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Investigation of Water Salinity Effect on Asphaltene Precipitation Using PC-SAFT EOS

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ABSTRACT

Asphaltene precipitation has attracted more attention in low-salinity water flooding processes in the last decade. In this study, ePC-SAFT equation of state has been used to investigate the effect of water salinity on asphaltene precipitation. To this end, a solid model with a synthetic oil containing heptane and toluene with a ratio of 70 to 30 was used to predict asphaltene precipitation. Three adjustable parameters in the Particle Swarm Optimization method were used to minimize the absolute average deviations (AAD) between experimental and modeling values. The role of water chemistry on asphaltene precipitation was addressed by changing the composition of seawater (SW) by tuning ionic strength and manipulating divalent ions. Also, to get further insights into the role of divalent ions (Mg^{2+} , Ca^{2+} , SO_4^{2-}), three makeup water containing $MgCl_2$, $CaCl_2$ and Na_2SO_4 salts were used. Results showed that in low concentrations of salts (5000 ppm), the asphaltene molecules migrate to the oil/water interface, leading to a decrease in asphaltene precipitation. Beyond this concentration, asphaltene precipitation was increased due to the breaks of the bonding between ion-asphaltene. As to results, a lower precipitation level was observed for the case of dilution seawater (0.5 SW and 0.1SW) that could be discussed in terms of electrical double-layer expansion. The results of the comparison between modeling and experimental data show that the proposed model can predict asphaltene precipitation for $MgCl_2$, $CaCl_2$ and Na_2SO_4 brine with absolute relative deviations less than 7.68%, 5.44% and 8.39%. The finding from this study elucidates the importance of water salinity to design an applicable low-salinity water flooding.

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1. Introduction

One of the distinguished methods in enhanced oil recovery (EOR) is low-salinity water flooding (LSWF) which improves oil recovery mostly through wettability alteration, multiple cation exchange, double layer extension, salting-in effect, IFT reduction, etc. (Amanabadi et al., 2020; Chai et al., 2022; Yutkin et al., 2022). Precipitation of asphaltene on the rock surface is one of the unwanted problems during LSWF. This phenomenon could be more challenging if the asphaltene precipitation influences oil recovery by permeability reduction, rock surface wettability alteration, and pipeline blockage (Speight, 2015). Mathematical modeling of this issue has been more attractive to have a better insight into how this phenomenon occurs, prevents, and treats.

The reduction of injected water salinity directly impacts asphaltene presented in the crude oil phase due to their polarity (Hu et al., 2015; Ameri et al., 2018). Hence, several studies have been conducted to address the role of fluid-fluid interaction. To this end, thermodynamic modeling of asphaltene with a different equation of states such as PC-SAFT is essential (Rodriguez, 2008; Sabeti et al., 2015; Meighani et al., 2016). There are two types of asphaltene modeling presented based on the literature. In the first one, it is assumed that asphaltene is an actual component in the oil composition and soluble in the oil. In the second approach, asphaltenes are colloidal in oil, and their stability depends on different factors such as pressure, temperature, and oil composition. Zhang et al. compared PC-SAFT and CPA EOS for the aspect of asphaltene modeling. They used SRK EOS for the physical part, while Wertheim was used for the associating part. They considered asphaltenes as a self-associating component and can cross-associate with resin. They studied six live oils and one heavy oil and found that CPA EOS has better matching with experimental data. The results contradict Alhammadi et al. (Zhang et al., 2012). Kariman Moghaddam and

Jamshidi have suggested a methodology to characterize fluid injections consisting of crude oil and evaluated the performance of the PC-SAFT in asphaltene behavior modeling during fluid injections into the oil reservoirs (Kariman Moghaddam & Jamshidi, 2022). Hosseinifar & Jamshidi modified a new model to estimate PC-SAFT parameters for different pure components. They created a relationship between the cubic equation of state parameters (critical pressure, critical temperature, and acentric factor) and PC-SAFT parameters (Hosseinifar & Jamshidi, 2015). Naseri et al. developed a new multicomponent, multiphase and dynamic tool to model the aggregation and deposition of asphaltene particles in a bulk medium. They developed a bespoke algorithm to predict asphaltene precipitation, aggregation, and deposition. Also, they used PC-SAFT equation of state to obtain asphaltene precipitation phase envelope (APE) (Naseri et al., 2020). Moeini et al. investigated the mechanisms of interfacial tension between oil/ water in the presence of different salt concentrations. Low salinity water flooding (LSWF) causes a reduction of water-oil IFT. They found that interfacial tension reaches its minimum value at a certain salinity which is called critical concentration. Beyond this concentration, diluting brine solution has a negative impact on IFT. The results showed that the amount of IFT decreases until 50% of the brine solution is mixed with deionization water. As soon as brine salinity decreases from critical concentration, the amount of interfacial tension increases (Moeini et al., 2014). Shojaati et al. studied the effect of water salinity on asphaltene behavior in the presence of water in oil emulsion. In order to investigate the effect of ions on the asphaltene instability, makeup waters from different salts were used in a diverse range of concentrations. It was found that divalent cations have more impact on the asphaltene instability compared to monovalent cations due to the chelation process. Furthermore, the presence of divalent anions can prevent the effect of cations on the asphaltene instability (Shojaati et al., 2017). Birkan Demir et al. studied the effect of water

salinity on asphaltene clustering in five different model oils. The brine solutions were prepared with various salts, including CaCl_2 and MgCl_2 at 2%, 4%, 6%, and 8% concentrations. The results showed that the makeup water with CaCl_2 salt results in bigger asphaltenes clusters than NaCl salt (Birkan Demir et al., 2016).

In our previous study, the mechanisms between rock/fluid in the presence of different water salinity was examined (Amanabadi et al., 2021). As to the literature on asphaltene precipitation for the purpose of LSWF, comparatively, few studies addressed modeling of asphaltene precipitation in the presence of makeup water compositions and model oil. In order to understand the exact mechanism behind the asphaltene precipitation, makeup water, including single salts (such as MgCl_2 and CaCl_2) in different ionic strengths, is used. Also, formation water and seawater have been used to simulate reservoir conditions better.

2. Material and Methods

2.1. ePC-SAFT

In this study, the ePC-SAFT EOS proposed by Cameretti et al. was used to model the electrolyte solutions (Cameretti et al., 2005). As offered by Gross et al., the original PC-SAFT was used to model the other components such as hydrocarbons and water (Gross et al., 2001).

$$\frac{A^{res}}{NKT} = a^{res} = a^{hc} + a^{disp} + a^{assoc} + a^{ion} \quad (1)$$

Where N is the total number of molecules, a^{hc} is the residual Helmholtz energy of hard-chain, a^{disp} , a^{assoc} and a^{ion} are Helmholtz energy for dispersive, associative, and ions, respectively. Finally, the Helmholtz energy of ions is defined as follows:

$$\frac{a^{ion}}{K_B T} = -\frac{\kappa}{12\pi K_B T \epsilon} \times \sum_j x_j q_j^2 X_j \quad (2)$$

Where K_B is Boltzman constant, x_j and q_j are the mole fraction and charge of ions, respectively. Finally, X_j and inverse of Deby length (κ) are defined as follows:

$$X_j = \frac{3}{(\kappa a_j)^3} \times \left[\frac{3}{2} + \ln(1 + \kappa a_j) - 2(1 + \kappa a_j) + \frac{1}{2}(1 + \kappa a_j)^2 \right] \quad (3)$$

$$\kappa = \sqrt{\frac{N_A}{K_B \epsilon} \times \sum_j q_j^2 c_j} = \sqrt{\frac{\rho_N e^2}{K_B T \epsilon} \sum_j Z_j^2 x_j} \quad (4)$$

Where N_A is Avogadro's constant, e is the elementary charge (c), and c_j molarity (mol/lit)

2.2. Calculation of thermodynamic properties with ePC-SAFT

In this study, to calculate the compressibility factor from residual Helmholtz energy, the following equation was used:

$$Z = \frac{\partial(a)}{\partial \ln(\eta)} = \eta \frac{\partial a}{\partial \eta} \quad \text{or} \quad Z = \frac{\partial a}{\partial \ln(\rho)} = \rho \frac{\partial a}{\partial \rho} \quad (5)$$

Where a is the total contribution of Helmholtz energy including a^{hc} , a^{disp} , and a^{assoc} , and η is residual density. Other residual Helmholtz energy is defined as follows:

$$\tilde{a}^{hc} = \bar{m} \tilde{a}^{hs} + \tilde{a}^{chain} = \bar{m} \tilde{a}^{hs} + \sum_i x_i (1 - m_i) \ln g_{ii}^{hs}(d_i) \quad (6)$$

$$\tilde{a}^{hs} = \frac{1}{\zeta_0} \left(\frac{3\zeta_1 \zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3} - \zeta_0 \right) \ln(1 - \zeta_3) \right) \quad (7)$$

$$\tilde{a}^{disp} = \frac{a^{disp}}{RT} = \frac{A_1}{RT} + \frac{A_2}{RT} \quad (8)$$

$$\frac{A_1}{NKT} = -2\pi\rho N_A \left[\sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{KT} \right) \sigma_{ij}^3 \right] \int_1^\infty \bar{u}(x) g^{hc}(m; \bar{x} \frac{\sigma}{d}) x^2 dx \quad (9)$$

$$\frac{A_2}{NKT} = -\pi\rho N_A \bar{m} C_1 \left[\sum_i \sum_j x_i x_j m_i m_j \left(\frac{\epsilon_{ij}}{KT} \right)^2 \sigma_{ij}^3 \right] \int_1^\infty \bar{u}(x)^2 g^{hc}(m; \bar{x} \frac{\sigma}{d}) x^2 dx \quad (10)$$

Where a^{hs} is Helmholtz energy of the hard-sphere, m_i is the number of the segment that is equal to 1 for ions, $g_{ij}^{hs}(d_i)$ is the radial distribution function, ϵ_{ij}/KB is the pairing segment energy parameter, A_1 and A_2 are depend on density, compositions, and size of molecules. The liquid-liquid flash calculation for oil/water was used to find the fugacity of precipitated asphaltene in the liquid phase (at atmospheric pressure and 353.15 k).

$$f_i^h = f_i^w \quad (11)$$

$$\phi_{i,p} = \exp \left(\frac{a_p^{res}}{RT} + (Z_p - 1) + \frac{\partial(a_p^{res}/RT)}{\partial x_i} - \ln(Z_p) - \sum_{j=1}^N x_j \left(\frac{\partial(a_p^{res}/RT)}{\partial x_i} \right)_{T,Y,x_{i \neq j}} \right) \quad (12)$$

Where $\phi_{i,p}$ is the fugacity coefficient of phase p .

2.3. Nghiem model

In this study, the Nghiem model (Nghiem et al., 2000) was used to predict asphaltene precipitation in the presence of water salinity. This model relies on the fugacity coefficient compared to other thermodynamic models (colloidal, activity coefficient base model). Also, the fugacity of asphaltene is expressed as a pure solid phase as follows:

$$\ln f_s = \ln f_s^* + \frac{v_s(P - P^*)}{RT} \quad (13)$$

Where f_s is the fugacity of asphaltene, f_s^* is the fugacity of asphaltene at a reference pressure, P^* , T , and R are reference pressure, temperature,

and the universal gas constant, respectively.

Three adjustable parameters in the Particle Swarm Optimization algorithm that was implemented in the Csharp language were used to minimize the AAD percentage between experimental and modeling data. Asphaltene's fugacity in the pure solid, interaction between asphaltene and ions, and interaction of asphaltene with water are considered as adjustable parameters where the objective function is defined as follows:

$$AAD\% = 100 \frac{\sum_{i=1}^N (abs(Prec\%_{exp,i} - Prec\%_{model,i}) / Prec\%_{exp,i})}{N} \quad (14)$$

Where $Prec\%_{exp,i}$ is asphaltene percentage of asphaltene precipitate obtained from experimental data, $Prec\%_{model,i}$ is the amount of asphaltene precipitate from the model, and N is the number of experimental data. The schematic of asphaltene precipitation calculation with respect to Nghiem model is shown below.

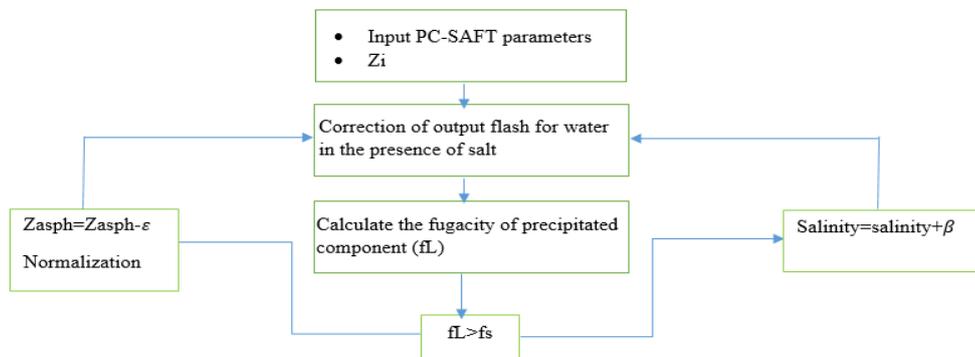


Figure 1. The schematic of asphaltene precipitation calculation

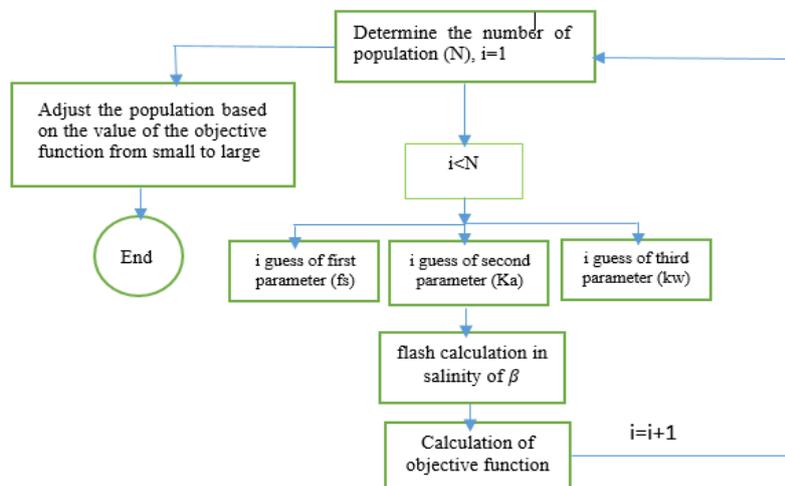


Figure 2. The procedure of optimizing adjustable parameter

2.4. Fluids

In this study, to check the effect of divalent ions on the asphaltene precipitation, three types of makeup water were used that in each solution, only one of the divalent salts became present. Also, to check the effect of seawater and

formation water on asphaltene precipitation, two solutions, including different salts, were used. Furthermore, in order to check the impact of salinity, two (0.5SW) and ten (0.1SW) time dilutions of seawater were used. See Table 1.

Table 1. Composition of seawater and formation water (Hosseini, 2018)

Brine: Formation water		Brine: Seawater			
Salt	Amount (gr/L)	Salt	SW (gr/lit)	0.5SW (gr/lit)	0.1SW (gr/lit)
NaCl	137.2735	NaCl	1.4212	0.71	0.1421
KCl	0	KCl	0.04125	0.02	0.0041
CaCO ₃	1.6278	MgCl ₂	0.3215	0.16075	0.0321
MgCl ₂	53.37	CaCl ₂	0.0692	0.045	0.0069
CaCl ₂	6.098	Na ₂ SO ₄	0.2245	0.1121	0.0224
Na ₂ SO ₄	2.587	NaHCO ₃	0.0053	0.0042	0.005
NaHCO ₃	2.587				
TDS (gr/50cc)	9.4844	TDS(gr/50cc)	2.08	1.04171	0.208

2.5. Oil

Due to the complex structure of crude oils, the observed changes in interfacial tension and asphaltene precipitation cannot be accurately attributed to the effect of a particular component. In such cases, the model oil can be used to facilitate the study of mechanisms. It is easier to interpret the observed phenomena when model oil is used because only one parameter is considered to change in the model oil. To this end, model oil containing heptane and toluene in a ratio of 70 to 30 was used to examine the effect of water salinity on asphaltene precipitation. The density of model oil is 0.84 (gr/m³), and asphaltene was measured as 0.6 of its total weight percent. Also, to prepare the input data for makeup water, a specific amount of salts (1000, 5000, 15000, 30000 and 45000 ppm) was added to the water (Hosseini, 2018).

3. Results and discussion

In general, it is necessary to pay attention to the reactions between water and salts in aqueous solutions, while it produces new ions in water. These ions migrate to the contact surface of water and oil. As a result, interactions between asphaltene and ions lead to a change in surface tension and consequently in the final amount of asphaltene precipitation.

Figure 3 shows the effect of makeup water in MgCl₂ salt on asphaltene precipitation. Based on the result, asphaltene precipitation decreased with increasing concentration up to 5000 ppm at low concentrations. Beyond this concentration, increases in salt concentration lead to increases in the amount of asphaltene precipitation that can be explained by the concept of salting-in and salting-out effect. Asphaltene molecules in the oil phase can play the role of polydentate ligand in the presence of cations. According to the definition, ligands are molecules or atoms with a

lone pair of electrons that can have neutral and negative electron charges in the external layer. Therefore, ligands usually interact with metal ions and make a complex structure. Generally, the relationship between metal and ligand involves one or more pairs of ligand electrons. In other words, at low salinities, the mobility of asphaltene molecules towards the interface of water and oil increases due to the presence of ions in the aqueous phase. Among these ions, cations play an essential role in binding to the structure of ligands (asphaltenes). Therefore, at low salinities, the asphaltene separates from the resins surrounding them and moves toward the interface. The Brownian motion of the asphaltene molecules toward the interface causes them to collide and makes their aggregation possible. On the other hand, due to the negative charge in the external structure of asphaltene, they have a function similar to surfactants and communicate with water molecules at the interface, the interaction between water-ion and water-asphaltene in the interface leading to a decrease in interfacial tension that could be proven by measuring interfacial tension by Hosseini et al. Beyond 5000 ppm, with increasing the ionic strength of aqueous phase relative to the interface, the thermodynamic equilibrium of the system is disturbed leading to increased demand of ions for ionization. Eventually, the bonding created at the interface is broken, and a layer of asphaltene with Brownian motion returns to the oil phase leading to the aggregation and precipitation of asphaltene. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018.

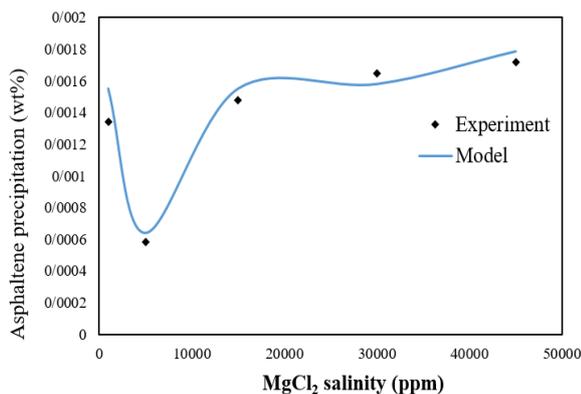


Figure 3. The effect of makeup water with MgCl₂ salt on asphaltene precipitation

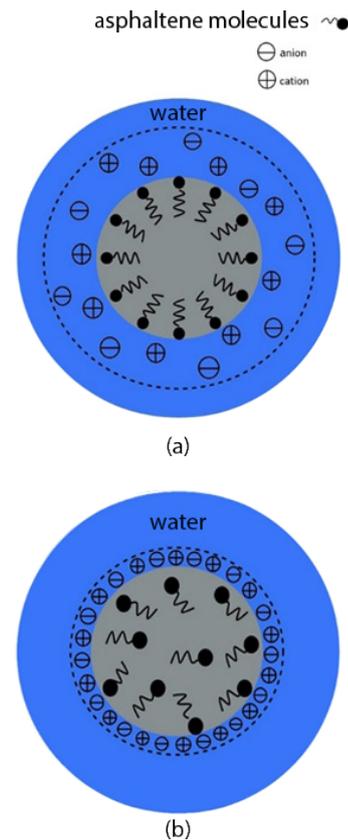


Figure 4. The effect of salinity on electrical double layer expansion. a) low salinity b) high salinity

Figure 5 shows the effect of makeup water in CaCl₂ salt on asphaltene precipitation. The mechanism of asphaltene precipitation in the presence of CaCl₂ salt is similar to MgCl₂, but the reason for the difference between the two trends could be discussed in terms of activity coefficient. The activity coefficient of each salt is unique for any particular concentration. Furthermore, the degree of ions hydration considered in terms of dispersive energy is different at any ionic strength of the solution leading to attract water molecules located in the interface toward the bulk phase of water. This attraction increases as the ratio of cation charge to cation surface increases. According to the results, in low concentrations of CaCl₂ (1000 and 5000 ppm), the asphaltene molecules are ionized by Ca²⁺ cations leading to the migration of asphaltene molecules toward to interface. Asphaltene molecules behave as a surfactant and reduce the interfacial tension. Beyond this concentration, increasing the

salinity, the electrical double layer becomes very thin, leading to the negative surface excess asphaltene concentration, which ultimately increases precipitation. In high concentrations, with a close look at the asphaltene precipitation diagram versus $MgCl_2$ and $CaCl_2$ concentration, understand that the rate of increase in precipitation is higher for $MgCl_2$ than $CaCl_2$ because the ratio of cation charge to cation surface is higher for Mg^{2+} than Ca^{2+} leading to a higher amount of hydration in the aqueous phase. The obtained results indicate that the model is in good agreement with experimental data. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018.

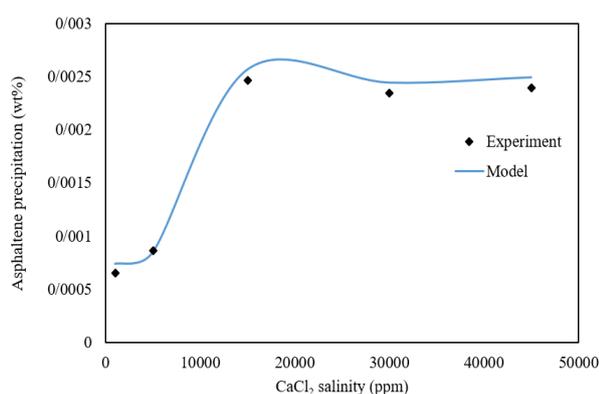


Figure 5. The effect of makeup water with $CaCl_2$ salt on asphaltene precipitation

Figure 6 shows the effect of makeup water in Na_2SO_4 salt on asphaltene precipitation. In order to investigate the effect of salinity on asphaltene precipitation, five brine solutions with Na_2SO_4 were used in different concentrations (1000, 5000, 15000, 30000, 45000 ppm). The result screens out, from the salinity of 1000 ppm to 5000 ppm, asphaltene precipitation decreases due to ionization of asphaltene molecules and their migration toward the interface. Beyond this point, the asphaltene precipitating was reduced by salting-out effect mechanism with a further increase in salinity. Generally, it has been proven 2:1 electrolyte (divalent cation in the presence of monovalent anion) like $MgCl_2$ and $CaCl_2$ have a higher activity coefficient than 1:2 electrolytes (divalent anions in the presence of

monovalent cations) like Na_2SO_4 , which can be related to the higher electron density of divalent cations than divalent anions. Also, the dispersive energy parameter confirms mentioned logic (Mg^{2+} and Ca^{2+} have a higher value than SO_4^{2-}). Consequently, Na_2SO_4 salt has less ability to ionize asphaltene toward the interface. Thus, IFT changes are less than in previous cases. However, in low salinities, the amount of asphaltene precipitation decreases due to the presence of asphaltene in the interface. Also, as mentioned before, according to the salting-out effect, asphaltene precipitating was reduced due to an increase in salinity. The obtained results indicate that the model is in good agreement with experimental data. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018.

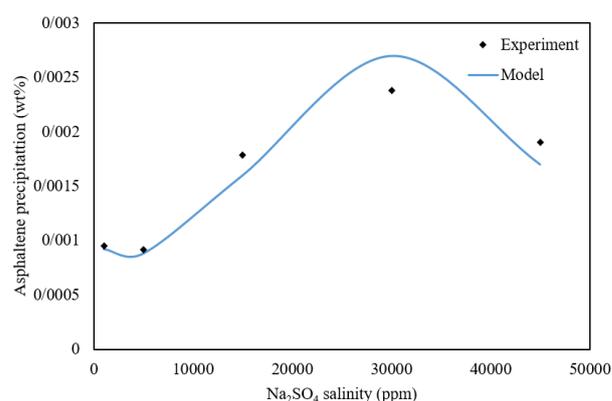


Figure 6. The effect of makeup water with Na_2SO_4 salt on asphaltene precipitation

In the previous three sections, the impact of monovalent and divalent salt on asphaltene precipitation was observed. But in reality, the water that exists in the reservoir is a combination of different salts with different impacts on the precipitation mechanism. To this end, modeling of asphaltene precipitation in the presence of seawater and formation water was conducted.

Figure 7 shows the impact of formation water and Persian Gulf seawater salinity in different dilutions of salts on asphaltene precipitation. The compositions of salts are given in Table 1. Based on the results, in the formation water, due to the presence of different concentrations

of ions, the ionic strength of water increased, leading to a decrease in Deby length. The water molecules return to the aqueous phase to hydrate more ions. Afterward, asphaltene molecules immigrate to the oil phase, which causes precipitation. Also, from formation water to ten times seawater dilution, the asphaltene precipitation decreases due to an increase in Deby length, which causes a regular arrangement of asphaltene in the interface. However, many articles studied the nonmonotonic behavior of interfacial tension versus salinity. But it is necessary to mention that the oil that has been used in this study consist of heptane and toluene and does not contain acidic components such as naphthenic acid. The competition between asphaltene molecules and naphthenic acid makes optimum conditions for IFT. Also, the results obtained from the model were validated by the experimental data in Hosseini, 2018 and Shojaati et al., 2017.

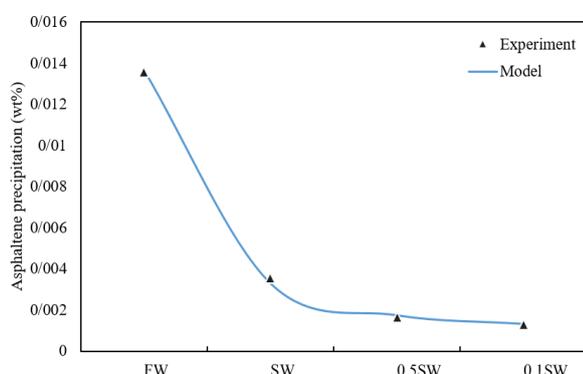


Figure 7. The effect of salinity on asphaltene precipitation in the presence of formation water (FW), Persian Gulf seawater (SW), two times dilution of seawater (0.5SW), and ten times dilution of seawater (0.1SW)

4. Conclusion

In this paper, ePC-SAFT equation of state was applied to many electrolyte systems. The aim of this work was modeling of asphaltene precipitation in the presence of different brines such as makeup water with $MgCl_2$, $CaCl_2$, and Na_2SO_4 , salts, formation water, and seawater with different dilutions (two and ten times diluted), Also, to get a better understanding

from the mechanisms during precipitation, model oil containing heptane-toluene was used. Results of the comparison showed that the proposed model is capable of predicting asphaltene precipitation for $MgCl_2$, $CaCl_2$ and Na_2SO_4 , brine with absolute relative deviations less than 7.68%, 5.44% and 8.39%, respectively. At low concentrations, the salting-in effect mechanism was observed due to the ionization of asphaltene molecules toward the oil-water interface. Also, asphaltene molecules act as a surfactant and bond with water molecules in the interface leading to a decrease in precipitation. Furthermore, in high salinity, the water molecules cannot support the bonding between ion and asphaltene due to the thin electrical double layer. It breaks down and leads to the return of asphaltene molecules to the oil phase. Eventually, the Brownian motion of asphaltene molecules in the oil phase and collisions lead to aggregation and precipitation. Furthermore, due to the presence of different ions, in the formation water and seawater, the ionic strength is high, and the electrical double layer is very thin, causing the further hydration of cations in the aqueous phase.

Nomenclature

a	Reduced Helmholtz free energy
d	Temperature-dependent segment diameter
D	A^0
$g^{hs}(r)$	Diffusion Coefficient
\bar{m}	Radial distribution function for hard-sphere
N	sphere
N_{av}	mean segment number in the system
fL	Total number of molecules in the system
	Avogadro's number
Z_i	Fugacity of precipitating component in the hydrocarbon phase
P	
q_j	Charge number
T	Pressure (pa)
x	Charge of ion j (C)
	Temperature (k)
	Mole fraction

Greek letters

$\frac{\varepsilon}{k_B}$	Pure component segment energy parameter
$\frac{\varepsilon_{ij}}{k_B}$	Pair segment energy parameter
ζ_k	Density function (for $k = 0:3$)
$\eta(=\zeta_3)$	Reduced density
π	Irrational number (3.14159265)
ρ	Molar density ($\frac{mol}{A^3}$)
σ	Temperature independent segment diameter
Ψ	Electron potential
ε	Dielectric constant of a medium, $\varepsilon_r \varepsilon_0 (\frac{C}{Vm})$
\emptyset	Fugacity coefficient

References

- Amanabadi, J., Simjoo, M., & Mousapour, M. (2021). Role of Water Chemistry on the Adsorption Behavior of a Saponin-based Biosurfactant on the Sandstone Surface. Paper presented at the IOR 2021.
- Ameri, A., Esmailzadeh, F., & Mowla, D. (2018). Effect of low-salinity water on asphaltene precipitation. *Journal of Dispersion Science and Technology*, 39(7), 1031-1039.
- Demir, A. B., Bilgesu, H. I., & Hascakir, B. (2016). The effect of clay and salinity on asphaltene stability. Paper presented at the SPE Western Regional Meeting.
- Gross, J., Sadowski, G. (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & Engineering Chemistry Research*, 40(4), 1244-1260.
- Hosseini, A. (2018). Experimental study of asphaltene precipitation and its deposition in Enhanced Oil Recovery by low salinity and smart water. Department of Chemical & Petroleum engineer. Sharif university of Technology, (51823).
- Hosseinfar, P., Jamshidi, S. (2015). Determination of perturbed-chain statistical association fluid theory parameters for pure substances, single carbon number groups, and petroleum fractions using cubic equations of state parameters. *Industrial & Engineering Chemistry Research*, 54(45), 11448-11465.
- Hu, C., Sabio, J. C., Yen, A., Joshi, N., & Hartman, R. L. (2015). Role of water on the precipitation and deposition of asphaltenes in packed-bed microreactors. *Industrial & Engineering Chemistry Research*, 54(16), 4103-4112.
- Kariman Moghaddam, A., & Jamshidi, S. (2022). Performance evaluation and improvement of PC-SAFT equation of state for the asphaltene precipitation modeling during mixing with various fluid types. *Fluid Phase Equilibria*, 554, 113340.
- Lake, L. W., Johns, R., Rossen, B., & Pope, G. A. (2014). *Fundamentals of enhanced oil recovery* (Vol. 1): Society of Petroleum Engineers Richardson, TX.
- Meighani, H. M., Ghotbi, C., & Behbahani, T. J. (2016). A modified thermodynamic modeling of wax precipitation in crude oil based on PC-SAFT model. *Fluid phase equilibria*, 429, 313-324.
- Moeini, F., Hemmati-Sarapardeh, A., Ghazanfari, M.-H., Masihi, M., & Ayatollahi, S. (2014). Toward mechanistic understanding of heavy crude oil/brine interfacial tension: The roles of salinity, temperature, and pressure. *Fluid phase equilibria*, 375, 191-200.
- Naseri, S., Jamshidi, S., & Taghikhani, V. (2020). A new multiphase and dynamic asphaltene deposition tool (MAD-ADEPT) to predict the deposition of asphaltene particles on tubing walls. *Journal of Petroleum Science and Engineering*, 195, 107553.
- Nghiem, L., Hassam, M., Nutakki, R., & George, A. (1993). Efficient modeling of asphaltene precipitation. Paper presented at the SPE Annual Technical Conference and Exhibition.
- Rodriguez, D.L.G. (2008). Modeling of asphaltene precipitation and deposition tendency using the PC-SAFT equation of state: Rice University.

- Sabeti, M., Rahimbakhsh, A., Nikookar, M., Mohammadi, A. H. (2015). Estimation of asphaltene precipitation and equilibrium properties of hydrocarbon fluid phases using the PC-SAFT equation of state. *Journal of Molecular Liquids*, 209, 447-460.
- Shojaati, F., Mousavi, S. H., Riazi, M., Torabi, F., Osat, M. (2017). Investigating the effect of salinity on the behavior of asphaltene precipitation in the presence of emulsified water. *Industrial & Engineering Chemistry Research*, 56(48), 14362-14368.
- Zhang, X., Pedrosa, N., Moorwood, T. (2012). Modeling asphaltene phase behavior: comparison of methods for flow assurance studies. *Energy & fuels*, 26(5), 2611-2620.

بررسی اثر شوری آب بر روی رسوب آسفالتین به کمک معادله‌ی حالت PC-SAFT

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چکیده

رسوب آسفالتین در فرآیندهای تزریق آب کم‌شور در دهه‌ی اخیر توجه بسیاری داشته است. در این مطالعه برای بررسی تاثیر شوری آب بر روی رسوب آسفالتین از معادلات ePC-SAFT استفاده شده است. در این راستا، برای پیشبینی رسوب آسفالتین از یک مدل جامد با نفت مدل شامل هپتان و تلوئن با نسبت ۷۰ به ۳۰ استفاده شده است. با هدف کمینه سازی تابع هدف AAD بین داده‌های آزمایشگاهی و داده‌های بدست آمده از مدل در الگوریتم بهینه‌سازی ازدیاد ذرات از سه پارامتر قابل تنظیم استفاده شد. نقش شیمی آب در رسوب آسفالتین با تغییر ترکیب آب دریا (SW) از طریق تنظیم قدرت یونی با یون‌های دو ظرفیتی مورد بررسی قرار گرفت. برای درک بهتری از نقش یون‌های دو ظرفیتی (SO_4^{2-} و Ca^{2+} ، Mg^{2+})، سه آب نمک ساختگی شامل نمک‌های $CaCl_2$ ، $MgCl_2$ و Na_2SO_4 مورد استفاده قرار گرفت. نتایج نشان می‌دهد که در شوری‌های پایین نمک‌ها (۵۰۰۰ ppm) مولکول‌های آسفالتین به سمت سطح تماس آب/نفت مهاجرت می‌کنند که منجر به کاهش رسوب آسفالتین می‌شود. بعد از این غلظت به سبب شکستن پیوند بین آسفالتین- یون رسوب آسفالتین کاهش پیدا می‌کند. طبق نتایج، میزان رسوب آسفالتین پایین‌تری برای آب دریای رقیق شده (۲ و ۱۰ بار رقیق شده) مشاهده شد که می‌تواند از نظر انبساط لایه‌ی الکتریکی دوگانه تشکیل شده مورد بحث قرار گیرد. نتایج مقایسه بین داده‌های آزمایشگاهی و مدل نشان می‌دهد که مدل پیشنهادی قادر به پیش‌بینی رسوب آسفالتین برای آب نمک‌های $CaCl_2$ ، $MgCl_2$ و Na_2SO_4 با خطای نسبی مطلق کمتر از ۷٫۶۸٪، ۵٫۴۴٪ و ۸٫۳۹٪ است. یافته‌های حاصل از این مطالعه اهمیت طراحی یک فرآیند تزریق آب کم‌شوری کاربردی را روشن می‌سازد.

واژگان کلیدی: مدل جامد، رسوب آسفالتین، معادله حالت ePC-SAFT، تزریق آب کم‌شور