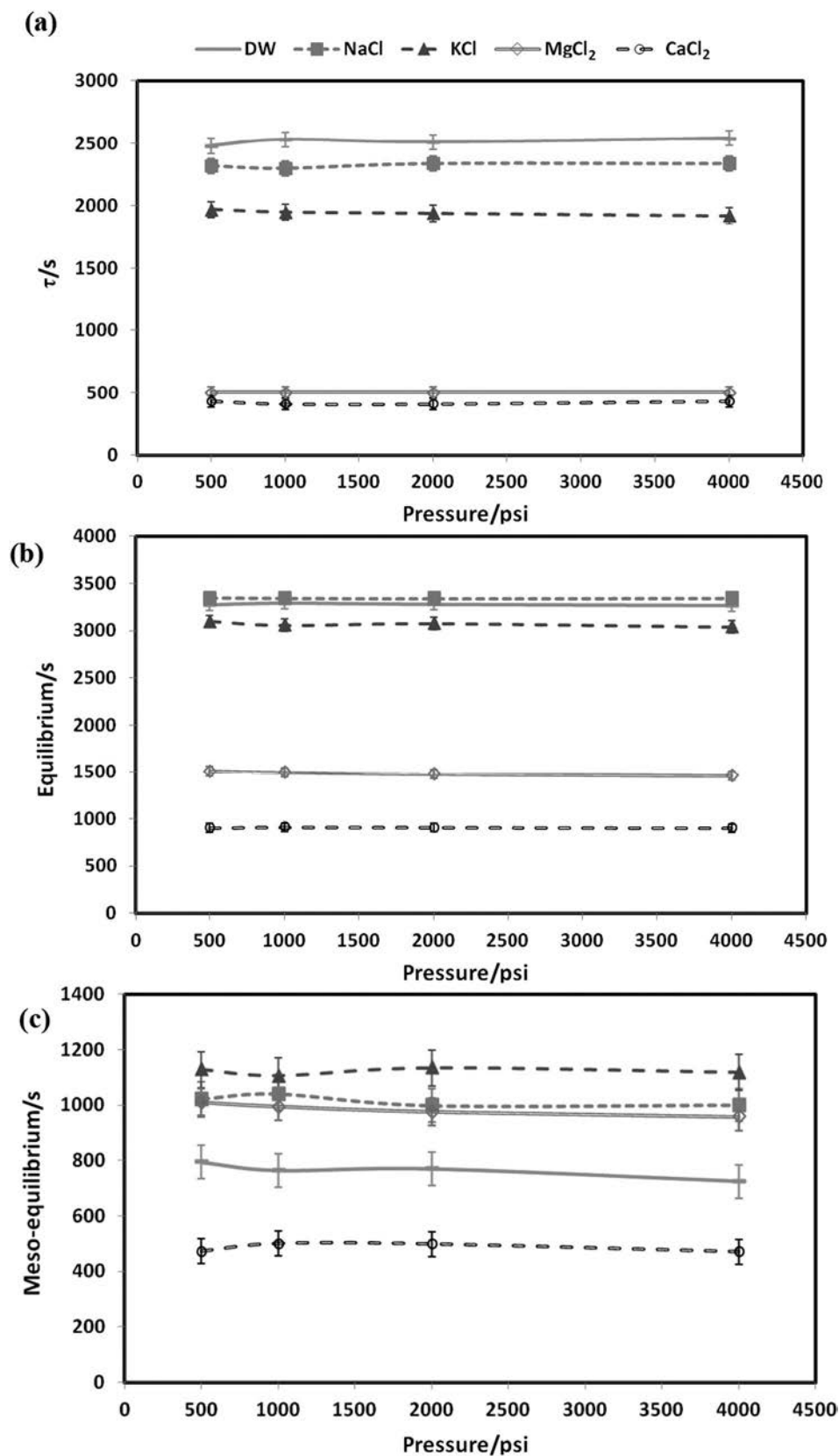


Fig. 6. Comparison between (a) adsorption, (b) equilibrium and meso-equilibrium and (c) times of used crude oil/different aqueous solutions as function of pressure (1 psi = 6.895 kPa).

time when monovalent salts were added to the solutions compared to DW. In addition, the attained results revealed that the adsorption time significantly reduces if the addition of $15000 \text{ mg} \cdot \text{kg}^{-1}$ of divalent salts to the aqueous solution occurs (~ 500 and 410 s for MgCl_2 and CaCl_2 , respectively) compared with monovalent ions. In other words, the following conclusion can be extracted for the adsorption time:

Adsorption time of : $\text{DW} > \text{NaCl} > \text{KCl} > \text{MgCl}_2 > \text{CaCl}_2$

An almost similar trend was observed for equilibrium time, although equilibrium time of $15000 \text{ mg} \cdot \text{kg}^{-1}$ of NaCl is slightly more than DW. But in the case of MgCl_2 interesting results are obtained considering its meso-equilibrium time. In more details, although adsorption and equilibrium times of MgCl_2 are considerably lower than DW and monovalent salts, its meso-equilibrium time is higher than DW and is near the monovalent salts. This observed trend is related to this fact that the complex ion of Mg^{2+} and polar organic component of asphaltene and resin [15] is rapidly formed, but the packing of these complex ions at the interface needs higher time.

The packing of the surface active agents at the interface in the meso-equilibrium region is the most important parameter to experience the lower meso-equilibrium region. As it was previously reported, the affinity of Mg^{2+} to the resin molecules is higher than Ca^{2+} while the

affinity of Ca^{2+} to the asphaltene molecules is higher than Mg^{2+} [14]. Therefore, the time of packing of the surface active agents is lower for Ca^{2+} due to the higher polarity of asphaltene molecules and higher affinity of them to Ca^{2+} cation.

The values of equilibrium IFT of crude oil with different solutions (with different concentration of salts) are demonstrated in Fig. 7(a) as a function of pressure. According to the outcomes (see Fig. 7), it can be concluded that the monovalent ions introduce a slight effect on the equilibrium IFT, whereas the effect of divalent ions on the equilibrium IFT is more apparent.

The point that must be mentioned is that the volume of drop is different from drop to drop for all of the examined salts. As can be seen from Fig. 7b, for CaCl_2 and MgCl_2 smaller drop was used. Due to lower IFT of crude oil in these solutions compared to DW, KCl and NaCl (see Fig. 7a), it was not possible to form a large drop. In other words, the smaller crude oil drop is needed for systems with lower IFT. In details, the increase of IFT for salt solutions containing the anion Cl^- for pressure of 500 psi ($1 \text{ psi} = 6.895 \text{ kPa}$) is as follows:

$\text{DW} > \text{KCl} > \text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$

As the pressure increases, the rate of IFT enhancement for $15000 \text{ mg} \cdot \text{kg}^{-1}$ of KCl solution is higher than that for DW.

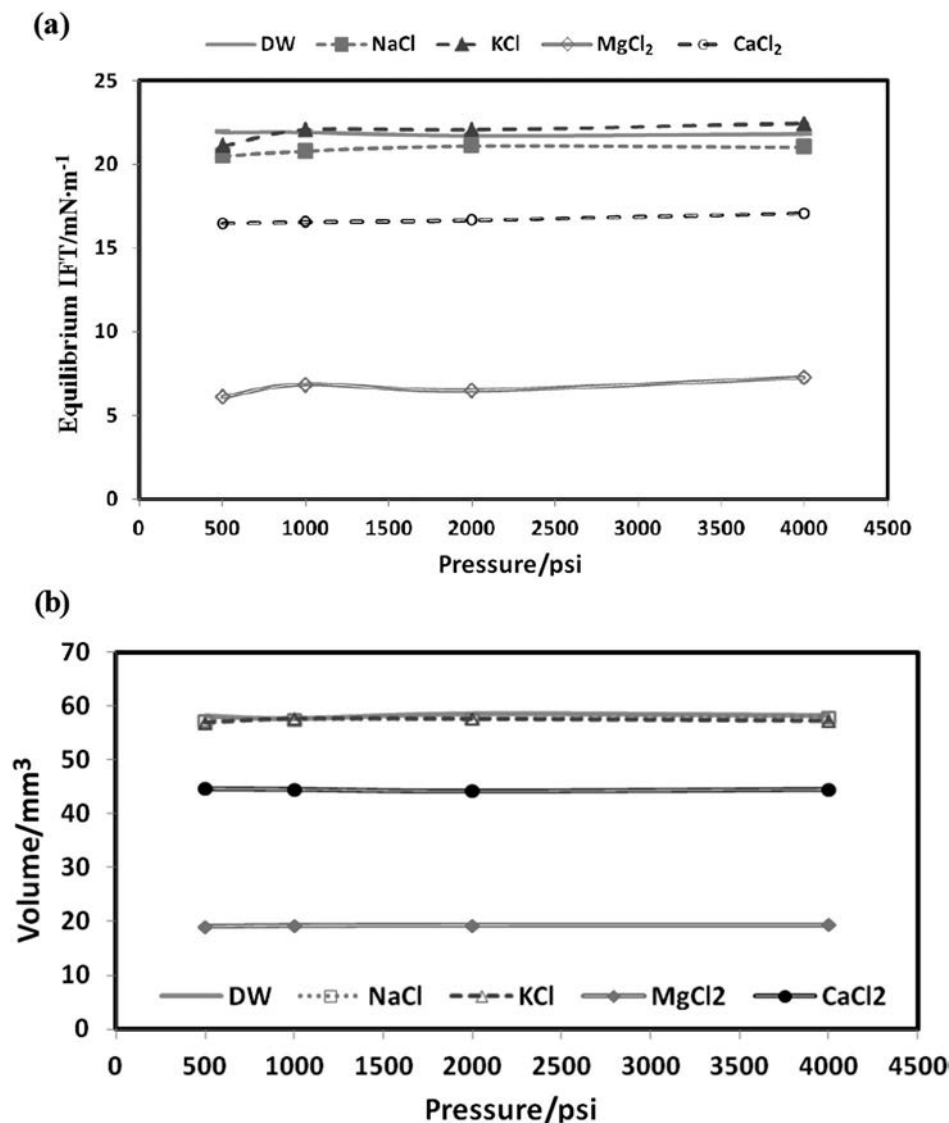


Fig. 7. Comparison between (a) equilibrium IFT of used crude oil/ $15000 \text{ mg} \cdot \text{kg}^{-1}$ of different brine solutions and (b) volume on crude oil drop as a function of pressure ($1 \text{ psi} = 6.895 \text{ kPa}$).

Table 4

Errors of equilibrium IFT measurement and the used models for prediction of dynamic IFT of divalent salts (1 psi = 6.895 kPa)

Model			CaCl ₂				MgCl ₂			
			P/psi	500	1000	2000	4000	500	1000	2000
Equilibrium IFT		EIFT/mN·m ⁻¹	16.47	16.55	16.64	17.04	6.09	6.83	6.46	7.23
		SD	0.11	0.11	0.11	0.19	0.05	0.06	0.07	0.10
Mono exponential decay		τ/s	430	410	390	430	500	500	500	500
		AARD/%	1.4	0.8	0.9	1.9	7.8	5.9	6.9	6.38
Empirical equation		n	1.715	1.715	1.715	1.715	1.329	1.329	1.329	1.329
		t*	108.6	108.6	108.6	108.6	119.1	119.1	119.1	119.1
		AARD/%	2.4	1.8	1.6	2.4	4.2	4.7	3.6	2.6
DAM	STA	Slope	0.568	0.568	0.568	0.568	0.838	0.839	0.792	0.784
		γ ₀ /mN·m ⁻¹	28.23	28.22	28.70	29.33	20.72	21.17	19.54	21.23
		AARD/%	<τ	0.8	0.8	1.1	1.5	16.9	16.2	18.3
	Total	17.1		16.4	17.1	17.3	161.8	150.2	154.8	126.2
	LTA	Slope	70.12	68.19	65.05	65.08	82.67	75.05	78.57	83.37
		γ _e /mN·m ⁻¹	14.03	14.30	14.51	14.92	4.19	5.04	4.64	5.37
		AARD/%	>τ	1.7	1.4	1.1	1.9	0.8	1.6	1.2
	Total	3.2		2.9	2.8	3.8	2.3	2.8	2.8	2.8

To understand which mechanism is dominant, dynamic adsorption models based on short and long term approximations were used. Comparisons between the error of fitting of short and long time

approximations used for correlating the dynamic IFT values of crude oil/15000 mg·kg⁻¹ of different brine are tabulated in Table 4. The point that must be mentioned is that in Table 4, for diffusion-controlled

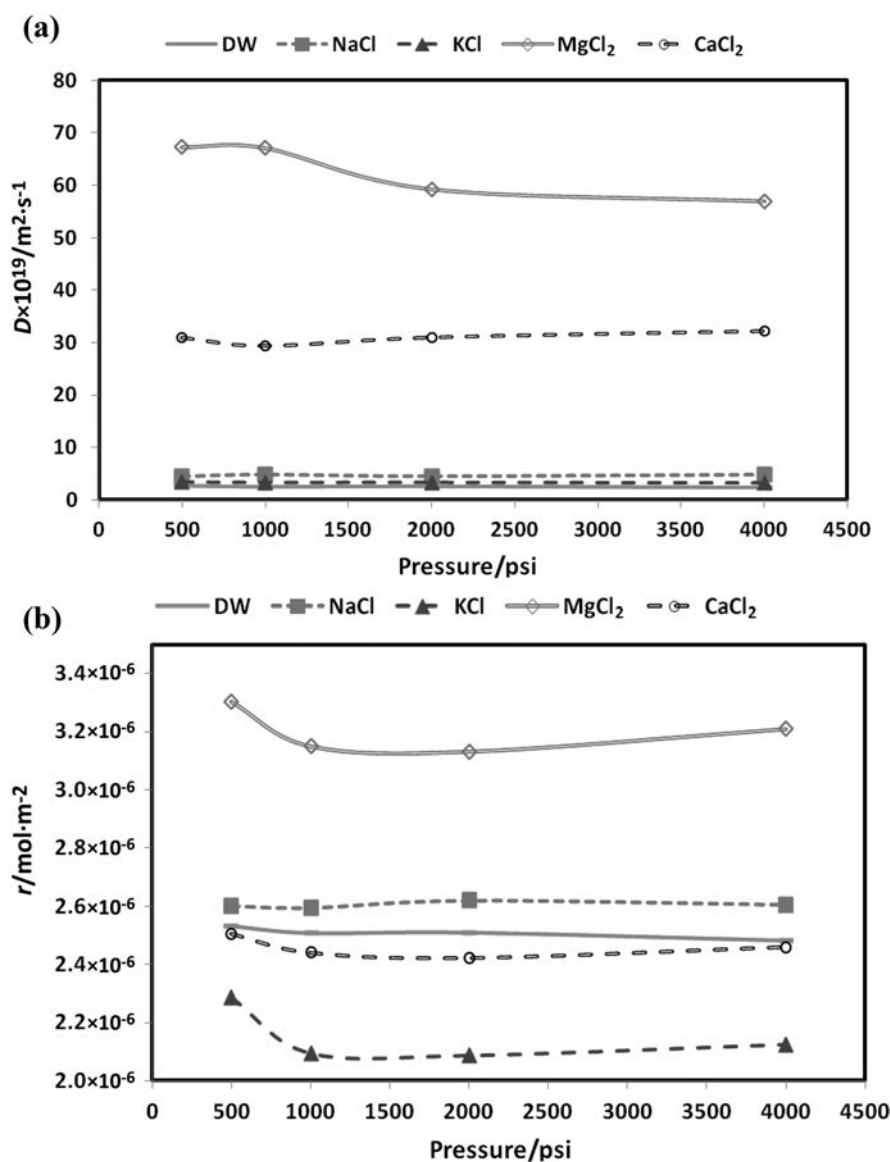


Fig. 8. Comparison between a) diffusivity of surface active agents to the crude oil/different aqueous solution interface and b) surface excess concentration of surface active agents at crude oil/different aqueous solution interface as function of pressure (1 psi = 6.895 kPa).

models, AARDs/% of predicted IFT are given based on the adsorption time and the entire range of time.

As it is clear from Table 4, the short-time approximation showed a satisfactory prediction of the experimental IFT data before adsorption time while the prediction results experienced a worse deviation as time increases after adsorption time. Contrariwise, the long-time approximation correlates the experimental IFT data after adsorption time and prediction become worse with decreasing times before adsorption time especially for initial times. As suggested by Joos *et al.* [23], at the start of the adsorption process the short-time approximation was utilized in which diffusivity of surface active agents to the fluid/fluid interface was calculated (see Fig. 8a). On the other hand, at the end of the process the long-time approximation was used and surface excess concentration of surface active agents at the interface was calculated (see Fig. 8b).

As the results presented in Fig. 8a and Table 5, the diffusivity values of asphaltenes and resins in the crude oil are between $D \sim 10^{-18}$ and $10^{-19} \text{ m}^2 \cdot \text{s}^{-1}$. These values of diffusion showed that the process is non-diffusion-controlled process as Pradilla *et al.* [40] reported for their findings regarding the Brij®-93 (model demulsifier) and asphaltene in xylene. In these cases, a decrease in the IFT is not clarified through the diffusion of surfactant molecules to the interface, but as an alternative it is probable that an adsorption barrier is present [40]. In addition, Rane *et al.* [41,42] using the oscillating pendant drop technique found that at water–oil interfaces, adsorption from largely aliphatic oils appeared to be governed at early times by molecular diffusion and at later times by molecular random sequential adsorption.

In addition, a close examination in Fig. 8 a revealed that the effect of salt on the diffusivity of surface active agents follows the current sequence: $\text{MgCl}_2 > \text{CaCl}_2 > \text{NaCl} > \text{KCl} > \text{DW}$. The presence of divalent ions including Mg^{2+} and Ca^{2+} changes significantly the adsorption process. The presence of divalent ions in the aqueous solutions decreases adsorption time while increases diffusivity of surface active agents to the crude oil/aqueous phase interface. As it was expected, the surface excess concentration of surface active agents can be a positive parameter due to the presence of asphaltene and resin at the interface of aqueous solution and crude. Besides, this parameter is higher for CaCl_2 aqueous solution compared with DW and monovalent salts due to low equilibrium IFT. In particular, many complex ions constructed by divalent ions (calcium and magnesium salts) and of a polar organic component, which have N- and O-bearing moieties, are soluble in aqueous solutions, which can consequently enhance the surface excess concentration [15]. Although positive values were obtained for surface excess concentration of surface active agents based on the dynamic adsorption model, surface excess concentration of surface active agents at CaCl_2 aqueous solution/crude oil interface is lower than DW and NaCl aqueous solutions (see Fig. 8b).

Through the Gibbs adsorption isotherm, the IFT is linked to the composition of the system. The change in IFT as a function of chemical activity of the components can be obtained through the Gibbs equation [43–45]:

$$d\gamma = -RT \sum_i \Gamma_i d \ln a_i \quad (8)$$

Table 5

Comparison of adsorption parameters of different systems with the current investigation

System	Surfactant concentration/mol · m ⁻³	$\Gamma/\text{mol} \cdot \text{m}^{-2}$	$D/\text{m}^2 \cdot \text{s}^{-1}$
SDBS in water solution [38]	0.5	7.48×10^{-6}	4.76×10^{-10}
SDBS in water solution [39]	0.5	4.83×10^{-6}	1.97×10^{-11}
Asphaltenes in xylene [40] ^①	2.94×10^{-3}	$\sim 10^{-7}$	1.49×10^{-12}
Asphaltenes in xylene [40] ^①	7.37	$\sim 10^{-7}$	2.15×10^{-18}
Brij®-93 in xylene [40] ^②	2.43×10^{-4}	$\sim 10^{-6}$	4.68×10^{-12}
Brij®-93 in xylene [40] ^②	1.21	$\sim 10^{-6}$	2.35×10^{-15}
Asphaltenes and resin in the crude oil	173	$\sim 10^{-6}$	$\sim 10^{-18}$ to 10^{-19}

^① Based on the short time approximation.

^② Based on the long-term approximation.

where $d\gamma$ is the change in IFT of the solution, R is the gas constant, T is the absolute temperature, and Γ_i and a_i are the surface excess concentration and the activity of the i th component in the solution, respectively.

Equilibrium IFT of crude oil, 8 wt% of extracted of asphaltene and resin in toluene and 15000 mg · kg⁻¹ of different brine solutions at ambient conditions [15] are shown in Fig. 9. It is shown that equilibrium IFTs of aqueous solutions/crude oil conform the following sequence:

$\text{KCl} > \text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2$

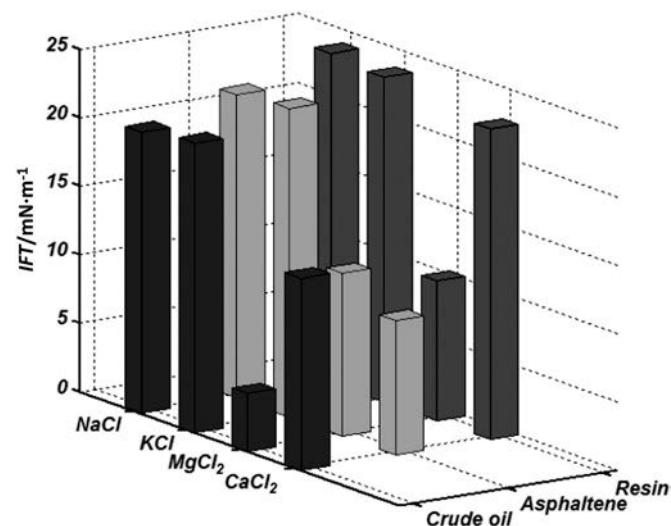


Fig. 9. Effect of ion type and surface active component (8 wt% of extracted of asphaltene and resin in toluene) in equilibrium IFT of crude oil.

The measured IFT of toluene/deionized water, 8 wt% extracted asphaltene and resin in toluene compared to deionized water were $35.4 \text{ mN} \cdot \text{m}^{-1}$, 23.9 and $24.1 \text{ mN} \cdot \text{m}^{-1}$, respectively. It was also observed that ions especially divalent cations because of synergetic effect of asphaltene and resin with salt leads to more IFT reduction.

The IFT of crude oil/brine solutions and the surface excess concentration of the surface active agents (*i.e.* asphaltene and resin) did not follow the same trend. For more investigation, dynamic IFT of crude oil/15000 mg · kg⁻¹ of different brine solutions are at temperature of 30°C and pressure of 500 psi are depicted in Fig. 10. A glance on the depicted results one can find out that initial IFTs of aqueous solutions/crude oil conform the following sequence:

$\text{NaCl} > \text{DW} > \text{KCl} > \text{CaCl}_2 > \text{MgCl}_2$

Therefore, polar organic components of surface active agents (*i.e.*, asphaltene and resin) react with the Ca^{2+} cations consequently producing complex ions [14,46,47] leading to an enhancement in the activity coefficient of the surfactant in the aqueous phase. Hence, based on the Gibbs adsorption isotherm (Eq. (8)), equilibrium IFT

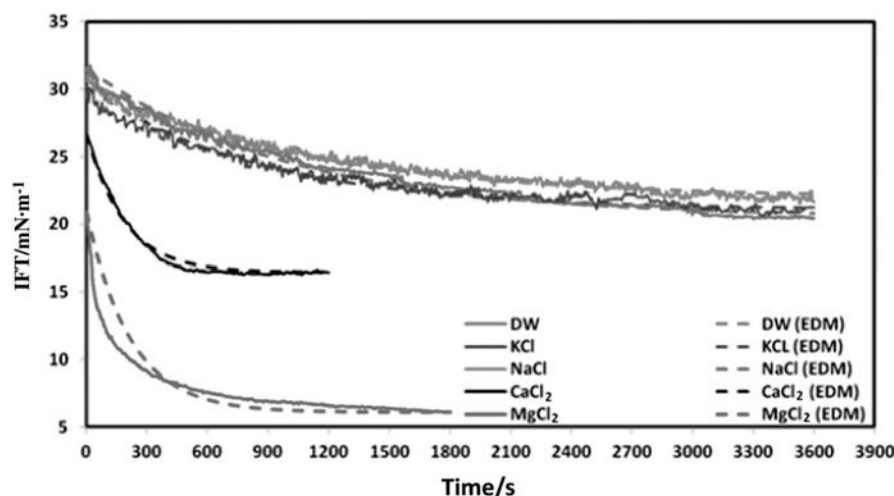


Fig. 10. Comparison of dynamic IFT of crude oil/15000 mg·kg⁻¹ of different brine solutions at $T = 30\text{ }^{\circ}\text{C}$ and $P = 500\text{ psi}$ (1 psi = 6.895 kPa) with exponential decay model (EDM).

decreases compared with DW as the activity of the surfactant in the aqueous phase increases. For MgCl_2 , two important parameters including surface excess concentration and activity of surface active agents increase compared with other studied salts consequently leading to a significant IFT reduction for MgCl_2 compared with the other salts. Although the equilibrium surface excess concentration of CaCl_2 case is obtained lower than DW, NaCl and KCl cases (see Fig. 8), not only the higher activity of surface active agents (is equal to lower initial IFT (see Fig. 10)) in the aqueous solution containing CaCl_2 leads to lower equilibrium IFT for CaCl_2 solution but also the equilibrium time is considerably lower for CaCl_2 case (see Figs. 6 and 10). In other words, the initial IFT of the used crude oil/ CaCl_2 is obtained lower than DW, NaCl and KCl systems due to higher activity of resin and asphaltene in the Ca^{2+} solution. Therefore, the activity of the surface active agents in the presence of Ca^{2+} is dominant mechanism compared with the equilibrium surface excess concentration. Moreover, due to low impact of pressure on the equilibrium surface concentration (see Fig. 8 b) and activity of surface active agent (see initial IFT on Figs. 2, 4 and 5), equilibrium IFTs (Fig. 7 a) were not changed based on Eq. (8). In addition, based on the obtained results it can be concluded that the presence of salt, especially divalent cation, is able to alter the distribution of surface active agents between crude oil and aqueous phase and enhances the adsorption of them at the interface and consequently leads to the IFT reduction.

As it is obvious in Fig. 10, deviation between the dynamic IFTs calculated by mono-exponential decay model and the experimental values is higher for MgCl_2 compared with other studied salts. Digging on the results tabulated in Table 4 revealed that the empirical equation for MgCl_2 leads to higher accuracy compared with the mono-exponential decay model. A closer examination in Tables 3 and 4 illustrated that for aqueous solutions which had low diffusivity of surface active agents including DW, NaCl, and KCl, not only short time approximation prediction in entire times is satisfactory but also it demonstrated higher accuracy than the long time approximation model. In contrast, the long-time approximation model predicts dynamic IFT better than the short time approximation for divalent cations including Ca^{2+} and Mg^{2+} which have high diffusivity.

4. Conclusions

The different models are used to predict the dynamic IFT of asphaltenic–acidic crude oil over aqueous phase containing chloride anion bonding to Na^+ , K^+ , Mg^{2+} and Ca^{2+} cations. In addition, the Gibbs adsorption isotherm and dynamic adsorption model were utilized to describe the impact of activity and surface excess concentration of surface active agents (i.e. asphaltene and resin) in the IFT behavior of

different ions. Totally, the following conclusions are extracted from the performed experiments and modeling:

- ✓ Although, pressure has no considerable effect on dynamic behavior of IFT for different saline solution/crude oil, the value of equilibrium IFT slightly increased as the pressure increased.
- ✓ The measured dynamic IFT properly qualified the variations on the crude oil/saline solution interface.
- ✓ The divalent ions reduce the adsorption time more than monovalent ions.
- ✓ The short time approximation model experience more deviation at the end of the process as the activity of surface active agents at the fluid/fluid interface increases.
- ✓ It was found that the aqueous solution containing Mg^{2+} is more effective compared to others, however the arrangement of the surface active components at the interface, hence the IFT reduction needs more time for this case.
- ✓ Although the surface active agents surrounding Ca^{2+} solution pose lower surface excess concentration than water, higher IFT reduction was observed due to the high activity of surface active agents for CaCl_2 .
- ✓ The next phase of this study would be design of experiments to investigate the effect of temperature, pH and crude oil type to clarify smart water injection applicability in the reservoir. Comparison of the crude oil sample from Iran with samples from other places (i.e. of different composition) may also be a subject of interest.

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