Gas Permeability of Foam Films Stabilized by an α-Olefin Sulfonate Surfactant

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The gas permeability of equilibrium foam films stabilized with an α-olefin sulfonate surfactant was measured. The permeability coefficient, \( K \) (cm/s), was obtained as a function of the electrolyte (NaCl) concentration, surfactant concentration, and temperature. The addition of salt to the film-forming solution leads to a decrease of the film thickness, which was complemented by an increase of \( K \) up to a certain value. Above that critical salt concentration, the gas permeability decreases even though the film thickness also decreases. We explain this effect as a result of interplay of the film thickness and the adsorption monolayer permeability for the permeability of the whole film, i.e., the thermodynamic state of the film. The classical theories that explain the process were applied. The gas permeability of the film showed an unexpected increase at surfactant concentrations well above the critical micelle concentration. The origin of this effect remains unclear and requires further studies to be clarified. The experiments at different temperatures allowed the energy barrier of the permeability process to be estimated.

1. Introduction

Foam is a dispersion of gas in a continuous liquid phase, stabilized by surfactants and/or nanoparticles.\(^{1,2}\) It is a complex fluid with numerous applications, including control of flow through pipes,\(^3\) cleanup of polluted soils,\(^4\) and the extraction of oil and gas from deep earth formations.\(^{5,6}\) In strongly water-wet porous media, the continuous liquid phase coats the porous rock surfaces, whereas gas is broken into bubbles by thin liquid films or lamellae.\(^{6,7}\) Sufficiently large pressure gradients are required to maintain lamellae moving in porous media: if the pressure gradient is not high enough, a fraction of the foam may be trapped in the pores and gas flow is blocked.\(^{8-9}\)

It is important to know the stability of the foams for different applications, i.e., the stability of single liquid lamella—foam films, which separate the gas bubbles. Many studies have been performed to investigate the foam stability over short and long times.\(^{2,10}\) The short-term stability is governed by the dynamics of foam formation and drainage of the films, while the long-term stability depends on the properties of the equilibrium foam films. Larger bubbles are formed at the expense of the smaller ones with time. Rupture of the foam films (coalescence) is one of the reasons for this process. On the other hand, the interbubble gas diffusion (Ostwald ripening) from smaller to larger bubbles changes the dispersity of the foam, and the bubbles coarsen.\(^11\)

When gas and surfactant solution are pushed through a porous pack, it is observed that a fraction of the foam varying between 0.60 and 0.95 is trapped in the porous system.\(^{12,13}\) Gas transport through the system is dominated by diffusion through the foam films.\(^{8,9,12}\) These processes demonstrate the importance of detailed knowledge of the foam properties for precise tuning of different applications.

Despite a host of investigations of foam films, measurements of the gas permeability are relatively scarce in the literature. The first measurements of the gas permeability of foam films were performed in the middle of the 20th century.\(^{14,15}\) Detailed investigations of the basic relations between the gas permeability of the foam films and the thermodynamic parameters of the system have been performed over the past 20 years. The influences of the film thickness, the surfactant adsorption density, the surfactant chain length, the surfactant hydrophilic group, and the temperature on the gas permeability of single foam films have been reported.\(^{16-21}\) Detailed theoretical and experimental studies have reported the permeability of gas through a series of foam films. Such studies are of high importance for the stability of foams in porous media.\(^{8,9,22}\) It has also been shown that measurements of gas permeability of the foam films deliver valuable information.

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Figure 1. Schematic view of two equilibrium states of a foam film. Left: A common black film has a central aqueous layer, which is sandwiched between two monolayers of usually adsorbed surfactant. Right: A Newton black film has a bilayer structure where two surfactant monolayers are close to each other separated only by a few layers of hydration water.

The stability of these films is governed by the interplay of the surface forces are operative.23 A comprehensive review of the works devoted to the gas permeability of foam films can be found in the recently published ref 24.

There are two equilibrium states of foam films that are defined by the thermodynamic conditions (see Figure 1). Common films are usually formed when the salt concentration in the film-forming solution is low. These films have a sandwich-like structure and consist of two monolayers of adsorbed surfactant molecules, which stabilize the film and are separated by an aqueous layer. The film thickness decreases when the salt concentration in the film-forming solution increases. The reflectivity from the film decreases so much that at a certain film thickness (respectively, salt concentration) the films look black in the reflected light. These films are called common black films (CBFs). Their stability, according to the classical DLVO approach,25 is due to the interplay between the repulsive electrostatic (\(\Pi_{EL}\)) and the attractive van der Waals (\(\Pi_{vW}\)) components of the disjoining pressure, \(\Pi\). \(\Pi_{EL}\) decreases with the further addition of salt to the film-forming solution until it is fully suppressed. Very thin Newton black films (NBFs) are formed at that point. These films have bilayer structures; i.e., the two surfactant monolayers are close to each other and are separated only by a few layers of hydration water. The stability of these films is governed by the interplay of the short-range interaction forces. The application of DLVO theory to such thin foam films is not possible because this theory does not take into account spatial and/or surfactant density fluctuations.26,27

A measure of the gas permeability of a foam film is the permeability coefficient, \(K\) (cm/s),\(^{14,15,24}\) defined by

\[
\frac{dN}{dt} = -K_S \Delta C_g
\]  

Here, \(N\) is the number of moles of gas that permeate through the film, \(t\) is time, \(S\) is the area of the film, and \(\Delta C_g\) is the concentration difference of the gas on both sides of the film. Considering the film structure, an expression for the permeability was proposed by Princen et al.:\(^{15}\)

\[
K = \frac{D_w H}{h_2 + 2D_w/k_{ml}} \tag{2}
\]

Here, \(D_w\) is the diffusion coefficient of the gas in the aqueous core of the film, \(H\) is the Ostwald coefficient of the solubility of the gas in the aqueous solution, \(k_{ml}\) is the permeability coefficient of a single surfactant monolayer, and \(h_2\) is the film aqueous core thickness (see Figure 2E). For thick films, \(h_2 \gg 2D_w/k_{ml}\) and the permeability is characterized by the transport properties of the gas through the aqueous core. The film permeability increases with decreasing film thickness, whereas the thickness of the monolayers remains constant. If \(h_2 < 2D_w/k_{ml}\), the gas permeability is governed by the permeability of the adsorbed monolayers by \(k_{ml}\). Different mechanisms for the permeation through surfactant monolayers and their advantages in explaining foam film permeability are proposed in the literature.24,29,30

Foam stability in porous media depends on several factors. The choice of surfactant with respect to the injected gas and type of the porous medium is an important key in the success of a foam injection project. In general, a candidate surfactant must have a low adsorption on the rock and should produce an oil-tolerant foam. \(\alpha\)-Olefin sulfonate (AOS) surfactants have shown relatively lower adsorption on sandstones,\(^{31}\) making them good candidates for foam applications. In our previous paper\(^{32}\) we summarize the results on studies of basic properties of aqueous solutions of AOS in the presence or absence of salt (NaCl) and the foam films prepared from those solutions. The film thickness and contact angle, which is formed at the transition between the film and the bulk solution (Figure 2E), were measured as a function of the NaCl and surfactant concentrations. The concentrations

\[K_{ads}H\]

\(h_2 + 2D_w/k_{ml}\)

\(K\)

(2)

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\(^{(31)}\) Du, D. X. Personal communication, 2007.

at which the NBFs are formed were determined. The measurements of the contact angle were used to calculate the free energy of film formation. In the present paper we summarize the results on the gas permeability of foam films stabilized by AOS (C14–C16) as a function of the surfactant concentration, NaCl concentration, and temperature.

2. Experimental Section

2.1. Measurements of the Gas Permeability. The “diminishing bubble” method described earlier in detail \(^{16,17,33,34}\) was used to measure the film permeability. A small floating bubble with radius \(R = 100–600 \mu m\) is formed on the surface of the investigated solution. The bubble is observed from the bottom by using a reflected light microscope. On the top of the bubble a foam film is formed, and its radius, \(r\), is observed simultaneously with a second microscope. The gas pressure in the bubble is higher because of the capillary pressure, which varies from 700 to 1000 Pa during the experiment. This pressure gradient causes permeation of gas through the thin foam film, and \(r\) decreases with time. A sketch of the experimental procedure is presented in Figure 2.

The film permeability coefficient is calculated from the experimentally obtained time-dependent \(R(t)\) and \(r(t)\) using the following expression:\(^{33}\)

\[
K = \left(\frac{P_d}{2\alpha}\right)(R_0^4 - R^4) + \frac{8}{9}(R_0^3 - R_r^3)\int_0^t r^2 \, dt^{-1} \tag{3}
\]

Here, \(R_0\) and \(R_r\) are respectively the values of \(R\) at the beginning \((t = 0)\) and at the end \((t = t)\) of the experiment. The denominator of eq 3 is solved numerically from the experimental \(r(t)\) dependence. An example of such dependence is shown in Figure 3. The experimental resolution of the technique is ±0.002 cm/s. The experiments were performed at a constant temperature controlled with a precision of ±0.1 °C. All presented \(K\) values are arithmetical mean values from more than 10 single experiments. The standard deviations of the mean values are presented as error bars in the figures. The permeating gas was always air.

2.2. Materials. The surfactant used was AOS (C\(_{14}\)–C\(_{16}\)) (Stepan Co.). This surfactant is anionic and was used as received. The general structure of olefin surfactants is \(R-\text{SO}_3^\text{\text{Na}}^+\), with a molar mass of

\(\approx 315\) g/mol. All solutions were exposed to sonication (SONOREX RK52, Bandelin, Berlin, Germany) before the experiments.

Sodium chloride (NaCl) GR grade (Merck, Darmstadt, Germany) was roasted at 600 °C for 5 h to remove surface-active contaminations. All solutions were prepared with water with Milli-Q quality (Elga Labwater, Germany, purification setup). The specific resistance of the water was better than 18.2 MΩ cm, the pH was 5.5, and the total organic carbon (TOC) value was less than 10 ppb.

3. Results and Discussion

3.1. Effect of the NaCl Concentration. The film permeability is strongly influenced by the film thickness (see eq 2). The film thickness can be precisely tuned by changing the concentration of the electrolyte in the film-forming solution according to the predictions of the classical DLVO theory. The gas permeability of the films was measured in a large range of electrolyte (NaCl) concentrations. Two AOS concentrations were used to stabilize the films, \(3.0 \times 10^{-4}\) M and \(9.5 \times 10^{-3}\) M (for the solutions in the presence of \(0.50\) M NaCl) (see Table 1).

<table>
<thead>
<tr>
<th>NaCl concn (M)</th>
<th>(\text{cmc} \times 10^{-4}) M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>1.3</td>
</tr>
<tr>
<td>0.20</td>
<td>2.2</td>
</tr>
<tr>
<td>0.05</td>
<td>5.7</td>
</tr>
<tr>
<td>0.00</td>
<td>31.7</td>
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\(M_w\) is the molar mass of the surfactant. The results show a sharp increase of the film permeability with the increase of the salt concentration up to \(1.3 \times 10^{-4}\) M (for the salt-free solutions). The cmc varies in this range of NaCl concentrations between \(3.17 \times 10^{-3}\) M (for the salt-free solutions) and \(1.3 \times 10^{-4}\) M (for the solutions in the presence of \(0.50\) M NaCl) (see Table 1).\(^{32}\)

The NaCl concentration was varied from 0 M (salt-free solution) to \(0.50\) M. Our previous study\(^{32}\) shows that the film thickness varies from ca. 50 nm (CBF) to 5 nm (NBF) in this range of electrolyte and surfactant concentrations. The dependence of the film permeability on the NaCl concentration is presented in Figure 4. The results show a sharp increase of the film permeability \(K\) with the increase of the salt concentration up to a certain point, followed by a decrease in \(K\). This result is similar to that observed for films stabilized with sodium dodecyl sulfate (SDS). The film thickness was varied in these earlier experiments.
either by changing the NaCl concentration \( \times 10^{-3} \) M (0.3 wt %). The increase of the NaCl concentration in the film-forming solution has a dual effect. First, it suppresses the repulsive electrostatic double-layer component of the disjoining pressure in the film, and the film thickness decreases. \(^{2,32}\) The film permeability has to increase with decreasing film thickness according to eq 2. The dependence of the film permeability on the film thickness is shown in Figure 5. The figure shows that indeed the film permeability slightly increases when the film thickness decreases to a thickness of 15 nm, where CBFs start to form. In this range of thicknesses, the gas permeability of the films is governed by the permeability of the central aqueous layer of the film. After that point the gas permeability strongly decreases, most probably because the permeability of the surfactant adsorbed monolayers controls the permeability rate of the whole film. Second, the salt concentration influences the adsorption of the surfactant (in the case of ionic surfactants) due to the screening of the electrostatic repulsion between the adsorbed ions. Generally, the surfactant adsorption has to increase when the salt concentration increases. Higher adsorption at the film surfaces has to decrease the film permeability, as predicted from different theories of the permeability of gas molecules through layers of surfactant molecules. \(^{24}\)

However, our earlier paper \(^{32}\) shows that, at a given mean ionic activity, the surfactant adsorption is independent of the electrolyte concentration, i.e., the ionic atmosphere contribution to the surface pressure is negligible. Data about the surfactant adsorption on the surface of a bulk solution of AOS at different NaCl concentrations are presented in ref 32. As pointed out, for solutions of a single ionic surfactant with inorganic electrolyte the measurements of the surface tension vs the mean ionic activity \( c^* \) at different electrolyte concentrations coincide on a single curve. The mean ionic activity accounts for the concentration of all ions (surfactant and electrolyte) in the solution. It is defined as \( c^* = \gamma_{4}(c_{AOS}(c_{AOS} + c_{NaCl}))^{1/2} \), with \( \gamma_{4} \) being the mean ionic activity coefficient and \( c_{AOS} \) and \( c_{NaCl} \) the surfactant and salt concentrations. This was confirmed in ref 32 for AOS solutions and in ref 36 for SDS solutions.

The adsorption of AOS, \( \Gamma_s \), continuously increases with the addition of either salt or surfactant by changing \( c^* \). \(^{35}\) However, precisely in this range of surfactant and NaCl concentrations the film permeability increases first and then sharply decreases. One has to remember that the concentration of surfactant, respectively the adsorption, changes only up to the point of the cmc, which changes with the addition of salt. The higher surfactant concentration we used \( (9.5 \times 10^{-3} \) M (0.3 wt %)) is always above the cmc of AOS, independent of the salt concentration of the solution. The lower surfactant concentration \( (3.0 \times 10^{-4} \) M (0.1 wt %)) is above the cmc of the higher salt concentration of 0.50 M NaCl and below the cmc of the lower salt concentration of 0.05 M NaCl. These data allowed the surfactant adsorption at the conditions of our experiments to be estimated using the surface tension and adsorption data presented in ref 32. \( c^* \) varies between \( 4.3 \times 10^{-3} \) and \( 1.5 \times 10^{-2} \) M, and respectively, the adsorption varies by less than 10% from \( 4.8 \times 10^{-6} \) to \( 5.2 \times 10^{-6} \) mol/m² (see Figure 5 in ref 32). This minor increase in the surfactant adsorption cannot explain the 2-fold decrease of the gas permeability of the films at higher salt concentrations. This could also imply that the change in the surfactant adsorption with the increase of the surfactant concentration at the film surfaces is different from that at the surface of a bulk solution of AOS.

An alternative explanation of the sharp decrease of the gas permeability of the films is given in ref 23. It has been shown that the gas permeability is influenced by increasing the adsorption of the surfactant at the film surfaces when the free energy of film formation increases. This energy is negative. Its absolute value increases when the salt concentration increases, and respectively, the thickness of the equilibrium films decreases. \(^{32}\) This quantitatively explains the remarkable finding that the film permeability decreases with decreasing thickness. The monolayer permeability, which governs the permeability through very thin films, depends on the area in the monolayers accessible for gas molecules to pass through. This area can be described by the number of unoccupied sites in the adsorption layer. At the transition to the Newton black film, this number—and therefore the accessible area—decreases significantly due to the effect of the film interaction on the state of the monolayers. The proposed mechanism describes the variation of film permeability at the CBF to NBF transition. Indeed the transition in the gas permeability occurs at salt concentrations of ca. 0.05 M, which is lower than what was estimated to be defined as critical for the transition from CBF to NBF \( \left( C_{NaCl} = 0.35\text{ to }0.40 \text{ M} \right) \). A similar effect was also observed in ref 35 and might be explained by the assumption that the strong attractive interaction between the film surface can change the surfactant adsorption at the film surfaces even before the transition from CBF to NBF, defined as a change in the film thickness, occurs.

### 3.2. Effect of the Surfactant Concentration

The film permeability coefficients were determined experimentally for different AOS concentrations at a constant NaCl concentration \( C_{NaCl} = 0.50 \) M. The dependence of the foam film permeability on the AOS concentration is presented in Figure 6. The temperature remained constant during the experiments \( (T = 24^\circ\text{C}) \). Newton black films with an equilibrium thickness of ca. 5 nm are formed at this NaCl concentration. \(^{32}\) The surfactant concentration was changed from \( 9.5 \times 10^{-5} \) to \( 1.3 \times 10^{-2} \) M. The entire studied range of concentrations was above the cmc, which is \( 1.3 \times 10^{-4} \) M at the conditions of the experiment, since formation of stable films was not possible below the cmc. This is most likely due to the fact that the adsorption surfactant monolayers are not saturated below the cmc. \(^{27}\) Another reason might be existence of impurities in the surfactant solution, which

was confirmed by formation of a minimum in the surface tension vs surfactant concentration curves.\(^{32}\)

The permeability of the film remains constant for concentrations above the cmc, similar to other experiments with different surfactants,\(^{16,17}\) as predicted theoretically.\(^{24}\) However, above a certain AOS concentration of \(3.0 \times 10^{-3}\) M the permeability increases with increasing surfactant concentration. This observation contradicts the previous theoretical predictions and experimental observations. The mechanism of this effect is not known. One can speculate and propose different mechanisms to explain the experimental observation. In general, the micelles can change the properties of the adsorbed surfactant monolayers, the aqueous layers, or the whole films. The solubility of air in the bulk solution increases when the surfactant concentration increases, similar to the observation reported for SDS solutions.\(^{37,38}\) Therefore, some part of the gas diffuses into the bulk to satisfy the enhanced solubility. This explanation is, however, unlikely because the solutions were made at least one day prior to the experiments and left at least for 24 h for gas saturation.

The films which we studied are very thin NBFs. In general, they have to only consist of two surfactant layers separated by a few layers of hydration water. However, at high surfactant concentrations when the concentration of micelles in the film-forming solution is high, some micelles could be captured in the film during the thinning process. Similar behavior has already been observed and is reported in the literature.\(^{39}\) The existence of such captured micelles can change the properties of the films and their permeability. We have no direct observation of such effects in our films because in our earlier paper\(^ {32}\) the film thickness was measured at much lower surfactant concentrations. Even though, we believe that presence of micelles in the NBF at very high surfactant concentration might be possible and can explain the increased permeability.

The nucleation theory of formation of holes in the NBF\(^ {2,16,24}\) postulates that gas permeability occurs through small holes, which are formed from other surfactant solutions,\(^ {17-20}\) some of them with consist of molecular vacancies in the film.\(^ {24}\) The formation of these holes depends on the work used for their formation. One of the important contributions to this work is the linear energy at the line that separates the hole from the nondefect film. If this line binds to a micelle attached to the film surface, the linear energy might be decreased, thus increasing the probability of formation of a hole in the film. This will increase the rate of the permeability through the film.\(^ {29}\)

Another hypothesis could be that the micelles captured in the film enhance its permeability, similar to mechanisms presented in several recent studies which have reported that the presence of micelles enhances the mass transfer between emulsion droplets. According to the hypothesis, micelles facilitate mass transfer by acting as carriers of oil molecules.\(^ {40,41}\) Therefore, it is possible that micelles act as carriers of gas molecules, thus increasing the permeability of foam films.

### 3.3. Effect of the Temperature

To investigate the effect of the temperature, the gas permeability coefficient of AOS films was measured in the temperature range from 22 to 32 °C at a constant AOS concentration of \(c_{\text{AOS}} = 3.2 \times 10^{-4}\) M and a constant NaCl concentration of \(c_{\text{NaCl}} = 0.50\) M. Throughout the whole range of temperatures, NBFs were formed. The results are presented in Figure 7.

The foam film permeability increases with increasing temperature. According to the gas kinetics theory, with increasing temperature the average energy of the gas molecules and the collision frequency of the gas molecules with the surfactant molecules at the interface increase. Therefore, the number of gas molecules that can overcome the energy barrier and pass through the film increases. The energy barrier theory\(^ {25}\) relates the film permeability to the temperature:

\[
K = \alpha \exp(-\Delta E/RT)
\]

where \(\Delta E\) is the free energy that the gas molecules must overcome to permeate through the film and \(\alpha\) is a constant that depends on the type of gas. Using the Arrhenius coordinate, \(\Delta E\) was calculated to be \(\Delta E = 35.5\) kJ/mol in the case of the NBF stabilized with AOS. This energy is different from that estimated for NBFs formed from other surfactant solutions,\(^ {17-20}\) some of them with

\[\text{(38) Matheson, I. B. C.; King, A. D., Jr. J. Colloid Interface Sci. 1978, 66, 464.}\]
\[\text{(39) Bergeron, V. Langmuir 1996, 12, 5751.}\]
4. Conclusions

We studied the gas permeability of foam films stabilized with AOS (C_{14}-C_{16}) to air. According to the film permeability model of Princen,\textsuperscript{15} the permeation process depends on the permeability and thickness of the film aqueous core and the permeability of the surfactant adsorption layers that form the film. In varying the film thickness by changing the electrostatic double-layer repulsion in the film, we changed the contribution of these different components to the whole permeability of the films. We observed that the gas permeability of the films increases when the film thickness decreases until a certain value. The film permeability coefficient sharply decreases after that critical value. We conclude that after that critical point the film permeability is governed by the monolayer permeability, respectively by the adsorption density of the surfactant monolayers. The decrease of $K$ can be explained by decreased permeability of the monolayers. This might be a result of increased adsorption upon an increase of the electrolyte concentration. On the other hand, increased adsorption could be a result of the stronger attractive interactions between the film surfaces at small film thickness.

The film permeability shows an unexpected increase at high surfactant concentrations well above the cmc. We hypothesize that this is a result of faster gas transport via the films facilitated by micelles which can be captured in the very thin NBF during the process of film thinning. Experiments at different temperatures allowed the energy of the permeability process to be estimated using the simple energy barrier theory.\textsuperscript{14,19,24} Comparison with other similar systems shows that the pre-exponential factor in the theoretical description also plays an important role in the whole gas permeability.

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