

## Foam film permeability: Theory and experiment

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### Abstract

The mass transfer of gas through foam films is a prototype of various industrial and biological processes. The aim of this paper is to give a perspective and critical overview of studies carried out to date on the mass transfer of gas through foam films. Contemporary experimental data are summarized, and a comprehensive overview of the theoretical models used to explain the observed effects is given. A detailed description of the processes that occur when a gas molecule passes through each layer that forms a foam film is shown. The permeability of the film-building surfactant monolayers plays an important role for the whole permeability process. It can be successfully described by the models used to explain the permeability of surfactant monolayers on aqueous sub-phase. For this reason, the present paper briefly discusses the surfactant-induced resistance to mass transfer of gases through gas–liquid interface. One part of the paper discusses the experimental and theoretical aspects of the foam film permeability in a train of foam films in a matrix or a cylinder. This special case is important to explain the gas transfer in porous media or in foams. Finally, this paper will highlight the gaps and challenges and sketch possible directions for future research.

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**Keywords:** Foam film; Gas permeability; Monolayer; Surfactant; Gas–liquid interface

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## 1. Introduction

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 gas permeability of the foam films [1–3]. The measurement of the gas permeability of the foam films gives valuable information about the stability and lifetime of the foams. The permeation of gas through foam films is a matter of interest in many physical, chemical, and biological studies, as well as in many technological applications. Examples include gas separation processes [4–8], chemical sensing [9–12], medical research-(breathing) [13–15], stabilization of ultrasonic contrast agents for medical diagnostics [16,17], cosmetics (stabilization of foams against coarseness) [18], and petroleum engineering, where, for instance, gas bubbles arise as the pressure decreases below the bubble point during the production of (highly) viscous and dense oils, and inter-bubble diffusion gives rise to the coalescence of the gas bubbles, which is undesirable [19,20], etc.

Foam films are suitable tools for studying the interactions between interfaces [21]. Detailed knowledge about their structures is needed in such studies. Part of this information can be obtained from gas permeability experiments with foam or single foam films. Even more, as it was shown in Ref. [22], the interaction between the adsorbed monolayers forming the foam film changes the film structure and its gas permeability accordingly.

The structure and the properties of the foam films have been intensively studied, and they are well documented in the literature. The main results are summarized in books and review articles [e.g. 23–29]. There are two equilibrium states of foam films that are defined by the thermodynamic conditions. 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 stabilizing the film 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 at certain film thickness (respectively, salt concentration) that the films look black in reflected light. These films are called Common Black Films (CBF). The interactions in these films are described by the classical DLVO approach. Their stability is due to the interplay between the repulsive electrostatic ( $\Pi_{EL}$ ) and the attractive van der Waals ( $\Pi_{VW}$ ) component of the disjoining pressure,  $\Pi$ . The  $\Pi_{EL}$  decreases with the further addition of salt to the film-forming solution until it is fully suppressed. Very thin Newton Black Films (NBF) are formed at that point. These films have bilayer structures: the two surfactant monolayers are

close to each other, separated only by 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 limited because this theory does not take into account both spatial and or surfactant density fluctuations [29,30]. The two states of foam films are shown schematically in Fig. 1. In both cases the transition from thicker common film to the thinner black films (either CBF or NBF) occurs through the formation of black spots in the thicker film.

The transfer of gases through a foam film depends on the gas permeability of the two surfactant monolayers, which build the film and the central aqueous core (Fig. 2). This paper is focused on detailed description of the processes that occur when a gas molecule passes through each of the foam film-forming layers. It summarizes up to date experimental data in the area and gives a comprehensive overview of the theoretical models used to explain the observed effects. The permeability of the film-forming surfactant monolayers plays an important role for the whole permeability process. It can be successfully described by the models used to explain the permeability of surfactant monolayers on an aqueous sub-phase. For this reason, the paper briefly discusses the surfactant-induced resistance to the mass transfer of gases through gas–liquid interface in Section 2 and reviews the theories proposed in the literature to interpret the experimental observations. Sections 3 and 4 present the main topic of the review, i.e., the permeability of foam films stabilized by surfactants. Various mechanisms and models, which have been

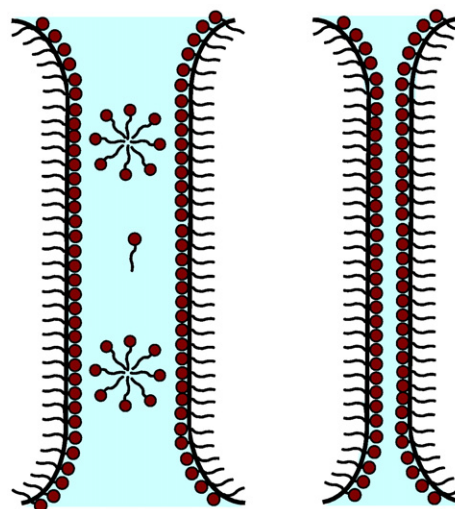


Fig. 1. Schematic of two equilibrium states of the foam films: A common black film (left) has a central aqueous layer which is sandwiched between two surfactant monolayers. A Newton black film (right) has a bilayer structure where two surfactant monolayers are close to each other separated only by few layers of hydration water.

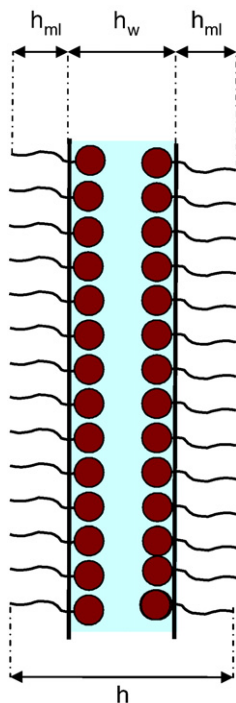


Fig. 2. A single foam film consists of an aqueous core with thickness  $h_w$  sandwiched between two adsorbed monolayers of surfactant with the thickness of  $h_{ml}$ . In this model the Plateau borders are neglected. The liquid layer and the surfactant monolayers are assumed to be homogenous.

proposed in the literature to treat the experimental data, are critically reviewed. Furthermore, the effect of different parameters on the permeability of foam films is discussed in detail. A special case of interest is a train of foam films in a matrix or a cylinder (Fig. 3). This case is very important for explaining the gas transfer in porous media or in foams. One part of the paper discusses the experimental and theoretical aspects of foam film permeability in this special case.

## 2. Gas permeability of single surfactant monolayers

The first studies on gas permeation through foam films were reported in 1924 by Hedestrand [31]. The author undertook repeated efforts to determine the influence of surfactant monolayers on the evaporation rate of water. He found no measurable effect; however, his technique was subject to criticism from Adam [32] and Rideal [33]. These authors pointed out that

the stagnant air over the water surface might have had a greater effect on the water evaporation than the spread monolayer. In 1925, Rideal [33] modified Hedestrand's technique [31] and demonstrated for the first time that the presence of a monolayer at the water–air interface retards the water evaporation, although the mechanism of the retardation was not completely clear. Subsequently, in 1927 Langmuir and Langmuir [34] reported the effect of an insoluble monolayer on the evaporation of ethyl ether from saturated solutions in water (5.5%). They observed that the rate of evaporation of ether from the solution in the presence of an insoluble oleic acid monolayer was 10 times lower than the case when no monolayer was present. Moreover, Langmuir and Langmuir [34] proposed for first time the energy barrier theory for the permeation of the water molecules through the layer covered by fatty acids and alcohols. The theory was later modified by Langmuir and Schaefer [35] and has been extensively used since.

The effect of surfactant monolayers on the water evaporation rate has been studied extensively [for example, see Refs. 36–51]. Most of the concepts, which describe the effect of surfactant monolayers on the water evaporation rate, remain the same for the mass transfer rate of other gases into a surfactant solution [52–68]. The common view is that when a surfactant is spread onto a quiescent liquid, the total resistance to the passage of the gas molecules is a sum of a series of three resistances: liquid phase resistance, gas phase resistance, and interfacial resistance, which arises from the adsorption of surfactant molecules to the interface (Fig. 4). The retardation of the mass transfer of gas through a gas–liquid interface by addition of surfactant to the liquid phase is often specified as “*monolayer resistance*” or its reciprocal “*monolayer permeability*”. The magnitude of the monolayer permeability is related to the molecular structure of the surfactant: the polarity of the hydrophilic group [53,62], the molecular weight of the hydrophilic group and the hydrophobic chain length (number of the  $\text{CH}_2$  group) [47,54], temperature [54–56], the monolayer surface pressure [57], and the size of the permeant (gas molecule) [58].

Many experiments support the view that insoluble surfactants impede the mass transfer of gas molecules through the gas–liquid interfaces. Nevertheless, there is a difference between the probable effects of soluble and insoluble surfactants. Relatively little work has been done on the effects of the soluble surfactants on the mass transfer of gas molecules. Some papers even suggest that the soluble surfactants have no measurable resistance on the mass transfer of gas across gas–liquid interfaces [53,69–73].

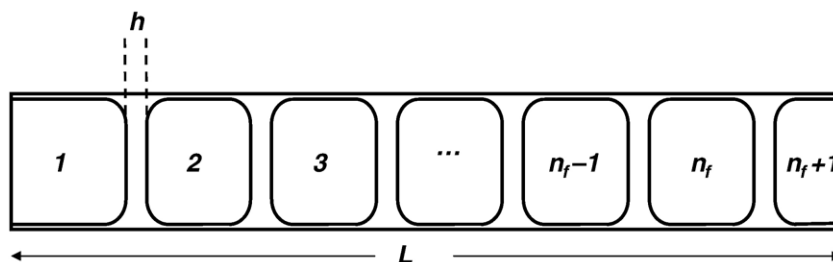


Fig. 3. Schematic of a train of foam films with the equal thickness of  $h$  in cylinder with the length of  $L$ . In the presence of  $n_f$  intervening foam films the 1-D gas space is separated to  $n_f + 1$  sections.

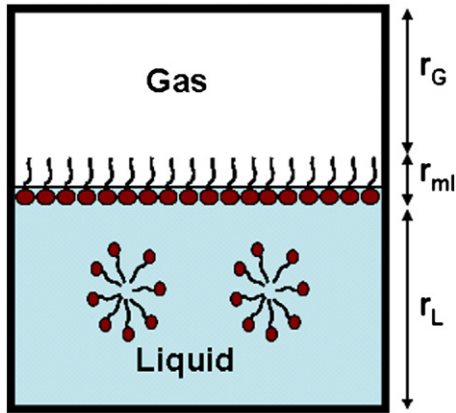


Fig. 4. Surfactant solution: when a surfactant is added to a quiescent liquid there are three main resistances to the mass transfer of gas: the gas phase resistance ( $r_G$ ), the interfacial resistance induced by surfactant molecules ( $r_i$ ), and the resistance in the bulk liquid ( $r_L$ ).

Different theories describe the permeability of surfactant monolayers. The main theories are the simple diffusion theory, the energy barrier theory, the density fluctuation theory, and the accessible area theory, which will be discussed subsequently.

### 2.1. Simple diffusion theory

The first simple approach to treat the experimental data is to assume that the monolayer is a homogenous phase with a thickness  $h_{ml}$ . The gas molecules diffuse through this thin uniform layer with a diffusion coefficient  $D_{ml}$ . According to Fick's first law, the rate of mass transfer is inversely proportional to the monolayer thickness:

$$\frac{dN_g}{dt} = -\frac{D_{ml}}{h_{ml}} \Delta C_g = -k_{ml} \Delta C_g \quad (1)$$

where,  $N_g$  is the number of moles of gas passing across the film per unit area and time  $t$ ,  $\Delta C_g$  is the difference in the gas concentrations on the both sides of the monolayer, i.e. the driving force for the diffusion process, and  $k_{ml} = D_{ml}/h_{ml}$  (cm/s) is the permeability coefficient for a monolayer [74,75].

The thickness of the monolayer can be related to the length of hydrocarbon chain of the surfactant molecule by the simple relation of

$$h_{ml} = a_{hg} + b_{hc}(n_C - 1) \quad (2)$$

Here,  $n_C$  is the number of carbon atoms in a linear hydrocarbon chain of a surfactant molecule. The constant  $a_{hg}$  accounts for the size of the polar group as well as the terminal methyl group of the alkyl chain. The constant  $b_{hc}$  accounts for the size of a single methylene group in the chain. According to Eqs. (1) and (2), gas permeability has to be inversely proportional to the length of its hydrocarbon chain, i.e.

$$k_{ml} = D_{ml}/h_{ml} = f(1/n_C) \quad (3)$$

Langmuir and Schaefer [35] could explain some of their experimental data, mainly those for gas permeation through thick

oil films on water surface, using the above theory based on Fick's law. Nevertheless, several works [35,37] have shown that the relationship between monolayer permeability and the chain length is exponential. This raises doubts about the accuracy of the simple diffusion theory in interpreting the experimental results. Seemingly when the size of permeant gas molecules is comparable to the thickness of the barrier (surfactant monolayer), Fick's law is not adequately accurate. Even more, it was observed that the diffusion coefficient of monolayers differs from that of the bulk material from which the monolayer is prepared [61]. However, Fick's law is a good approximation for thick films [53] and can be also applied to explain the effects of impurities and external additives on liquid surface that enhance the permeability of the monolayers [44].

### 2.2. Energy barrier theory

The concept of the existence of an activation energy barrier due to the presence of surfactant monolayers at the gas–liquid interface was first introduced by Langmuir and Langmuir [34] and developed further by Langmuir and Schaefer [35]. Their experimental results showed that gas permeability of a surfactant monolayer is exponentially proportional to the length of the surfactant hydrocarbon chain and inverse of the temperature. Although Archer and La Mer [37] proved that the low permeability coefficients obtained by Langmuir and Langmuir [34] were a result of impurities on the water surface, they confirmed the existence of an energy barrier that opposes the penetration of the gas molecules into the monolayer or some part of it. Consequently, they proposed the following relationship for the coefficient of monolayer gas permeability:

$$k_{ml} = \kappa \alpha_c \exp\left(\frac{E_a}{R_B T}\right) \quad (4)$$

where,  $E_a$  is the activation energy,  $R_B$  is the universal gas constant,  $T$  is the absolute temperature,  $\alpha_c$  is the condensation coefficient which accounts for the condensation of water molecules on a monolayer free surface and cannot exceed unity, and  $\kappa$  is a constant that depends on the cross-sectional area of the permeant molecule [34]. According to the gas kinetics theory [76], each gas molecule carries a certain amount of energy. When this molecule reaches a surfactant monolayer, it needs space to pass through the monolayer. The gas molecules in the gas phase strike the surfactant molecules in the monolayer. Some of the molecules are reflected back to the gas phase, and only a certain fraction of the molecules that have certain energy can permeate. This activation energy is dependent on the length of the hydrocarbon chain, the surface pressure, the cross-sectional area of the permeant, and some properties intrinsic to the monolayer (phase state, compressibility, free surface area, and polar group) [34,35,77–79].

By combining the gas kinetics theory and energy barrier theory, Eq. (4) can be modified to

$$k_{ml} = \frac{\chi H}{(2\pi M_g R_B T)^{1/2}} \exp(-(\Delta E_a + \Pi_s \Delta A)/R_B T) \quad (5)$$

where  $\chi$  is a constant and depends on the frequency of collision,  $M_g$  is the molecular weight of the gas,  $H$  is Henry's solubility coefficient, and  $\Pi_s$  is the surface pressure. Eq. (5) provides a direct relation between the monolayer permeability and the properties of the permeating gas, and the characteristics of the monolayer.

A modified version of the energy barrier theory was proposed by considering the dependence of the monolayer permeability in terms of the activation free energy,  $\Delta G'$  [77,78]. This model formulates the coefficient of monolayer permeability as

$$k_{ml} = \kappa' \exp(\Delta G' / R_B T) \quad (6)$$

where  $\kappa'$  is a constant. The excess Gibbs energy of activation is given by  $\Delta G' = \Delta U - T\Delta S + \Pi_s \Delta A$  with  $\Delta U$ ,  $\Delta S$  and  $\Delta A$  internal energy, entropy, and area of activation, respectively.  $\Delta A$  is the area by which the monolayer must expand to form the required space between the surfactant molecules to let the gas molecules pass through. The value of  $\Delta A$  decreases with decreasing packing density of the monolayer [78].

### 2.3. Density fluctuation and accessible area theories

The large number of factors that influence the energy barrier make the energy barrier theory problematic for giving a unified physical mechanism for the permeability of the monolayers. Blank [80], Blank and Britten [81], and Barnes [41,42] pointed out that the permeation is allowed only when the permeating molecule reaches a hole with a sufficiently large size to pass through, i.e. the permeation process is assumed to be all-or-none. Respectively, the gas permeability is related to the probability  $P$  of a gas molecule finding such hole in the monolayer. Thus, the monolayer permeability coefficient is defined as

$$1/k_{ml} = r_{ml} = \left( \frac{1}{\alpha_v Q} \right) \left( \frac{1}{P} - 1 \right) \quad (7)$$

where,  $Q = \sqrt{R_B T / 2\pi M_g}$  and the condensation coefficient  $\alpha_v$  is the fraction of the gas molecules which can enter the monolayer. Eq. (7) shows that the permeability of a monolayer can be predicted if the probability of finding a free space in the surfactant monolayer is known.

Blank [80] proposed a “density fluctuation theory” by which he could explain his experimental results. The model was derived in terms of equilibrium properties of the monolayers. Blank [80] and Blank and Britten [81] stated that the free space in the monolayer can arise by three different mechanisms: (i) the natural free area in the lattice; (ii) local fluctuations in the monolayer concentration; and (iii) the kinetic energy of the permeant molecule forcing the monolayer molecules apart.

The probability of a gas molecule finding a free space formed by mechanisms (i) and (ii) is proportional to the entropy change,  $\Delta S$ , due to expansion of the monolayer

$$\Delta S = \int \frac{dE'}{T} - \int \frac{\sigma dA}{T} \quad (8)$$

where  $E'$  is the enthalpy of monolayer expansion,  $\sigma$  is the surface tension of the bulk surfactant solution, and  $A$  is the area of monolayer.

Thus,

$$P = P_0 \exp\left(-\frac{\sigma_i \Delta A}{k_B T}\right) \quad (9)$$

with  $\sigma_i = fA - T \frac{d\sigma}{dT}$ ,  $f$  is a constant and is related to the monolayer compressibility,  $k_B$  is the Boltzmann constant, and  $P_0$  is the probability of the equilibrium ( $\Delta S=0$ ). In Eq. (9),  $\Delta A$  is the local expansion of the area necessary for the gas molecules to pass through.

The density fluctuation model gives reasonable results when dealing with equilibrium properties of the monolayers such as surface pressure (as part of the fluctuation frequency calculation), the diffusion coefficient, and the permeability. However, the model does not provide useful information when dealing with the dynamic properties such as the viscosity of the monolayer and thermal conductivity. The permeability obtained by the density fluctuation model is smaller than the experimental values. It appears that the calculation of the probability of a hole formation from the bulk entropy of the expansion of the monolayer [80] underestimates the number of permeable gaps. To get closer values, Bockman [82] suggested using experimental entropy values rather than calculated ones, which makes the model more accurate. There is no explicit allowance for the temperature or the alkyl chain length, and the model does not explain the impurity effects.

The *accessible area theory* [41,42] also calculates the probability of a gas molecule finding a gap between the surfactant molecules. The only difference to the “density fluctuation theory” is that in this theory the gaps exist in the monolayer because of the non-perfect arrangement of the molecules. The sum of areas of the available holes is called *accessible area*. These holes are formed spontaneously at the surface.

According to this theory, the probability for a gas molecule to meet a gap is

$$P = \frac{A_{ac}}{A} \quad (10)$$

where  $A_{ac}$  is the accessible area and  $A$  is the area of the monolayer. Any decrease in the rate of gas transfer is due to the reduction of the accessible area.

A model for the monolayer structure is required in order to predict the accessible area. Barnes et al. [41] proposed a random hard-disk model in which the surfactant molecules are represented by hard disks that are randomly distributed on the liquid surface. Liquid (water) molecules are represented by hard spheres. The interaction energy between a surfactant molecule and a liquid molecule is equal to that between two liquid molecules. However, this model ignores the interaction forces between the surfactant molecules and, as a result, the clumping of the surfactant molecules into closely packed clusters. Gas molecules can permeate through the existing holes, but they cannot form other holes. This model does not include the effect of the hydrocarbon chain length of the surfactants in the gas permeation rate, while experiments show the dependency of the

permeability of monolayers to the chain length [34,35]. The absolute value of the calculated permeability by this model is in a satisfactory agreement with the experimental data, and it is remarkably successful in predicting the dependence of the monolayer permeability on the surface density, although it is inaccurate in high concentrations due to the small numbers of holes in the arrays.

In Ref. [42] it was assumed that the surfactant molecules are not randomly distributed and exist in loose hexagonal packing so that the centers of the molecules form a regular hexagonal lattice with areas per molecule larger than the crystallographic values. The holes are formed because of the independent vibrations of the disks about their mean positions. Examining of the calculated values from this model with experimental results reveals that it cannot accurately predict the permeability of monolayers to gas molecules. The model presented in Ref. [41] was more satisfactory, giving more realistic permeation rates.

### 3. Gas permeability of foam films

#### 3.1. Sandwich model

A single foam film consists of an aqueous core with thickness  $h_w$  sandwiched between two adsorbed monolayers of surfactant with the thickness of  $h_{ml}$  (Fig. 2). The permeability of such a foam films at equilibrium can be calculated by [83,84]

$$k = \frac{DH}{h_w + 2D/k_{ml}} \quad (11)$$

taking into account the solubility of gas and applying Fick's first law for a *homogenous* layer, while neglecting the gas resistance on both sides of the film.

Here,  $k$  is the permeability of the whole foam film to gas,  $D$  is the diffusion coefficient of the gas in the liquid phase,  $H$  is the Henry's solubility coefficient, and  $k_{ml}$  is the permeability of the monolayer to gas. This equation shows that the permeability of the foam films depends on the thickness of the aqueous layer as well as on the solubility and diffusion of the gas in the aqueous phase. Higher  $D$  and  $H$  of the bulk liquid results in higher permeation rates, respectively  $k$ . It appears from Eq. (11) that for thick foam films ( $2D/k_{ml} \ll h_w$ ) the rate of permeation is controlled by the liquid layer via  $D$  and  $H$  ( $k=DH/h_w$ ), while for thin foam films ( $2D/k_{ml} \gg h_w$ ) the permeability of monolayer ( $k=Hk_{ml}/2$ ) is the limiting permeability process. Eq. (11) shows that the total foam film resistance is the sum of the resistance in the liquid core and the resistance of the monolayers. This is similar to the equations proposed in [85,86] for the permeation of rubber membranes by gases and polymer membranes by water vapor.

Princen et al. [83,84] performed detailed measurements on the gas permeability of foam films, varying concentrations of the surfactant and salt and also the temperature. The authors emphasized that Fick's law is applicable in macroscopic systems and accounts for the transport of gas through soluble monolayers. The sandwich model is adequately accurate for soluble monolayers, and the values calculated by this theory are

in good agreement with experimental data, although such a simple model may not be accurate for the permeation of gases through insoluble monolayers [83]. The authors reported some values for the permeability of various gases through foam films. It was observed that the permeability of monolayers inversely changes with the collision diameter of the gas molecules, a fact that cannot be explained by the simple Fick's mechanism they proposed.

#### 3.2. Nucleation theory of fluctuation formation of holes

The sandwich structure model of the film (Fig. 2) used by Princen and Mason [83] to explain the foam film permeability is not adequate to describe the structure of the very thin Newton Black Films (NBF). These films consist only of two monolayers of adsorbed surfactant molecules and some layers of hydration water. The properties of such films (e.g. electroconductivity [87]) are very different to those of the thicker CBF, which means that the mechanism of their permeability could be different than that of single surfactant monolayers. Several authors [88–90] have mentioned that a possible mechanism of permeability of such surfactant bilayers (NBF) is the existence of microscopically small holes in the bilayer. Nucleation theory of fluctuation formation of holes in the NBF assumes that molecular defects in the adsorbed monolayers exist. They are called vacancies. These vacancies move in the monolayers and aggregate, forming holes with different size  $i$  (here  $i$  is the number of vacancies which form a single hole). The theory gives relations to calculate the probability for the formation of holes of certain size  $i$  [91–93]. The permeability occurs by two regions in the foam bilayers (NBF): (a) hole-free area with a permeability coefficient  $k_0$  (coefficient of background permeability) and (b) area which consists of holes with different sizes. The gas flux of holes with size  $i$  is given by the permeability coefficient  $k_i$ . Thus, the permeability of a bilayer is a sum of the permeabilities of each part of the film  $k_0$  and  $k_i$  by:

$$k = k_0 + \sum_{i=0}^{\infty} k_i \quad (12)$$

where the permeability coefficients are defined as

$$k_0 = \frac{S_0 D_0}{Sh}, \quad k_i = \frac{S_i D_i}{Sh_i} \quad (13)$$

and in these equations  $h$  and  $S$  are the thickness and total area of a bilayer film, respectively.  $S_0 = S - \sum_{i=1}^{\infty} S_i$  is the hole-free area of the film,  $S_i$  is the overall area of the holes of size  $i$ , and  $D_0$  and  $D_i$  are the diffusion coefficients of the permeant gas through hole-free bilayer and holes of size  $i$ , respectively.

Eq. (13) is valid only in the case that the permeability obeys Fick's law. Earlier studies [34,35,37,53] on the permeability of insoluble monolayers and foam films [94] show that this usually is not obeyed. The permeability is not a linear function of the surfactant chain length, but  $D$  varies with the number of  $\text{CH}_2$  groups in the hydrophobic part of the surfactant molecules [35,37]. Thus, it is more suitable to describe the results as permeability rather than as diffusion.

The background permeability of the bilayer could be described by any of the mechanisms of permeability of surfactant monolayers. The problem of finding  $k_i$  and, respectively,  $k$  according to nucleation theory is reduced to that of finding

$$S_h = \sum_{i=1}^{\infty} S_i \quad (14)$$

The area  $S_i$  is determined using nucleation theory of hole formation in bilayers [91–93,95] as

$$S_i = (iA_{ef})n_iS \quad (15)$$

where  $A_{ef}=iA_m/2$  ( $A_m$  is the area occupied by a single surfactant molecule) is the effective area of an  $i$ -sized hole. The density of the  $i$ -sized holes in the bilayer  $n_i$  ( $m^{-2}$ ) is given by [91,92]

$$n_i = \left(\frac{1}{A_m}\right) \exp\left(-\frac{W_i}{k_B T}\right) \quad (16)$$

where  $W_i$  is the work of the formation of an  $i$ -sized hole in the bilayer. Eq. (16) is valid when  $n_i \ll (1/A_m)$ . The work of formation of an  $i$ -sized hole depends on the surfactant concentration in the solution and is calculated from the thermodynamics of fluctuation formation of holes in the bilayer [91–93]

$$W_i = -i\Delta\mu + P_i, \quad \Delta\mu = k_B T \ln\left(\frac{C_s}{C_{se}}\right) \quad (17)$$

where  $C_s$  is the surfactant concentration, and subscript e stands for the equilibrium surfactant concentration in the solution. At  $C_s=C_{se}$  there is no driving force for the formation of large holes in the film. Above this concentration the film is stable with respect to rupture by hole nucleation. Eq. (17) shows that the work  $-i\Delta\mu$  is gained ( $C_s < C_{se}$ ) or lost ( $C_s > C_{se}$ ) due to clustering of  $i$  single vacancies to form an  $i$ -sized hole, and during this process work  $P_i$  is needed to create the hole periphery. The quantity  $P_i$  can be determined only if the shape of the hole and the interaction energies of the molecules in the bilayer are known [95]. For large enough holes, it can be assumed that  $P_i$  is simply proportional to hole perimeter

$$P_i = (4\pi A_{ef}i)^{1/2}\gamma \quad (18)$$

where  $\gamma$  ( $Jm^{-1}$ ) is the specific free energy of the hole edge. Combining Eqs. (12)–(18) provides the following expression for the bilayer film permeability

$$k = \frac{D_0}{h} + A_{ef} \sum_{i=1}^{\infty} iD_i n_i \quad (19)$$

Eq. (19) states that the permeation of the gas through the holes of size  $i$  depends on the hole density  $n_i$ . The possibility of the formation of large holes in the bilayer is small, and their density is low. Therefore, the main contribution to the film permeability will be due to the existence of a large number of

sufficiently small holes. From Eqs. (16), (17), and (19) an equation is obtained, which expresses the relation between surfactant concentration and foam film permeability

$$k = k_0 + \sum_{i=1}^{\infty} \varepsilon_i \left(\frac{1}{C_s}\right)^i \quad (20)$$

where,

$$\varepsilon_i = \left(\frac{A_{ef}}{A_m h}\right) iD_i C_{se}^i \exp\left(-\frac{P_i}{k_B T}\right) \quad (21)$$

Physically  $\varepsilon$  is the permeability coefficient of certain holes of the bilayer at  $C_s=C_{se}$ . It can be obtained as a fitting parameter of the experimental data.

Eq. (20) shows that the foam film permeability increases with decreasing surfactant concentration because the required work for formation of a hole decreases. When the concentration of surfactant increases, the density of holes decreases, and the required work for the formation of a hole increases. As a result, permeability of the gases through the bilayer decreases. The permeability of the bilayers decreases with the increase of surfactant concentration until it reaches its minimum value, i.e.,  $k_0$ . After this, minimum permeability of the foam film is independent of surfactant concentration and remains constant. Furthermore, Eq. (20) implies that the dependence of foam film permeability on temperature is not a simple Arrhenius dependence. The nucleation theory of fluctuation formation of holes in foam bilayers also explains the stability of the NBF. It shows that there is a range of surfactant concentrations where the film is in metastable equilibrium. In this range the film is stable and permeable even though some holes are formed, which can rupture the film [92]. This can be seen from Fig. 5.

### 3.3. Freely standing film diffusion theory

Nguyen et al. [19,20] studied a special case of interest, e.g. a train of foam films in a matrix. They developed a *freely*

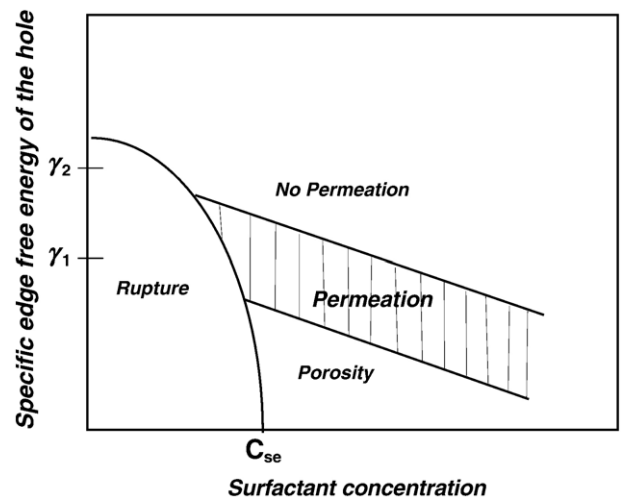


Fig. 5. Bilayer permeability: the shaded area shows the area in which the bilayer is permeable to gases.  $\gamma$  is the hole specific edge energy [92].

standing film diffusion model to investigate the resistance of one or more films to the mass transfer in this case. The model allows experiments on vapor components, extending the range of investigated gases. This mechanistic model relates the effective gas diffusivity to foam film density (number of foam films per unit of length) and permeability, which itself is a complex function of electrolyte concentration, gas solubility, surfactant concentration, and temperature.

In the presence of  $n_f$  intervening foam films with the equal thickness of  $h$ , the one dimensional gas space is separated to  $n_f + 1$  sections (Fig. 3). The gas flux will be reduced as a result of film resistance  $1/k_{\text{eff}}$  with  $k_{\text{eff}}$  being the effective coefficient of the gas transfer across  $n_f$  films. The whole system is assumed to have an effective diffusion of  $D_{\text{eff}}$ . The difference between  $D_{\text{eff}}$  and the diffusion coefficient of the gas in the gaseous mixture,  $D_g$ , is the measure of the film resistance. The effective resistance mass transfer coefficient of the gas  $k_{\text{eff}}$  through  $n_f$  foam films of thickness  $h$  in a cylinder with a length  $L$  can be written as

$$\frac{1}{k_{\text{eff}}} = \frac{(L - n_f h)}{D_g} + \frac{n_f H}{k} \quad (22)$$

where  $H$  is the Henry's coefficient of gas solubility in the aqueous core of the film.

Eq. (22) is obtained under steady-state condition, assuming that the mass transfer rate is linearly proportional to the driving force and the equilibrium relationship is a straight line. Assuming that the permeability of a single film follows the sandwich model, its permeability coefficient  $k$  is defined as

$$\frac{1}{k} = \frac{2}{k_{\text{ml}}} + \frac{1}{k_w} \quad (23)$$

where  $k_w$  is the background mass transfer coefficient in the bulk. When the film thickness is much smaller than the length of the cylinder, Eq. (22) reads

$$\frac{1}{k_{\text{eff}}} = \frac{1}{k_g} + n_f H \left( \frac{1}{k} \right) \quad \text{for } h \ll L \quad (24)$$

where,  $k_g = D_g/L$  is the mass transfer coefficient of the investigated gas in the gaseous mixture. Since the film thickness  $h$  is neglected in Eq. (24), the quantity  $k$  reduces to the permeability of a bilayer film (respectively Eq. (23) reduces to  $1/k = 2/k_{\text{ml}}$ ) and is determined from the adsorption density of the surfactant molecules at the film interfaces.

Nguyen et al. [19,20] assumed that the state of unsaturated monolayers varies considerably with the dynamic adsorption behavior of the surfactant, which depends in turn on the presence of electrolytes in the solution. As a result, similar to the monolayer permeability, the permeability of a foam film to gas is also dependent on the surface coverage of the surfactant or adsorption density.

The adsorption density,  $\theta$ , is defined as the ratio of the equilibrium density,  $n_{\text{eq}}$ , to the closed-packed density,  $n_0$ , of the surfactant molecules at the interface, provided that the effective area per molecule of the surfactant,  $A_m$ , is constant. However, it is well known that the effective area per molecule of surfactant in the interface varies significantly with surface pressure and

decreases with the increasing  $\theta$  [96]. The authors proposed the following form of the effective fraction of the occupied sites:  $\theta$  to the power of  $1/(\lambda - 2\theta)$  where  $\lambda (=4)$  shows the maximum change in the effective area per surfactant molecule with varying surfactant concentration. Therefore, from the kinetics theory, the overall penetration rate of gas molecules across this interface can be written as

$$k = \left(1 - \theta^{\frac{1}{\lambda-2\theta}}\right)^2 F e^{(-E_w/R_B T)} + \left(\theta^{\frac{1}{\lambda-2\theta}}\right) F e^{(-E_f/R_B T)} \quad (25)$$

where,

$$F = \frac{H}{\sqrt{2\pi M R_B T}} \quad (26)$$

and,

$$H = H_0 e^{\left(\frac{-\Delta H}{R_B} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \quad (27)$$

$E_f$  and  $E_w$  are respectively the penetration activation energies across the occupied and unoccupied sites, and  $\Delta H$  is the enthalpy of the solution. The power two of the unoccupied sites in Eq. (25) considers both of the film surfaces. However, depending on the overlapping structure of the two monolayers, a power other than 2 can be also taken. This number should be lower for sufficient thick films and vice versa. The fraction of occupied sites can be obtained by a Langmuir type of adsorption equation [97]

$$\theta = \frac{(B/n_0) C_s e^{(E_a/R_B T)}}{1 + (B/n_0) C_s e^{(E_a/R_B T)}} \quad (28)$$

where,  $E_a = \frac{521 n_{\text{hc}}}{N_A} + 12 \times 10^{-6} n_{\text{hc}} n_0^{0.5} - z e \psi_0$ .

In these equations  $C_s$  is the surfactant concentration,  $E_a$  is the desorption activation energy,  $B$  is the adsorption–desorption equilibrium constant,  $n_0$  is the closed-packed adsorption density, and  $z$  and  $e$  are the valence number and electric charges, respectively.  $\psi_0$  is the Gouy potential and is expressed as a function of electrolyte concentration, temperature, and effective area per surfactant molecule [96]. This model is capable of explaining the effect of surfactant concentration, the length of hydrocarbon chains, as well as the effect of temperature and electrolyte concentration.

#### 4. Permeability of foam films — A summary of experimental results

The gas permeability of surfactant monolayers spread on liquid/air surfaces had been studied intensively during the first part of the last century. Many studies have reported interesting experimental results, most of which have been summarized in books and reviews [e.g. 44,79]. Experimental studies on gas permeability of foam films are comparatively rare. First results were published by Brown et al. [75]. Princen and Mason [83] were the first to perform detailed experimental study on the permeability of foam films. The permeability was measured on the basis of non-steady-state diffusion kinetics. The method

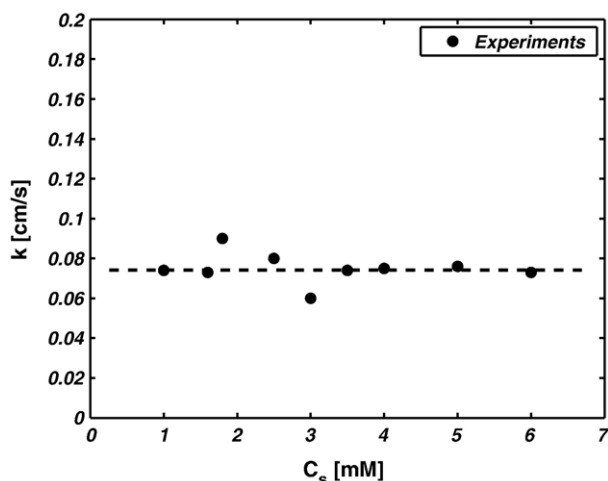


Fig. 6. Dependence of the permeability of the common black films on the surfactant concentration at a constant electrolyte concentration 0.1 M NaCl and  $T=25\text{ }^{\circ}\text{C}$ : The permeability value remains constant [94].

they used was an extension of the diminishing bubble method used by Brown et al. [75], where the size decrease of a free floating foam bubble on an interface is related to the outward diffusion of gas across the foam film at the top of the bubble. Originally, it was assumed that the bubble is spherical and exactly immersed halfway in the liquid. Princen and Mason [83] analyzed the shape of such bubbles and obtained a precise relation that allows the gas permeability of a foam film to be obtained from experimental data. Modified versions of the diminishing bubble technique were used extensively to study the gas permeability in later experiments [95]. Other techniques are based on the use of single foam films [4] or “trains of films” in glass tubes [20] as well as layers of single foam bubbles [5]. The main experimental observations obtained with these techniques and effect of different parameters on gas permeability of foam films are summarized in the following.

#### 4.1. Surfactant concentration

Usually the foam films are stabilized by soluble surfactants. Changes in the surfactant concentration in the film-forming solution are directly related to changes of the surface tension or the surfactant density at the film surfaces. Princen et al. [83,84] reported that varying the surfactant concentration in the absence of salt has no significant effect on the value of the permeability of the foam film, as long as the concentration is above 0.25% hexadecyl ammonium bromide (HDTABr). However, they observed that at 0.1%, the value of permeability was much lower. The unusual decrease in the permeability coefficient with decreasing surfactant concentration was explained by the presence of admixtures in the technical surfactant used [83,84]. The reason for such unexpected dependence could be also the action of the cationic surfactant HDTABr as an electrolyte. The ionic strength of the surfactant solution is postulated by the surfactant concentration in the case of a salt-free solution. The increase in the surfactant concentration increases the ionic strength of the solution, thus decreasing the foam film thickness

according to the DLVO theory. This can result in an increase in the film permeability, which could be stronger than the decrease in it created by the higher surfactant concentration. This shows the necessity of precise control on the parameters that control the foam film structure and can influence the gas permeability of the films. Detailed measurements on gas permeability of foam films can resolve very fine effects if performed at well-defined conditions. Such experiments were performed [94] with CBF prepared from sodium dodecyl sulphate (SDS) in the presence of 0.1 M NaCl as an electrolyte. The salt concentration was comparatively low and assured formation of CBF, but it was always higher than that of the anionic surfactant used. The choice of conditions allowed the experiments to be performed with foam films with defined structures. The results are presented in Fig. 6. The permeability of the CBFs does not change significantly with the increasing surfactant concentration and remains constant. This behavior cannot be explained by the nucleation theory or freely standing film diffusion theory; because both models assume that the permeability of a foam film is a strong function of the surfactant concentration. A possible reason could be that CBFs are stable at surfactant concentrations higher than the critical micelle concentration (CMC), and any addition of surfactant to the film-forming solution does not change the surfactant density at the film surfaces. An alternative reason could be that the thickness of the aqueous core of a CBF is so large that practically only the aqueous core governs the permeability of the whole film (see Eq. (11)), and it does not depend on the permeability of the surfactant monolayers.

Several detailed studies on the permeability of NBFs were also performed [e.g. 20,95,98,99]. Fig. 7 shows the results for NBF stabilized by SDS in the presence of 0.5 M NaCl. The experiments were performed at four different temperatures in a wide range of surfactant concentration,  $C_s$ . The permeability coefficient,  $k$ , is practically constant in a wide range of higher  $C_s$ . It increases sharply at lower concentrations and also changes with the temperature. Similar dependencies were obtained when other surfactants were charged or non-ionic surfactants were used

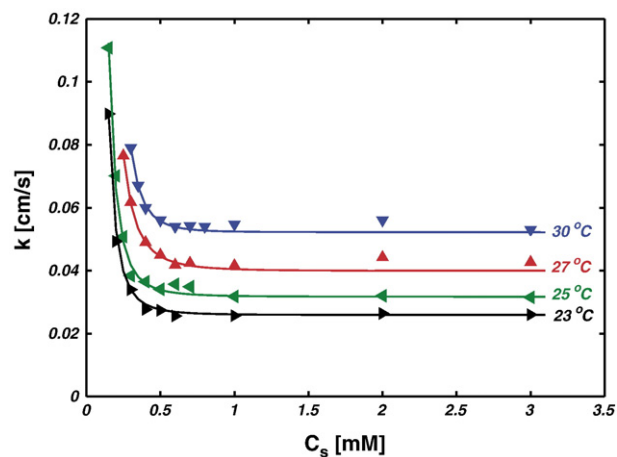


Fig. 7. Gas permeability coefficient,  $k$ , as a function of surfactant concentration,  $C_s$ , at four temperatures for films prepared from solutions of SDS and containing 0.5 M NaCl. The lines denote the theoretical curves fitted to the experimental points [99].

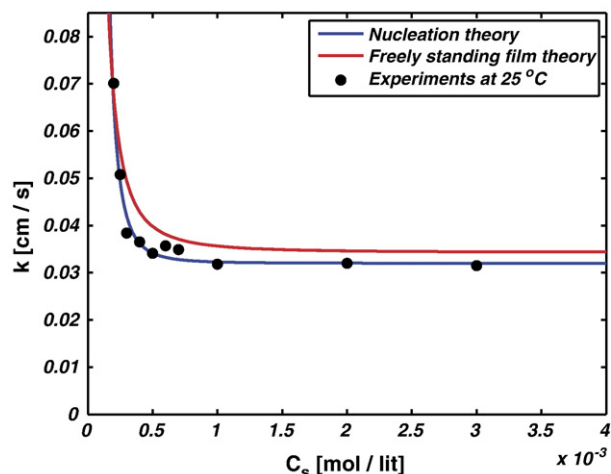


Fig. 8. Comparison between nucleation theory and freely standing film diffusion theory: two models are in good agreement with each other and experimental data [20,99].

[100], which confirms the general trend that the gas permeability decreases when the surfactant concentration increases.

The experimental data were usually treated using the nucleation theory of fluctuation formation of holes in bilayer NBF and freely standing film theory. It should be mentioned, as shown in Fig. 8, that the two models give similar results for the NBF gas permeability and match the experimentally obtained data. According to the nucleation theory, the bilayer film is considered populated by microscopically small holes consisting of  $i=1, 2, 3$ , etc. vacancies of surfactant molecules. The gas permeability coefficient is a sum of the permeability coefficient  $k_0$  through the hole-free bilayer surface and the permeability coefficient  $k_i$  through the holes of  $i$  molecular vacancies (Eq. (20)).

The statistical treatment of the  $k(C_s)$  data for each temperature was done including  $k_0$  and all possible combinations of the other summands up to  $i=6$ . Formation of holes larger than those consisting of 6 vacancies was disregarded due to the small probability of formation of such holes. The experimental curves were fitted only to the experimental points for  $C_s < 0.6$  mM SDS, i.e. in the concentration range where  $k$  strongly depends on  $C_s$  and is close but below that reported in the literature value of CMC for the system. The curve lines in Fig. 7 present the best theoretical fits to the experimental data. The curves coincide well with the experimental points also in the concentration range where  $k$  is practically constant for the lower temperatures 23 °C and 25 °C. However, the experimental points lie above the fitted theoretical curves in this range of higher surfactant concentrations for the both high temperatures 27 and 30 °C. A new quantity  $k_{pl}$  was introduced, which is the constant  $k$  value obtained experimentally from the  $k(C_s)$  curve plateau as an arithmetical mean from all points at  $C_s > \text{CMC}$  for each temperature. These  $k_{pl}$  values practically coincide with the horizontal part of the fitted theoretical curve in the cases of 23 and 25 °C. However, at temperatures 27 and 30 °C,  $k_{pl}$  values are larger than the constant  $k$  values corresponding to the fitted theoretical curve.

This is demonstrated in Fig. 9, where the  $k_{pl}$  values are denoted by dotted lines. It was assumed that the constant  $k$

value obtained from the horizontal part of a fitted theoretical curve is the background permeability coefficient  $k_0$ . For both lower temperatures of 23 °C and 25 °C,  $k_0$  and  $k_{pl}$  practically coincide, while for the higher temperatures of 27 °C and 30 °C,  $k_0 < k_{pl}$ .

Permeability of the NBFs dramatically decreases with increasing surfactant concentration until it reaches a constant permeability after a certain concentration (see Figs. 7 and 8). In some papers, this concentration is considered to be the critical micelle concentration (CMC) of the surfactant [20,97,101], whereas in some other papers it is referred to as characteristic concentration [92–95,98,99]. This is due the fact that CMC does not vary with the variations in temperature, while the background permeability,  $k_0$ , changes with temperature variation. This means that the concentration in which the foam film permeability becomes constant is different than the CMC of the surfactant. According to the nucleation theory, at lower surfactant concentrations the work required for the formation of holes decreases, and thereby the density of holes and the accessible area for the passage of gas increases. In contrast, at higher surfactant concentrations the number of available sites for gas molecules decreases, since they are mostly occupied by surfactant molecules. In the concentrations close to the CMC, the striking gas molecules encounter a close-packed surface in which the surfactant molecules have occupied all available sites, and consequently, the gas permeability of the foam film remains constant. The same behavior is expected in the freely standing film diffusion theory [20].

#### 4.2. Electrolyte (salt) concentration

Princen and Mason [83] carried out experiments in the system of 4% HDTABr+1% NaBr. In contrast to the system without salt, the permeability of foam films appeared to increase slightly during the initial stages of the experiment and then became constant. According to their explanation this might be related to the continuing drainage after the black film had covered the cap and when the experiment was started. For

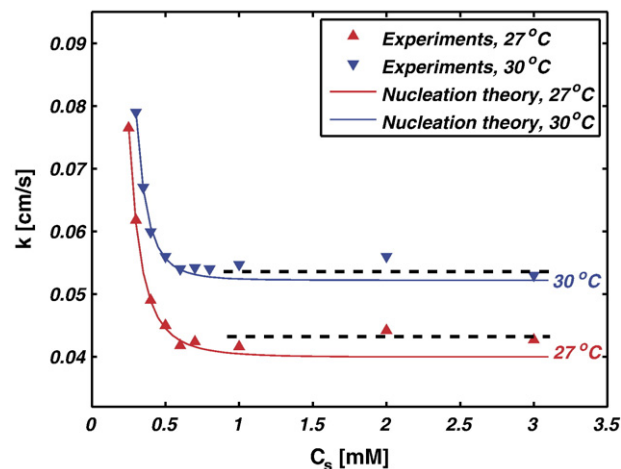


Fig. 9. Experimental points and fitted curves using nucleation theory for permeability of NBF at 27 and 30 °C. The mean  $k_{pl}$  values are presented as dotted lines [99].

monatomic and diatomic gases, the presence of the salt resulted in slightly higher permeabilities. This can also be related to  $h$  (film thickness), which decreases with increasing salt concentration [23,26].

The addition of electrolytes has a dual effect on the film structure. It increases the adsorption density of the surfactant (in the case of ionic surfactants) due to the screening of the electrostatic repulsion between the molecules. On the other hand, the addition of electrolytes suppresses the repulsive electrostatic double-layer component of the disjoining pressure in the films, and the film thickness decreases [23]. Thus, the transition from the thicker CBF, where the sandwich model could be applied, to the thinnest bilayer NBF occurs. The experimental results have shown unexpected dependence of the permeability of the films stabilized by SDS on the film thickness. Generally, one would expect the permeability to increase with decreasing thickness of the aqueous core, but contrarily, the experimental results show that the thicker CBF from SDS solutions has higher gas permeability than the thin NBF from the same solution. Fig. 10 shows the permeability of films formed by SDS solutions with different concentrations of two different electrolytes, NaCl and LiCl. In Refs. [94,98], it was concluded that the film permeability is mainly determined by the monolayer permeability of the adsorption layers, and the permeability of the monolayers increases with the increasing distance between the monolayers (Figs. 11 and 12). It appears that at small thicknesses the normal interactions between the monolayer molecules make the monolayer better ordered and less permeable. As can be seen from Figs. 11 and 12, the film permeability increases with the increasing film thickness until it reaches a maximum. After this jump, which is due to the transition from CBF to NBF, the film permeability decreases with increasing salt concentration until it reaches a constant value. The transition in the SDS+NaCl appears to be sharp, but in the SDS+LiCl system the permeability decreases gradually, and the transition is not clear, which is in agreement with the experimental data for the film thicknesses [102–106]. It is also

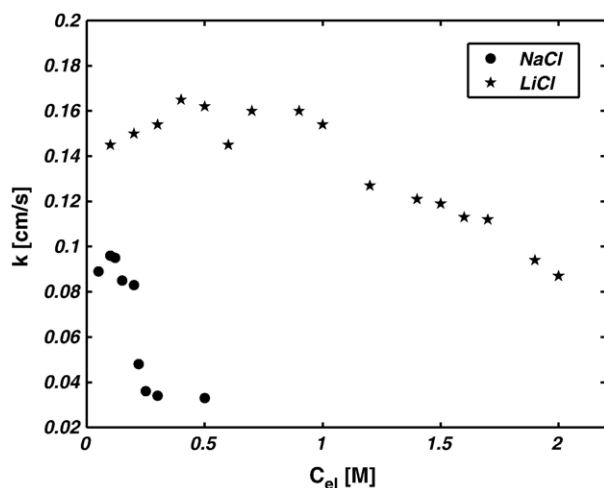


Fig. 10. Dependence of the film permeability coefficient on the electrolyte concentration. (● for NaCl and ★ LiCl) at a constant  $C_{SDS}=1.73$  mM and  $T=25$  °C [94].

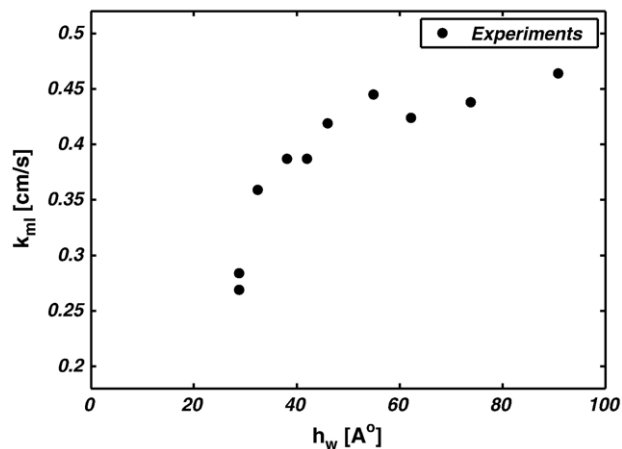


Fig. 11. Dependence of the monolayer permeability on the thickness of the inner aqueous layer of CBF stabilized by SDS and LiCl solutions [98].

clear from Fig. 10 that the film permeability in the presence of the  $Li^+$  is larger than in the presence of  $Na^+$ , because the  $Na^+$  ions are more strongly adsorbed at the dodecyl sulfate monolayer than the  $Li^+$  ions [105,106]. This makes the monolayers with adsorbed  $Na^+$  ions more compact, better ordered, and less permeable compared to the monolayers with adsorbed  $Li^+$ .

The free energy of the film formation faces a sharp increase in its absolute value while the permeability (and the thickness) decreases with the increasing electrolyte concentration [22]. This confirms the hypothesis proposed in Ref. [22] that the transition from the CBF to the NBF – which is connected to the increase in the strength of the interactions between two monolayers – causes an additional increase in adsorption density, resulting in an essential decrease in the film permeability. A model has been proposed by Krustev and Müller [22,107] to explain this behavior. The model takes into account the effect of the interaction of the two monolayers on the adsorption density of the surfactant molecules. By increasing the electrolyte concentration, the electrical double-

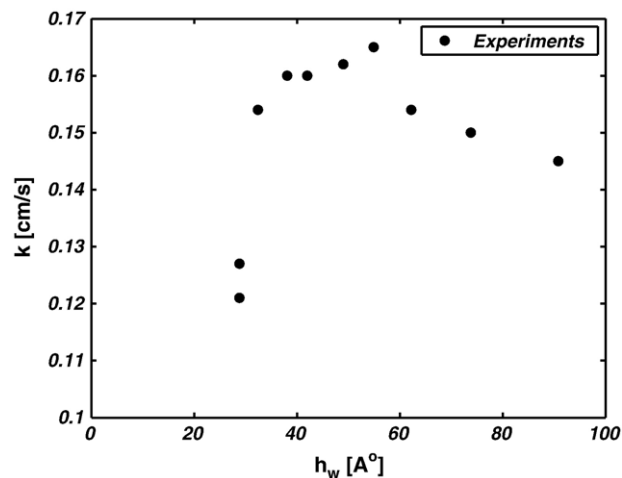


Fig. 12. Dependence of the film permeability on the thickness of the inner aqueous layer of CBF stabilized by SDS and LiCl solutions [98].

layer forces are screened, and film becomes thinner (Fig. 13). The Gibbs energy of film formation  $\Delta g^f$  is defined by the work done on the film per unit of area in brining its surface from infinity (no interaction between the surfaces) to the distance  $h$  (thickness of the film). The absolute value of free energy of film formation increases sharply in transition from CBF to NBF, indicating that  $\Delta g^f$  may influence the gas permeability of the film, because according to the theory of enhanced colloidal interactions the adsorption density of the surfactant is dependent on  $\Delta g^f$  [108]. The relation between the difference  $\Delta\Gamma_a$  between the adsorption density of the film and the bulk phase with  $\Delta g^f$  is

$$\Delta g^f = 2\sigma(\cos\beta - 1) + 2\mu_a\Delta\Gamma_a(h) \quad (29)$$

where

$$\Delta\Gamma_a = \Gamma_\infty^b \left[ \exp\left(\frac{\Pi(Z-1)}{RT\Gamma_\infty^b}\right) - 1 \right] \quad (30)$$

In these equations  $\beta$  is the measurable contact angle between the film surface and the surface of adjacent meniscus,  $\sigma$  is the surface tension,  $\mu_a$  is the chemical potential,  $\Gamma_\infty^b$  is the maximum adsorption density of the bulk phase, and the quantity  $Z$  is dependent on the value of  $\Delta g^f$ . It is shown that the adsorption density of the film surfaces starts to increase above that of the bulk phase surface ( $\Gamma_a^b$ ), if the transition from CBF to NBF occurs in the case of NaCl. The difference is about 3%  $\Gamma_a^b$  at 0.4 M NaCl. The films with LiCl show a similar effect; however, the difference is essentially smaller.

Moreover, according to the accessible area theory [41,42], the gas permeation of the surfactant monolayers are governed by the sites that are not already occupied by the surfactant molecules. The number density of the unoccupied sites is given by:

$$\Gamma_v = \Gamma_\infty^f - \Gamma_a^f = \Gamma_\infty^f - (\Gamma_a^b + \Delta\Gamma_a) \quad (31)$$

where  $\Gamma_\infty^f$  is the maximum number of the adsorbed surfactant molecules per unit area of the film and depends on the free energy of the film formation. In the case of the attractive interaction,  $\Gamma_\infty^f$  is smaller than  $\Gamma_\infty^b$ . For the CBF,  $\Gamma_\infty^f$  becomes equal to  $\Gamma_\infty^b$ . The combined effect of decreasing  $\Gamma_\infty^f$  and increasing  $\Gamma_a^f$  with increasing electrolyte concentration on  $\Gamma_v$  is dramatic. For the CBF with 0.1 M NaCl,  $\Gamma_v$  is roughly equal to  $1.5 \times 10^{-7}$  mol/m<sup>2</sup>. For the NBF practically all the sites are occupied by the surfactant molecules, and  $\Gamma_v \approx 0$ . The accessible permeation area  $A_{ac}$  in a surfactant monolayer can be calculated by

$$A_{ac} = A_m N_{Av} \Gamma_v A_t \quad (32)$$

where,  $N_{Av}$  is Avogadro's number, and  $A_m = 1/\Gamma_\infty^f N_{Av}$  is the effective area of one surfactant molecule in the monolayer. Therefore, the gas permeability of a monolayer can be calculated by

$$k_{ml} = \frac{D_{ml} A_{ac}}{h_{ml} A_t} \quad (33)$$

$A_t$  is the total area of the film, and  $D_{ml}$  is the diffusion coefficient of the gas through the monolayer, and since it is assumed that the gas diffuses through unoccupied sites it can be

considered to be the diffusion coefficient through the area that is not covered by the surfactant molecules. Thus, using the calculated values for  $A_{ac}/A_t$ , one is able to calculate the permeability of the monolayer. The calculated monolayer permeability as a function of the salt concentration together with the experimental values from Refs. [94,98] are presented in Fig. 14. This figure shows the good correlation between theory and experiment and implies that permeability decreases monotonically with the increasing adsorption density. The uncertainties in the model include the simple model used for the monolayer permeability, the constant diffusion coefficient, and the assumption of single dispersed vacancies. A model taking into account aggregates of vacancies may improve the results [93,109].

In the above studies the variation of the electrolyte concentration in the presence of an ionic surfactant resulted in the change of the film thickness. In another study [110], the film thickness was altered by changing the size of the hydrophilic

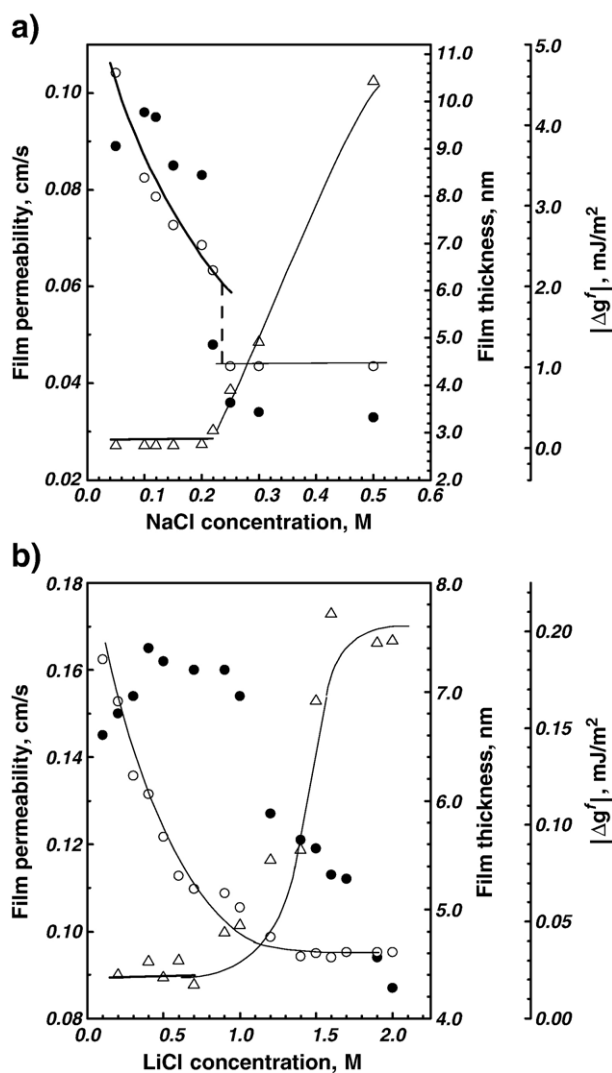


Fig. 13. Dependencies of (○) the film thickness  $h$ , (●) the permeability coefficient  $k$ , and (△) the free energy of film formation  $\Delta g^f$  on the concentration of (a) NaCl and (b) LiCl [22] Copied with permission. Copyright © 2007 American Chemical Society.

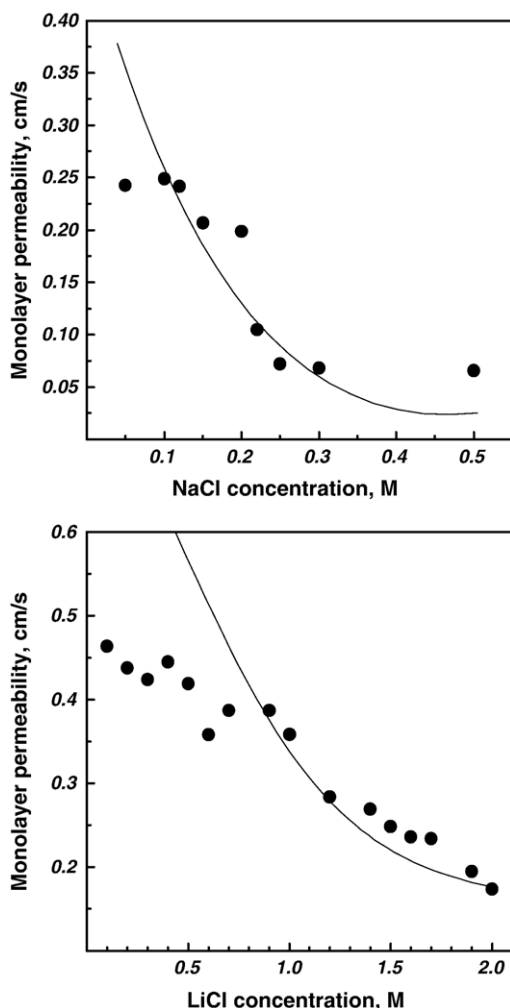


Fig. 14. Experimental dependencies of the monolayer permeability  $k_{ml}$  versus electrolyte concentration. Lines present the theoretical estimate, applying the accessible area theory for gas permeation and ECI theory [108] for the surfactant adsorption density on the film surface [22] Copied with permission. Copyright © 2007 American Chemical Society.

part of a non-ionic surfactant. The gas permeability of the films stabilized by those non-ionic surfactants increases linearly with the inverse of the film thickness as expected from Eq. (11).

#### 4.3. Temperature

It is proven that the gas permeability of the foam films increases with increasing temperature [20,53,84,94,98–100,111,112]. Early experiments on the monolayer permeability [e.g. 30,32,49,69] demonstrated that (at constant surface pressure) there is a linear relationship between  $\ln r_{ml}$  and  $1/T$ . This behavior was also observed for the permeability of foam films with a slight difference. Nedyalkov et al. [99] carried out several experiments at different temperatures while keeping the other parameters constant. They chose a limited range of temperatures, apparently because at lower temperatures the SDS solution becomes inhomogeneous and at higher temperatures the black film becomes unstable. Their measured permeabilities for a concentration above the CMC fitted the theoretical

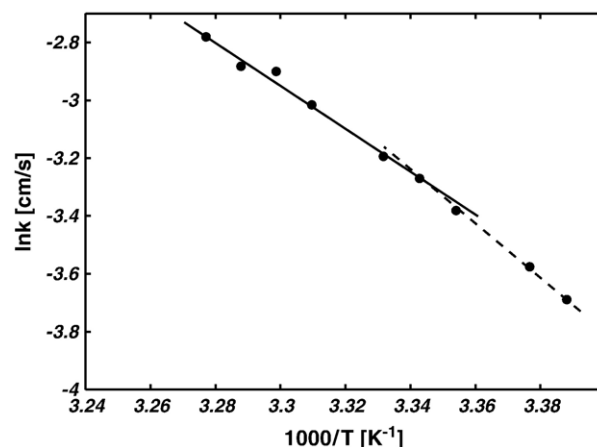


Fig. 15. Dependence of the film permeability,  $k$ , on temperature,  $T$ , in Arrhenius coordinates for NBF from 2 mM SDS+0.5 M NaCl aqueous solution. The experimental points (●) are fitted to two straight lines with different slopes [112] Copied with permission. Copyright © 2007 American Chemical Society.

predictions rather well for 23 °C and 25 °C but were slightly larger than the theoretical values for 27 °C and 30 °C (see Figs. 7 and 9). The same experiments were repeated later [112] for NBF in a wider range of temperatures (22–32 °C) while the surfactant concentration was kept above the CMC. Again, it was observed that the experimentally obtained permeability values for the NBF do not follow a straight line with a constant slope in the whole temperature range, and, as can be seen from Fig. 15, there is a kink in the  $\ln k - (1/T)$  dependence. It appears from Fig. 15 that the slope of the curve changes above  $T=26$  °C. The change in the slope of the lines suggests that there is a change in the mechanisms of gas permeation through the NBF. The experimental points were fitted into straight lines. From the slope of the dashed line in Fig. 15, the activation energy  $E_a = 73 \pm 4$  kJ/mol for lower temperatures (22–26 °C) and from the slope of the solid line the activation energy  $E_a = 63 \pm 3$  kJ/mol for higher temperatures (26–32 °C) are obtained.

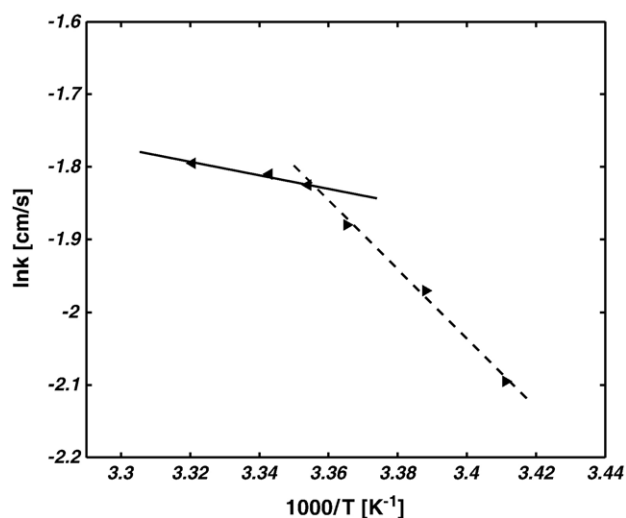


Fig. 16. Dependence of film permeability,  $k$ , on temperature  $T$  in Arrhenius coordinates for CBF from 1.73 mM SDS+0.5 M LiCl aqueous solution. The experimental points (◄) are fitted to two straight lines with different slopes [98].

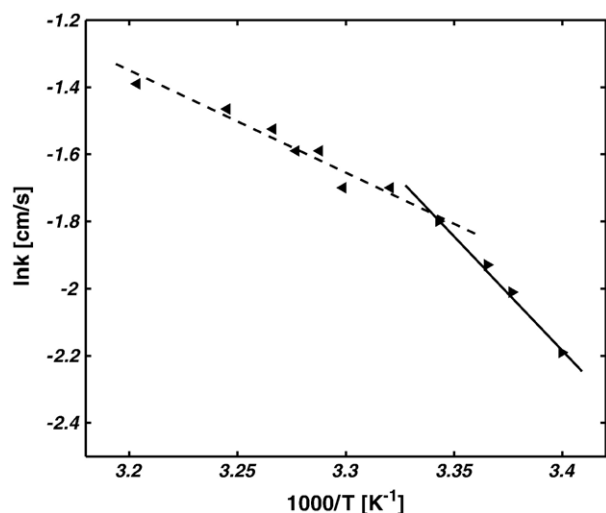


Fig. 17. Dependence of film permeability,  $k$ , on temperature  $T$  in Arrhenius coordinates for CBF from 1.73 mM SDS+0.1 M NaCl aqueous solution. The experimental points ( $\blacktriangle$ ) are fitted to two straight lines with different slopes [98].

According to these results, the authors [99,112] defined characteristic concentrations at which the permeability is equal to the background permeability, i.e.,  $k_0$ . Apparently characteristic concentration is lower than the CMC for lower temperatures (22–26 °C), while it is higher than the CMC for higher temperatures (26–32 °C). This behavior was related to the addition of the hole-mediated permeability to the background permeability (permeability of the hole-free area). However, it is possible that they did not consider the effect of micellization because they assumed that the concentration of surfactant monomer in the solution at concentrations larger than the CMC remains constant. Another explanation is that according to the nucleation theory at higher temperatures larger holes will be formed at the surface.

Figs. 16 and 17 show the temperature dependence of CBF from SDS solution in the presence of LiCl and NaCl, respectively. Similar to the NBF, the experimental points lie on two straight lines with different slopes. The cross point of two straight lines in the case of LiCl is 25 °C and in the case of NaCl is 26 °C. Therefore, at temperatures 25–26 °C, a change of the monolayer properties occurs, and the monolayer and, accordingly, the CBF becomes more permeable above these temperatures. It is interesting to note that at temperatures close to 26 °C, a phase transition was established in concentrated systems SDS+water-between gels and liquid crystalline phases [113]. An analogy between the temperature dependencies of the electroconductivity of concentrated systems such as SDS+water and the

corresponding black films properties was reported in Ref. [87]. A comparison between Figs. 15–17 illustrates that the change of the slope for CBF is more significant than for NBF. The same conclusion can be drawn from Table 1, where the activation energies calculated from the slopes of the experimental points are presented for CBF. As expected, the obtained activation energies are higher when NaCl is used as an electrolyte.

For some surfactants in a constant electrolyte and surfactant concentration, any increase in temperature decreases the adsorption density [114–119] and the absolute value of the specific interaction film free energy [120], which in turn increases the permeability of the foam film. Furthermore, 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 the gas molecules that can overcome the energy barrier and pass through the film increases.

Recently, an unexpected decrease in the gas permeability of the foam films stabilized by a non-ionic surfactant (Dodecyl Maltoside  $\beta$ -C<sub>12</sub>G<sub>2</sub>) was observed [111]. It can be observed from Fig. 18 that the gas permeability of the NBF stabilized by Dodecyl Maltoside in the presence of 0.2 M NaCl decreases with increasing temperature until it reaches a minimum (at  $T=25$  °C) and increases again with the increasing temperature. It seems that the surface density of  $\beta$ -C<sub>12</sub>G<sub>2</sub> increases below  $T=25$  °C due to the decrease in the dimension of the non-ionic surfactant head group (due to the dehydration) [121] and decreases above  $T=25$  °C as expected.

#### 4.4. Surfactant structure

The gas permeation rate of the foam films varies with different kinds of surfactants. Examination of the permeation rate of toluene through films stabilized by various surfactants showed higher rates for ionic surfactants compared to the non-ionic or weakly ionic surfactants [122]. In general, foam films stabilized by ionic surfactants are more permeable to gases than

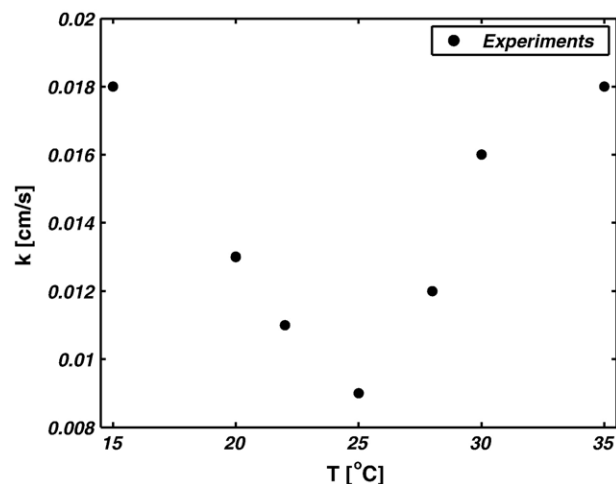


Fig. 18. Dependence of the monolayer permeability on the temperature for foam films prepared from a solution of 1 mM  $\beta$ -C<sub>12</sub>G<sub>2</sub> and 0.2 M NaCl [111] Copied with permission. Copyright © 2007 American Chemical Society.

Table 1

Electrolyte	Temperature range °C	Activation energy kJ/mol
LiCl	20–25	36±3
0.5 M	25–28	7±0.1
NaCl	21–26	59±0.2
0.1 M	26–39	26±3

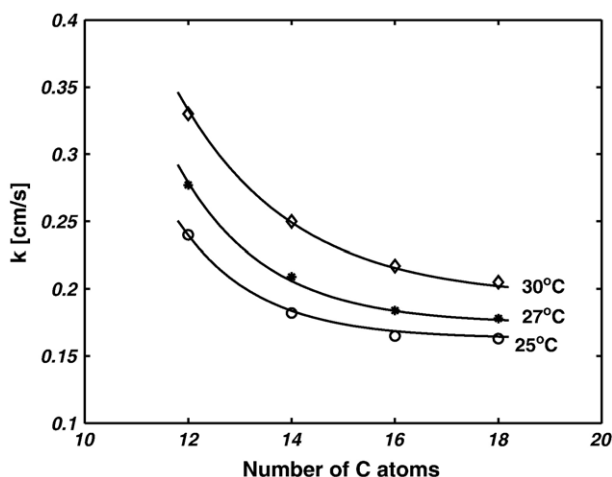


Fig. 19. The experimentally obtained film permeability of NBFs at three different temperatures as a function of number of carbon atoms in the alkyl chain of the alkyltrimethylammonium surface active cation [126].

the films stabilized by the non-ionic surfactants [100,111]. Besides the chemical properties of the surfactant, permeability of the foam films is influenced by the geometry of the adsorbed surfactant molecules. In addition to the type of the surfactant, for a certain surfactant two parameters are important in determining the permeability of the foam films: the length of the hydrophobic group and the size of the hydrophilic part.

#### 4.4.1. Chain length of hydrophobic tail

At a constant surface pressure, the permeation rate of the gases through the monolayers depends on the chain length. The permeability of the foam films decreases with increasing surfactant alkyl chain length [123,124]. The experimental results show that there is an exponential relationship between monolayer permeability and length of the hydrophobic part of the surfactant [37,41,125]. Archer and La Mer [37] found out that each  $\text{CH}_2$  group in the fatty acid monolayers contributes about 300 cal/mole to the energy barrier for water penetration, and its magnitude is independent of the surface pressure. Blank and Roughton [62] also found that depending on the geometry of the chains for penetration of carbon dioxide, oxygen, and nitrous oxide, about 200–350 cal./mol is added per  $\text{CH}_2$  group. This means that with increasing chain length of the hydrophobic part of the surfactant, the gas molecules will face higher energy barrier at the interface, i.e., it will be more difficult for gas molecules to make a hole between the surfactant molecules to pass through. Nevertheless, it is also possible that surfactants with the same number of  $\text{CH}_2$  group at the same surface pressure show different permeation rates to gases [51].

Krustev et al. [124] combined three theories of the film permeability – simple diffusion theory, energy barrier theory, and nucleation theory of fluctuation formation of holes – to explain the experimental results of the gas permeability of NBF stabilized by four alkyltrimethylammonium chloride homologues (Fig. 19). According to the *simple diffusion theory*, the hole-free part of the bilayer can be considered as a homogenous

phase. Hence,  $k_0$  should depend on the film thickness, i.e., the surfactant chain length according to Eq. (2)

$$k_0 = \frac{D_0}{a_{\text{hg}} + b_{\text{hc}}(n_C - 1)} \quad (34)$$

From the energy barrier theory [35,37,44],  $k_0$  should also depend exponentially on the number of methylene groups in the surfactant alkyl chain:

$$k_0 = \kappa \exp[(-E_r + E_{\text{CH}_2}(n_C - 1))/R_B T] \quad (35)$$

where  $\kappa$  is a constant,  $E_r$  is the activation energy due to the polar headgroup and the terminal methyl group, and  $E_{\text{CH}_2}$  is the activation energy required to separate any methylene group from the groups in the neighboring molecules. It is assumed that the change of hydrophobic chain length of the surfactant only changes the background permeability. Thus, replacing Eqs. (34), (35) and Eq. (12) provides

$$k = \kappa \exp[(-E_r + E_{\text{CH}_2}(n_C - 1))/R_B T] + \sum_{i=1}^{\infty} k_i \quad (36)$$

Therefore, permeability of the holes is not influenced by the length of hydrocarbon tail of the surfactant. The critical micelle concentration decreases with increasing chain length. This enhances the permeability of the foam films. However, on the other hand, with increasing chain length the interaction between the surfactant molecules and the thickness of the film increases. This effect decreases the permeability of the film. The simultaneous action of both effects will make the hole-mediated permeability independent of the surfactant chain length.

#### 4.4.2. Headgroup size

The permeability of foam films stabilized by a series of non-ionic oxethylated dodecanol surfactants ( $\text{C}_{12}\text{E}_n$ ) appears to change with different sizes of the headgroups. In the sandwich model, the headgroup of the surfactant molecules tend to stay in

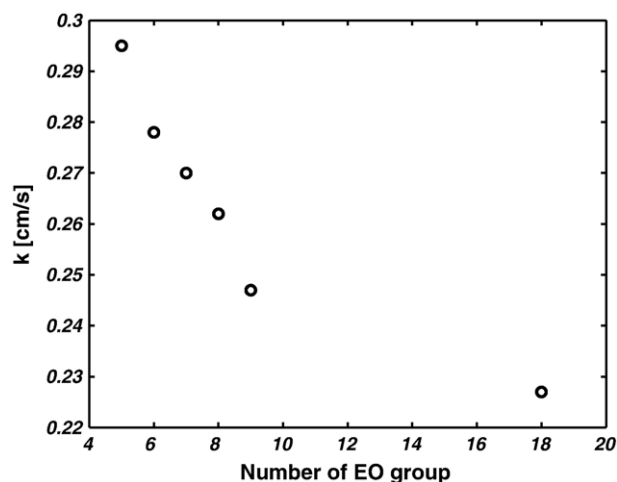


Fig. 20. Gas permeability of foam films depending on the number of EO groups in the stabilizing oxethylated dodecanole,  $C_s = 2 \times \text{CMC}$ ,  $T = 22^\circ\text{C}$  and  $C_{\text{NaCl}} = 0.1\text{ M}$  [110]. Copied with permission. Copyright © 2007 American Chemical Society.

the liquid core, which is between two monolayers of hydrophobic chains of surfactant molecules. In non-ionic surfactants of  $C_{12}E_n$  these headgroups are larger and may form a gel-like phase [110,126] inside the liquid core, which is less permeable to the gas molecules. Thus, as can be observed from Fig. 20, the permeability of the foam films decreases with increasing size of headgroups of non-ionic surfactants. In another study [122], the diffusion rates of the toluene through surfactants with different hydrophilic chain lengths were measured. The used surfactants were Igepal, which is composed of only a hydrophilic and hydrophobic part, and Pluronic, which is composed of a hydrophobic section connected at both ends to two hydrophilic sections. The diffusion rate of the toluene was found to increase with the increasing hydrophilic chain length of the Igepals and with the decreasing hydrophilic chain length of Pluronic. These results were interpreted as the net result of two counteracting effects, the extent of the surfactant chain entanglement and the thickness of the water layer with the chain entanglement effect favoring higher permeation rate, which is obviously in contrast to the findings about the oxethylated dodecanol surfactants.

#### 4.5. Number of foam films

Nguyen et al. [20] measured the diffusion of a gas (Ar) through a train of foam films in a cylinder, as shown in Fig. 3, to obtain the  $k_{\text{eff}}-n_f$  relationship and validate their model. Fig. 21 shows that the measured effective film resistance  $1/k_{\text{eff}}$  varies linearly with  $n_f$ , as expected from Eq. (22). The intersection between the straight line fit and the  $y$ -axis gives  $k_g$ , from which  $D_g$  can be obtained. From the slope of the line, one is able to calculate the value of  $k$ , which theoretically must be the same value as that obtained from the experiments with a single foam film. Fig. 22 shows the drastic decrease of  $k_{\text{eff}}$  for a few films. For an increasing number of the films,  $k_{\text{eff}}$  reduces only slowly,

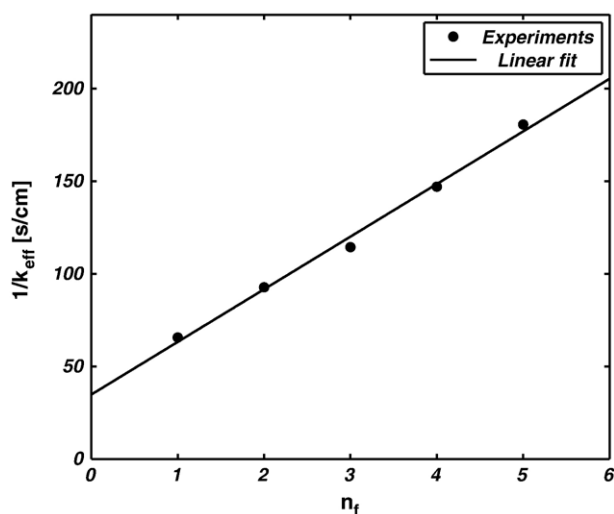


Fig. 21. Predicted and experimental reciprocal of the effective film permeability to Ar as a linear function of the number of the foam films (SDS surfactant solution of  $2 \times 10^{-3}$  M) [20].

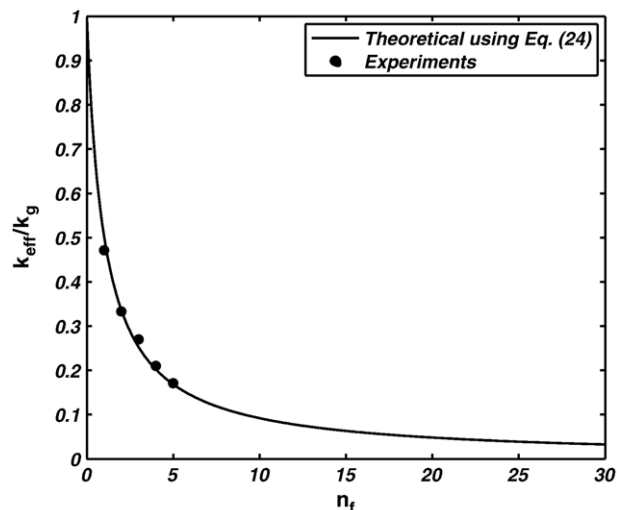


Fig. 22. Predicted and experimental film permeability reduction factor for Ar gas as a function of the number of films (2 mM SDS+0.5 M NaCl aqueous solution) [20].

since the resistance in the bulk gas phase becomes marginal relative to the total resistance of the films.

## 5. Conclusions and outlook

The measurement of the gas permeability of foam films is a powerful tool for studying the stability and lifetime of foams, the interaction between the foam film-forming adsorbed monolayers, and the structure of the film. It also facilitates the better understanding of the mass transfer of gases through gas-liquid interfaces, which is favorable in many fields of science and engineering. Owing to the similarities of foams and emulsions, the results of foam film permeability measurements can be effectively adopted to study the long-time stability of emulsions.

The gas permeability of a foam film is a complex phenomenon, which is a function of various parameters: the structure and state of the surface film, the nature and concentration of the surfactant, the electrolyte concentration, etc. Despite the importance of the gas permeability of the foam films, the number of studies devoted to this subject has remained limited.

The current models mostly give good explanations for the gas permeability of the Newtonian black films, which are missing the liquid core. Moreover, the current models are not able to describe the permeability of the foam films in the surfactant concentrations far below CMC. However, the permeability behavior of the thicker common black films is not fully described by the existing film permeability models and is yet to be fully identified. Apparently, the physico-chemical properties of the adsorbed surfactant molecules in the presence of a thick liquid core play a more significant role in the foam permeability than thus far believed. This hints to how further studies of the foam permeability should be oriented in the future.

Besides the investigation of the permeability of the inert gases through common black films, much more effort should be devoted to electrolyte gases, i.e. gases such as carbon dioxide

(CO<sub>2</sub>) and ammoniac (NH<sub>3</sub>), which produce ions upon dissolution in water. These produce a broader range of applicability, and their understanding is a necessary first step towards the study of more complex systems including large micellar entities and polymers. New intriguing effects are likely to arise when considering these systems.

In forming a global perspective on the future studies of foam films we need to consider more closely the experimental techniques employed. For both monolayers and foam films the experimental observations relied on measurements of the variations of the concentration of the diffusing species across the ‘barrier’, i.e. at the in-and out-flow sides of the thin liquid system. Hardly any attempt was made to measure simultaneously the structural characteristics and the permeability of the foam films. NMR and X-ray diffraction or microtomography could play a significant role in this endeavor. It is expected that attempting such kind of approach will give more directly access to the dynamic relation between the microscopic structure of the foam film and inherently macroscopic (phenomenological) film permeability. It will lift prevailing uncertainties concerning the validity of the mechanisms proposed for the gas permeation. On the theoretical side more should be devoted to harness the most recent development in molecular dynamics theory to capture the different aspects of the gas permeation.

Last, but not least, the rising interest in the foam films stabilized by solid (nano)-particles and the industrial importance of such systems, e.g. in the production of heavy oils, opens a new door to the study of the permeation of gases through such complex interfaces.

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