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Surfactant Induced Solubilization and Transfer Resistance in Gas-Water and Gas-Oil Systems

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SUMMARY

Typically, conventional reservoir simulators underestimate the recovery factor of heavy oil reservoirs under solution gas drive. We hypothesize that natural surfactants in oil (e.g. asphaltenes) cause this phenomenon in two ways: 1) by hindering the mass transfer rate of gas molecules through the gas-oil interface and 2) by enhancing the solubility of gas in the heavy oil.

We investigate effect of surfactants on mass transfer rate of gas through gas-water interface and on the solubility of gas in oil. In bulk experiments, we observe that the addition of sodium dodecyl sulfate (SDS) does not influence the gas transfer rate while in the presence of a porous medium the growth of gas bubbles becomes increasingly difficult with increasing SDS concentration, which indicates that the interaction of the grain with fluids is an essential element in bubble growth in porous media. The effect a non-ionic surfactant on the solubility of methane in n-dodecane is also examined. The bubble point pressures of the gas+oil+surfactant system are determined experimentally. It is found that the bubble point pressures of the system decrease with increasing surfactant concentration, i.e., the surfactant enhances the solubility of methane in the oil.

1. Introduction

It has been repeatedly observed that solution gas drive in heavy oil is more efficient for crude oil than for mineral oil of the same viscosity [1]. The two proposed hypotheses to explain this behavior are investigated in this study: 1) the bubble grows differently due to the presence of natural surfactants in crude oil and/or 2) surfactants increase the solubility of gas in oil. Both processes promote the oil recovery by reducing the oil viscosity. Therefore we have carried out experiments in various systems of liquid and surfactant (Fig. 1) to investigate the effect of surfactant on the transfer rate of gas in bulk and porous media and on the solubility of gas in bulk oil.

2. Bulk surfactant solution (CO₂+Water+SDS)

When surfactants are added to a quiescent liquid, the total resistance to the transfer of gas molecules is the sum of the liquid-phase resistance, the gas resistance, and the interfacial resistance that arises from the surfactant molecules adsorbed at the interface (Fig. 1-left). It has been shown that water insoluble surfactants hinder the mass transfer through the gas-liquid interface [2]; however, there is controversy on the effect on soluble surfactants on transfer rate [2].

In this study the quantification of the mass transfer rate is based on the measurement of the gas pressure in a closed volume containing a column of liquid below a gas column. The changes in the gas pressure are assumed to be only due to transfer of gas into the liquid phase.

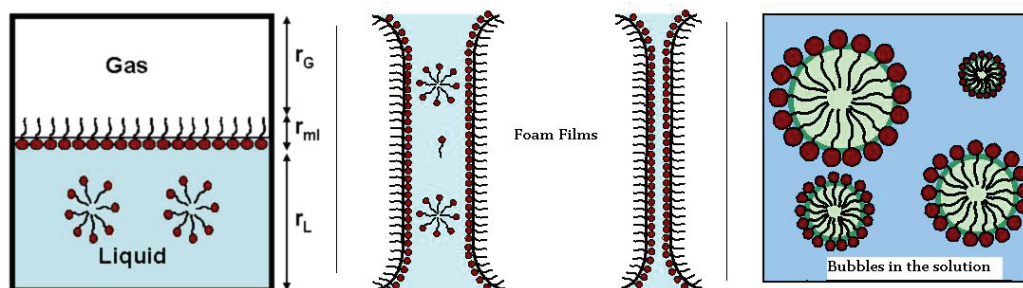


Figure 1 Different studied systems from left: bulk surfactant solution with and without surfactant and electrolyte; foam films stabilized by surfactants; gas bubbles generated in a 2-D micro-model.

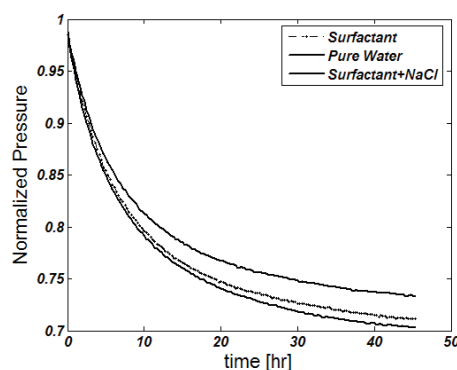


Figure 2 Change in the pressure in column of gas CO₂ in contact with different water solutions: pure water, solution of water+SDS and solution of water+SDS+NaCl versus time.

The details of the experimental set-up and procedure are explained in ref. [3]. The measured gas pressures versus time for both distilled water, surfactant solution, in which the surfactant concentration is above the critical micelle concentration (cmc), and the same solution with added NaCl with concentration of 0.5M are plotted in Fig. 2. It is evident the addition of SDS has no significant effect on the mass transfer rate of CO₂ into water. However, it seems that the addition of salt slightly retards the mass transfer most likely due to the fact that NaCl

decreases the solubility of CO₂ in the solution, and/or NaCl increases the viscosity of water and/or the NaCl makes the layer of adsorbed SDS molecules denser. Our results are consistent with the results of other researchers [2].

3. Foam films stabilized by surfactants

Foam is a dispersion of a gas phase in a continuous liquid phase stabilized by a surfactant. The gas breaks into bubbles that are separated by thin liquid films (lamella)– foam films. The long-term stability of foam is a result of the stability of the thin liquid films. One factor for the long-term stability of foam is the transfer rate of the foam films [2]. There are two equilibrium states of foam films. Common black films with the thickness 10-20 nm are formed when the electrolyte concentration is low. With addition of salt, the double layer electrostatic repulsion in the film is screened and film becomes thinner until Newton black films with the thickness of few nm are formed (Fig. 1 middle). Adsorption of the surfactant molecules on the gas-water interface in foam films offers significant resistance to the gas transfer. According to different theories the permeability of the foam films decreases with increasing surfactant concentration until cmc and remains constant afterwards [2]. This is explained by “mechanistic” theories assuming that a gas molecule can pass through the gaps in the surfactant monolayer (un-occupied sites).

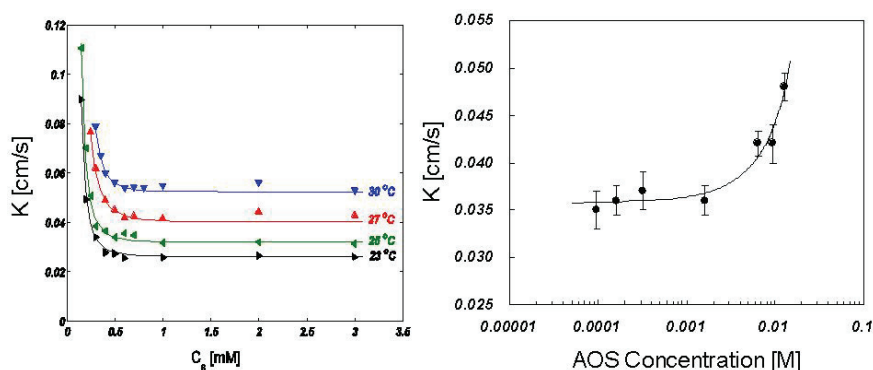


Figure 3 Gas permeability coefficient, K , as a function of surfactant concentration, C_s , at four temperatures for films prepared from SDS+0.5M NaCl solutions (left) and for films prepared from AOS+0.5M NaCl solutions at $T=24^\circ\text{C}$ (right). The lines are theoretical fits (left) and only guides for eyes (right).

We measured the gas permeability coefficient of foam films stabilized by (C₁₄-C₁₆)-alpha olefin sulfonate (AOS) in the presence 0.5M NaCl using “diminishing bubble” method. Below the cmc the formation of bubbles was not possible. The permeability of the film remains constant for concentrations above cmc similar to other experiments with different surfactants and predicted theoretically [2]. However, the permeability increases with increasing surfactant concentration above a certain AOS concentration of 3.0×10^{-3} M. The results are shown in Fig. 3. This observation contradicts the previous theoretical predictions and experimental observations. The reason causing this phenomenon is still unclear and requires further investigations. In general, the micelles can change the properties of either the adsorbed surfactant monolayers or the aqueous layer which separate them in the film. Note that the determined transfer coefficient is orders of magnitude smaller than the coefficient if no surfactant is present.

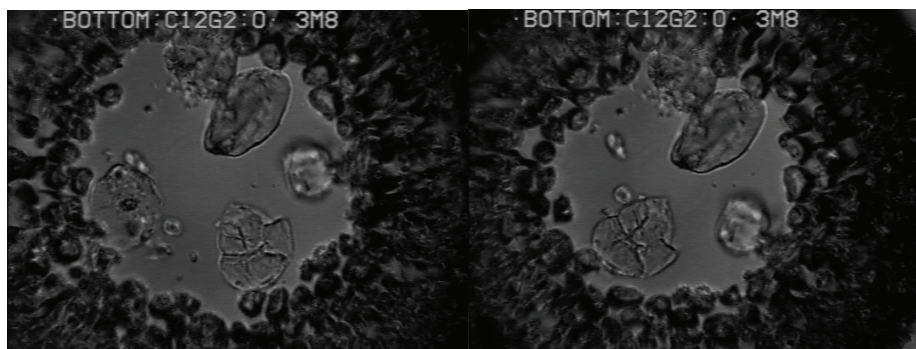


Figure 4 A bubble ($200\mu\text{m}$) stabilized by nano-particles at $t=0$ min (left) and $t=45$ min (right).

4. Foam films stabilized by nano-particles

It has been known for a long time that small particles can stabilize emulsions (Pickering emulsions). Recently, silica particles have been used to stabilize foams [4]. Figure 4 shows a bubble that is stabilized with nano-particles. Once the bubble is stabilized, the accumulation of particles at the water-gas interface reduces the transfer rate significantly and even more than due to the presence of surfactant. In our experiments the bubble stayed stable (sometime without any change in the radius) for hours. Unlike the surfactant-stabilized bubbles, these bubbles did not disappear due to the transfer of gas, but only due to the forces exerted by nano-particles possibly because of their high concentration. It is likely that in heavy oil, the solid particles accumulate at the interface and block the gas transfer through the interface.

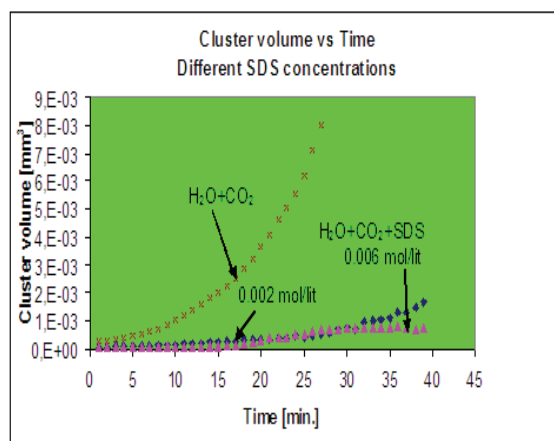


Figure 5 Comparison of gas bubble behavior in fluids with and without SDS. The bubble grows slowly in systems with SDS.

5. Gas bubbles in porous media (CO_2 +Water+SDS)

We have carried out visual experiments in glass micro-models to investigate the mechanisms of bubble growth in porous medium. Our model system uses CO_2 and water as flowing fluids. A piston pump was used to extract the fluids from the model in order to create the necessary pressure decrease inside the relevant area. The decrease of the pressure in the model mainly resulted in bubble expansion along the grain surface. The model shows that the contact angle of the bubble with the grain is different than 0° , i.e. the system is partially water wet. Further it is observed that the curvature of the growing bubble is not constant, indicating surface heterogeneity of the model. The same experiments were also carried out for systems containing surfactant. Figure 5 shows the bubble growth for solutions with and without surfactant. Note that the cmc of SDS at our experimental condition was measure to be 6 mM. It is obvious from Fig. 5 that unlike the bulk experiments addition of the SDS influences the transfer rate of the gas. Moreover, the results show a slower growth of the bubbles along the grain surface. The conclusion is that the interaction of fluids with the pore body plays an essential part in the growth of a bubble.

6. Effect of surfactant on solubility of gas in oil.

Using the ternary system $C_1+C_{12}+C_7E_5$, a series of experiments were performed to understand the effect of natural surfactant on the gas solubility in heavy oil in a variety of test conditions, temperature: 278.15 - 368.15 K and surfactant concentration: 0 – 13.8 weight percent. The gas solubility increases by increasing the concentration of the surfactant (Fig. 6). The bubble-point pressure for 0 weight percent surfactant at 298.15 K is 7.84 MPa while the bubble-point pressure for 13.8 weight percent surfactant, under similar conditions, is 7.49 MPa. The changes in bubble point pressure versus surfactant concentration between the mentioned range, show a similar trend: generally, surfactant enhances the solubility of gas in heavy oil.

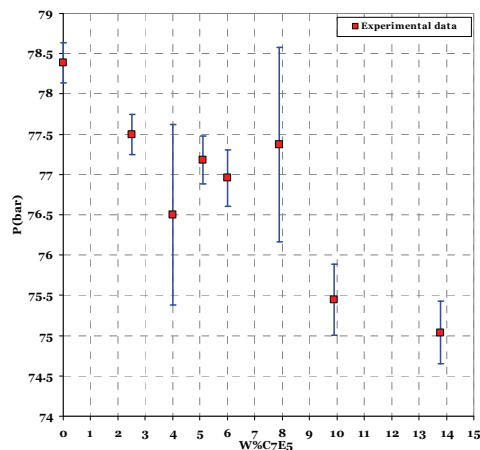


Figure 6 P/W% (weight percent) C_7E_5 - diagram at a temperature of 298.15 K of the system $CH_4+C_{12}+C_7E_5$ of all the experiments.

7. Conclusions

1. The addition of SDS has no measurable effect on the mass transfer rate of gas through the gas/bulk liquid surface but in the case of foam films it plays an important role.
2. In liquid films stabilized by surfactants, thermodynamic state of the film plays an important role in the transfer of the gas.
3. If solid particles are adsorbed at the interface, the mass transfer rate is significantly reduced.
4. The addition of SDS affects the bubble growth in the micro-model (virtual porous media).
5. The interaction of the grain with fluids is an essential element in bubble growth in porous media
6. Addition of a non-ionic surfactant enhances the solubility of gas in oil.
7. The higher than expected recovery in heavy oil reservoir can be explained by the fact that the natural surfactants/particles (asphaltenes) increase the gas content of the oil by resisting the gas transfer or enhancing the gas solubility.

8. References

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2. R. Farajzadeh, R. Krastev, P.L.J. Zitha, Adv. Colloid. Interf. Sci., 137 (1) (2008).
3. Farajzadeh, Barati, Delil, Bruining, Zitha, Pet. Sci. Technol., 25(12) (2007).
4. B. P. Binks and T. S. Horozov, Angew. Chem., Int. Ed., 2005, 44, 3722.