

# NANOSTRUCTURES AND STABILITY OF

# **THIN LIQUID LAYERS**

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PhD Thesis

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## Abstract

The Thesis is focused on determination and evaluation of importance of nanostructures of adsorption layers and hydrophobic solids surfaces on properties and stability of thin liquid films (TLF), formed at the liquid/gas and liquid/solid interfaces under dynamic conditions. Phenomena occurring during collision of the bubble with liquid/air and liquid/solid interfaces, were studied using a high-speed camera, working with a frequency 1040 Hz. Influence of surface active substances (SAS) and the dynamic architecture of the adsorption layer (DAL) formed over surface of the rising bubble on the bubble impact velocity, bouncing time and amplitude, the timescale of the bubble coalescence at liquid/gas interface, kinetics and mechanism of the three-phase contact (TPC) formation at hydrophobic solid surfaces was studied for two different locations (L=3 mm and L= 250 mm) of the interfaces, in respect to the point of the bubble formation (capillary orifice).

At extremely low SAS concentrations the bubble coalescence time  $(t_c)$ , was slightly shortened due to diminishing of the bubble bouncing time and amplitude. Further concentration increase, above a "threshold" value, resulted in significant prolongation of the bubble coalescence time, due to increased stability of the liquid film formed between the colliding bubble and solution/air interface. Thicknesses of the liquid films at the moment of their rupture, under dynamic conditions, were calculated on the basis of the experimentally determined the film lifetime  $(t_{film})$  values. It was found that at low of n-octanol concentrations the thicknesses of the rupturing films were of an order of a few µm, that is, much larger than the thicknesses measured, using microinterferometric method, for the films formed under static conditions. However, at high SAS concentrations the films rupture thicknesses were similar order for dynamic and static conditions. Surface roughness is the factor of crucial importance for the kinetic of the TPC formation at hydrophobic solid surfaces, both in absence and presence of the surface active substances. In solutions of SAS the time of the TPC formation  $(t_{TPC})$  was a bit shortened at low concentrations, and significantly prolonged at high concentrations due to a significant increase of the drainage  $(t_D)$  time of the films formed at the hydrophobic surfaces studied. The prolongation of the time of the TPC formation is attributed to air presence in the cavities and scratches of hydrophobic surface and mechanism responsible for prolongation of the  $t_{TPC}$  at high concentrations of surface active substances is proposed.

## Streszczenie

Praca doktorska jest poświęcona określeniu roli nanostruktur warstw adsorpcyjnych i hydrofobowych powierzchni ciał stałych w stabilności cienkich filmów ciekłych (TLF), powstających w warunkach dynamicznych na granicach międzyfazowych: ciecz/gaz i ciecz/ciało stałe. Zjawiska zachodzące w czasach milisekundowych w trakcie kolizji pęcherzyków powietrza z powierzchniami międzyfazowymi ciecz/gaz i ciecz/ciało stałe monitorowano przy użyciu szybkiej kamery o częstotliwości 1040 Hz. Badano wpływ stężenia substancji powierzchniowo aktywnych (SAS) oraz architektury dynamicznej warstwy adsorpcyjnej (DAL) na prędkość kolizji, czas i amplitudę odbić pęcherzyka, czasy koalescencji pęcherzyków na powierzchni swobodnej, kinetykę i mechanizm powstawania kontaktu trójfazowego (TPC) na hydrofobowych powierzchniach ciał stałych. Powierzchnie międzyfazowe umieszczane były w dwóch różnych odległościach (L= 3 i L= 250 mm) od punktu tworzenia pęcherzyka (kapilara).

W bardzo niskich stężeniach roztworów SAS, czasy koalescencji pęcherzyków ( $t_c$ ) ulegały skróceniu w wyniku zmniejszania czasu i amplitudy odbić pęcherzyków. Przy wyższych stężeniach, powyżej pewnej "granicznej" wartości, następowało znaczne wydłużenie czasu koalescencji spowodowane zwiększeniem stabilności cienkiego filmu powstającego pomiędzy pecherzykiem a powierzchnia międzyfazowa roztwór/powietrze. Grubości filmów ciekłych w momencie ich pękania w warunkach dynamicznych były wyznaczane w oparciu o eksperymentalne wartości czasów życia pecherzyka  $(t_{film})$ . Stwierdzono, że w wodzie i przy niskich stężeniach n-oktanolu grubości tych filmów były rzędu kilku µm, tj. znacznie wyższe niż zmierzone metodą mikrointerferometryczną grubości filmów powstających w warunkach statycznych. Jednakże, grubości filmów w momencie rozrywania były podobne w warunkach dynamicznych i statycznych dla wysokich stężeń SAS. Szorstkość powierzchniowa jest czynnikiem o kluczowym znaczeniu w kinetyce powstawania kontaktu trójfazowego na hydrofobowych powierzchniach, zarówno w wodzie jak i w roztworach SAS (jonowych i niejonowych). W roztworach o małych stężeniach, czasy powstawania kontaktu trójfazowego ulegały skróceniu w porównaniu do wartości zmierzonych w czystej wodzie. Natomiast, przy wysokich stężeniach badanych SAS, zaobserwowano znaczne wydłużenie czasów powstawania kontaktu trójfazowego związane z wydłużeniem czasów wyciekania filmów. W pracy przedstawiono mechanizm wydłużenia czasu powstawania kontaktu trójfazowego i wykazano, że efekt ten jest związany obecnością powietrza na hydrofobowych powierzchniach ciał stałych o różnej szorstkości powierzchniowej.

# List of Symbols and Abbreviations

## Latin Symbols

4	C C
A	area of surface
$A_b$	area of bubble surface
$A_R$	real area of surface
$A_G$	geometrical area of surface
$A^{\prime\prime}$	Hamaker constant
a	activity
$a_+$	activity of cationic surfactant ion
<i>a</i> _	activity of counterion
$a_F$	parameter of Frumkin isotherm
Ar	Archimedes number
$b_c$	channel dimension
С	coefficient in the atom-atom pair interaction
$C_D$	drag coefficient
$C_m$	mass coefficient
С	concentration
$C_c$	channel dimension
$C_{el}$	electrolyte concentration
$c_{el}^{+}$	cation concentration
$C_{el}$	anion concentration
$c_i^{\alpha}$	concentrations of the i-component in phase $\alpha$
$c_i^{\beta}$	concentrations of the i-component in phase $\beta$
<i>c</i> *	mean ionic product concentration
$\mathcal{C}_{R^+}$	concentrations of surfactant ion
$c_{X-}$	concentrations of counterion
$c_{i+}(x)$	local concentrations of all cations in double layer
$c_{i-}(x)$	local concentration of all anions in double layer
$c_{i+b}$	concentrations of all cations in bulk
C <sub>i-b</sub>	concentration of all anions in bulk
$c_0$	surfactant bulk concentration
$C_{SS}$	surfactant concentration in the "subsurface"
D	diffusion coefficient
$D_S$	surface diffusion coefficient
$d_b$	bubble diameter
$d_c$	inner diameter of capillary
$d_e$	equivalent diameter
$d_h$	horizontal diameter
$d_v$	vertical diameter
$E_k$	kinetic energy
$E_s$	streaming potential
е	elementary charge
Eo	Eovots number
F	Faraday constant
$F_B$	buoyancy force
$F_D$	drag force
$F_T$	driving force

Fl	Flow number
f	fraction of the projected area that is wet
$f_{\pm}$	average coefficient of ions activity
G	Gibbs free energy
$G^{lpha}$	Gibbs free energy of phase $\alpha$
$G^{eta}$	Gibbs free energy of phase $\beta$
$G^{\gamma}$	Gibbs free energy of interface $\gamma$
g	gravitational acceleration
H	hysteresis
$H_{S}$	parameter describing interactions between molecules at the surface
ĥ	film thickness
ha	foam film thickness
hcr	critical thickness of rupturing
$h_P$	Planck constant
$h_{wf}$	wetting film thickness
I	monochromatic light intensity
J	flux
i.	adsorption flux
ju Id	desorption flux
K K	adsorption equilibrium constant
$K_{a}$	cell electric conductivity
K <sub>H</sub>	Henry adsorption equilibrium constant
$K_I$	Langmuir adsorption equilibrium constant
$K_{F}$	Frumkin adsorption equilibrium constant
k	Boltzmann constant
<i>k<sub>ad</sub></i>	rate constants of adsorption process
<i>k</i> <sub>des</sub>	rate constants of desorption process
$k_\lambda$	interference order
$L_c$	channel dimension
l	number of domains or rings in the film
l <sub>im</sub>	capillary immersion depth
$l_D$	Debye length
Ly	Lyashchenko number
Мо	Morton number
n	refractive index of medium in the visible light
$n_i$	number of moles of i-component
$n_i^{\gamma}$	number of moles of i-component adsorbed at interface $\gamma$
$n_s$	number of moles of the surfactant adsorbed at the bubble surface
$n_{\lambda}$	refractive index of solution
P	pressure
$P_{0}$	pressure in the bulk liquid phase
$P_f$	pressure exerted by the dispersed phases on the interlayer
$P_m$	osmotic pressure
$P_{max}$	maximum pressure
$P_{\gamma}$	capillary pressure
$\Delta P$	pressure difference
$\Delta P_f$	"total" pressure causing film squeezing
$\Delta P_h$	hydrostatic pressure difference
R	gas constant
$R_c$	capillary radius
$R_e$	net electric resistance

$R_{cell}$	capillary radius in Scheludko-Exerowa cell
$R_{cur}$	curvature radius
$R_f$	film radius
r	distance between the point with given concentration and the bubble center
$r_s$	instantaneous radius of growing bubble
$\tilde{r_w}$	roughness ration
r <sub>f</sub>	roughness ratio of wet area
Re	Reynolds number
S	entropy
$S^{\alpha}$	entropy of phase $\alpha$
$S^{\beta}$	entropy of phase β
$S^{\gamma}$	entropy of interface $\gamma$
$S_{h}$	surface of projection on a horizontal plane of the body
$S_C$	spreading coefficient
T	temperature
t	time
thouncing	time of bubble bouncing
t <sub>C</sub>	time of bubble coalescence
tn	time of film drainage
t <sub>film</sub>	film lifetime
t <sub>TPC</sub>	time of three-phase conctact formation
U	internal energy
$U^{lpha}$	internal energy of phase $\alpha$
$U^{\!eta}$	internal energy of phase $\beta$
$U^{\gamma}$	internal energy of interface $\gamma$
$U_b$	bubble velocity
$U_f$	fluid velocity
$U_{imp}$	bubble impact velocity
$U_s$	expansion velocity
$U_T$	terminal velocity
$W_A$	work of adhesion
$W_C$	work of cohesion
We	Weber number
V	volume
$V^{\alpha}$	volume of phase $\alpha$
$V^{\beta}$	volume of phase $\beta$
$V^{\gamma}$	volume of interface $\gamma$
$V_b$	bubble volume
$V_f$	velocity of film thinning
$V_{Re}$	Reynolds velocity
$V_S$	Scheludko velocity
$V_{MTsR}$	MTsR velocity
$V_{RDI}$	RDI velocity
$V_{ShR}$	Sharma-Ruckenstain velocity
Ve	Velocity number
$X_i$	molar fractions of i-component
x	distance
$x_i$	bubble coordinate
$x_{\delta}$	Stern distance
$x_{\zeta}$	distance between surface and shear plane
${\mathcal Y}_i$	bubble coordinate

$Z_i$	charge of the	i-component
	-	-

- charge of surfactant ion charge of counterion
- $Z_s$  $Z_c$

## **Greek Symbols**

$\alpha_s$	"surface activity" of surfactant ion
$\alpha_c$	"surface activity" of counterion
β	coordinate relative of instantaneous position of the bubble surface
$\Gamma_i$	interfacial excess of i-component
$\Gamma_i^{\alpha\beta}$	surface concentration of i-component in interfacial layer $\alpha\beta$
$\Gamma_{\infty}$	maximum surface excess
$\Gamma_{R^+}$	surface excess of surfactant cation R <sup>+</sup>
$\Gamma_{X-}$	surface excess of counterion X
$\Gamma_{RX}$	surface excees of surfactant RX
$\Gamma_{RX\infty}$	maximum surface excees of surfactant RX
$\Gamma_s$	surface concentration of surfactant ion
$\Gamma_c$	surface concentration of counterion
$\Gamma_{s\infty}$	limiting surface concentration of surfactant ion
$\Gamma_{c\infty}$	limiting surface concentration of counterion
$\Gamma_{i^+}$	surface concentration of all cations
$\Gamma_{i}$ -	surface concentration of all anions
γ	surface tension
$\gamma^{0}$	surface tension of pure solvent
ŶSV	interfacial tensions of solid-vapor interface
ŶSL	interfacial tensions of solid-liquid interface
$\gamma_{LV}$	interfacial tensions of liquid-vapor interface
8	static dielectric constant
$\mathcal{E}_0$	vacuum permittivity
$\mathcal{E}_r$	relative permittivity
ζ	zeta potential
η	dynamic viscosity
$\eta_L$	liquid dynamic viscosity
$\eta_G$	gas dynamic viscosity
Θ	surface coverage
$\Theta_s$	relative surface concentrations of surfactant ion
$\varTheta_c$	relative surface concentrations of counterion
$\theta$	contact angle
$ heta_{ad}$	advancing contact angle
$ heta_{rec}$	receding contact angle
$ heta_Y$	Young contact angle
$ heta_W$	Wenzel contact angle
$ heta_{CB}$	Cassie-Baxter contact angle
κ	Debye-Huckel parameter
λ	wavelength
$\lambda_I$	parameter specific for the isotherm
$\mu_i$	chemical potential of i-component
$\mu_i^{\alpha}$	chemical potential of i-component in phase $\alpha$
$\mu^{\gamma\beta}$	chemical potential of i-component in phase $\beta$
$\mu_i^{\gamma}$	chemical potential of i-component at interface $\gamma$

v	absorption frequency
ξ	amplitude
Π	disjoining pressure
$\Pi_{vdW}$	van der Waals component of disjoining pressure
$\Pi_{el}$	electrostatic component of disjoining pressure
$\Pi_{non-DLVO}$	non-DLVO component of disjoining pressure
$\pi$	surface pressure
ρ	charge density
$ ho_L$	liquid density
$\Delta \rho$	density difference
σ	charge
$\sigma_0$	surface charge
τ	time
$\phi_s$	corrections related to the lateral interaction between surfactant ions
$\phi_c$	corrections related to the lateral interaction between counterions
$arphi_i$	number of atoms per unit volume of i-component
χ	bubble deformation degree
Ψ	electrostatic potential
$\Psi_0$	surface electrostatic potential
$\Psi_m$	electrostatic potential of mid-plane
$\Psi_\delta$	Stern potential
ω	area per molecule in the close-packed surface layer

## Abbreviations

AFM	Atomic Force Microscope
CB Eq.	Cassie-Baxter Equation
CBF	Common Black Film
CCC	Critical Coalescence Concentration
CMC	Critical Micelle Concentration
CTABr	Cetyltrimethylammonium Bromide
DBMM	Drop & Bubble Micro Manipulator
DLVO	Derjaguin-Landau-Verwey-Overbeek theory
EDL	Electric Double Layer
ftp	Frames per Second
IHL	Inner Helmholtz Layer
IHP	Inner Helmholtz Plane
LRHF	Long Range Hydrophobic Forces
MTsR	Manev-Tsekov-Radoev model
NBF	Newton Black Film
OHL	Outer Helmholtz Layer
OHP	Outer Helmholtz Plane
<i>P-B Eq.</i>	Poisson-Boltzmann Equation
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PZR	Point of Zeta Reversal
RDI	Radoev-Dimitrov-Ivanov model
Rh	Rhamnolipid
SAS	Surface Active Substance
SFA	Surface Force Apparatus

- Surface Quasi Two Dimensional Electrolyte model Thin Liquid Film Three-Phase Contact
- STDE TLF TPC

I. LITERATURE REVIEW

### 1. Introduction.

This PhD Thesis is focused on dynamic phenomena occurring during collision of the rising bubble with liquid/air and liquid/solid interfaces. When the bubble collides with liquid/air or liquid/solid interface a thin liquid film (TLF) between the bubble and interface is formed. If the TLF formed is unstable and the collision time is long enough for the draining film to reach a critical thickness of its rupture then (i) for liquid/air interface the coalescence take place or (ii) for solid surface the three-phase contact (TPC): gas-liquidsolid can be formed. Thus, the properties and stability of the thin liquid films formed plays significant role in kinetics of these processes. The formation and stability of the liquid films under dynamic conditions, i.e. during collision of the bubble with different interfaces, is of the great importance for variety of technological processes, i.e. froth flotation, pulp and paper industry, wetting/dewetting, foam separation, wastewater treatment and many others. The liquid films are fundamental elements of various dispersed system determining in a great extent conditions of their formation, final properties and applicability. Outcome of the bubble collisions depends on many mutually interconnected factors such as: bubble size, the bubble impact velocity and shape deformations, the collision contact time, presence and state of adsorption layer at the interacting surfaces, size and stability of the liquid film formed, surfactant adsorption kinetics and drainage velocity of the liquid films formed, etc. Thus, knowledge about influence of these factors on mechanisms and kinetics of the formation, drainage, stability and/or rupture of the liquid films formed under dynamic conditions are the fundamental questions to be understood.

In pure liquids, the velocity of the rising bubbles depends on the viscosity and density of the continuous phase and the bubble diameter, while in solutions of surface active substances (SAS) the bubble rising velocity is lowered as a result of formation of the motion induced dynamic architecture of adsorption layer (DAL) over the bubble surface, which retards fluidity of the interface. Thus, the kinetic of the film rupture in SAS

solutions of different concentration is changed not only due to lowering of the bubble impact velocity, but also as a result of (i) retardation of the film thinning velocity, and (ii) increased stability of the films formed against external disturbances.

Even in the case of pure liquids, as showed earlier, the coalescence of a bubble at free surface does not have to take place during the first collision. This phenomenon is related to the bubble bouncing, which occurs when the bubble collision time is shorter than the time needed for the film formed to drain to its critical thickness of rupture. In my PhD Thesis, influence of SAS concentration and dynamic architecture of the adsorption layer (DAL) on the bubble impact velocity, bouncing at the solution surface and stability of the films formed by the colliding bubble at liquid/gas and different solid surfaces, kinetics of the TPC formation at various solid surfaces and properties of the microscopic foam films was studied.

For the three-phase contact formation and attachment of the colliding bubble to a hydrophobic solid surface the liquid film needs to drain and rupture at its critical rupture thickness. In such processes, during bubble-solid collisions, stable TPC and bubble attachment occurs only, when thinning and rupture of the thin liquid layer separating the colliding entities is quicker than a collision time (millisecond scale). Otherwise, the bubble rebounds from the surface, what can significantly affect the attachment time. Thus, properties and stability of the thin liquid film formed between colliding bubble and a solid surface is a key-factor determining the time scale of TPC formation. Stability of thin liquid film is described by DLVO theory. Nevertheless, for hydrophobic surfaces interacting in aqueous solutions some "Long Range Hydrophobic Forces" (LRHF), not included in DLVO theory, were reported. Nowadays, it is rather commonly accepted that these additional "long range forces" were due to interactions between nanobubbles presence at the interacting surfaces due to high affinity of air to hydrophobic solids. As affinity to air is a typical feature of all hydrophobic surfaces, therefore, air can be always present at such

surface (in a form of micro- and nano bubbles) immersed into aqueous phase. The presence of air can affect the mechanism of the TPC formation and attachment of the colliding bubble. In this Thesis, new results obtained, which show importance of air entrapped at hydrophobic surfaces in kinetics and mechanisms of the TPC formation, are presented and discussed in details.

### 2. Liquid/Gas Interfaces.

A phase of a substance is defined as a form of matter that is uniform throughout in chemical composition and physical state. There are mainly three phases of matter namely solid, liquid and gas, separated from each other by the boundary region called interface. The physical properties of interfaces differ from those of the bulk. The intensive properties of the system change from those of one phase to those of another through the interfacial region. The positive free interfacial energy, which is a consequence of the unbalanced forces between the molecules in the interface vicinity, i.e. asymmetric forces acting on molecules and atoms (Fig. 2.1), is a condition of existence of the stable interface.



**Fig. 2.1.** Schematic illustration of the forces interacting between molecules at the surface and in the interior of the liquid.

The increase of the free surface energy is proportional to the area of the surface (A) and the molecules surface density. The surface excess of Gibbs free energy (G) can be expressed in form (Adamson and Gast, 1997; Butt et al., 2003):

$$dG = -SdT + VdP + \gamma dA + \sum_{i} \mu_{i} dn_{i}$$
(2.1)

where *S* is the entropy, *T* is the temperature, *V* is the volume of the system, *P* is the pressure,  $\mu_i$  is the chemical potential of *i*-component,  $n_i$  is the number of moles of *i*-component in the system and  $\gamma$  is the surface energy, called also surface or interfacial tension and presents the uncompensated intermolecular forces in the bulk phase. For the *i*-component forming the interface, when the *T*, *P* and  $n_i$  are constant, the  $\gamma$  can be given by (Butt et al., 2003):

$$\gamma = \left(\frac{\mathrm{dG}}{\mathrm{dA}}\right)_{\mathrm{P,T,i}} \tag{2.2}$$

The surface tension is linked with the concept of the adsorption. Adsorption is the accumulation of substances at the interface. There are two principal types of adsorption of molecules at interfaces: (i) physical adsorption, where the bonding is weak (van der Waals type forces) and (ii) chemisorption, where chemical bonds between the adsorbate and substrate are formed (Adamson and Gast, 1997). Adsorption of the substances called surface active agents (or surfactants) usually causes decreasing of the surface tension, due to lowering of the surface free energy of the system. This ability of the surface active substances (SAS) is the result of their characteristic structure, which consist of two main blocks: (i) hydrophilic "head-group" and (ii) hydrophobic "tail". The hydrophilic parts of the SAS molecules consist polar groups which interact strongly with water (hydroxyl, carboxyl, ionic groups), where the hydrophobic "tails" are non-polar and usually contain aliphatic and/or aromatic carbon chains of different lengths (Everett, 1988). Depending on type of the hydrophilic head group the four main groups of surfactants can be distinguished (Dukhin et al., 1995; Pletnev, 2001):

- nonionic (no ionic charge of the molecule)
- anionic (negatively charged head-group)
- cationic (positively charged head-group)
- zwitterionic (both charges can be presented in the molecule structure)

In highly concentrated solutions, when the surfactants molecules are packed so closely together at the interface, that no further adsorption is possible there, the surfactants show ability to self-assembly in the bulk into various structures, including the formation of micelles, bilayers, liquid crystals and many others. The concentration at which surfactants begin to form micelles is known as the Critical Micelle Concentration (CMC) (Everett, 1988; Adamson and Gast, 1997).

A characteristic property of solutions and dispersed systems is diffusion, defined as a random transport of the molecules or particles due to the concentration gradient. The rate of diffusion is proportional to the concentration gradient and is described by the Fick's first law:

$$J = -D\frac{dc}{dx}$$
(2.3)

where J is a flux of particle or molecule, D is the diffusion coefficient and c is a concentration and dc/dx is a concentration gradient in one dimension. Application of this equation is limited to the systems, where the concentration gradient (and diffusion flux) is constant, i.e. for the steady-state conditions. In most cases, however, J as well as c is the functions of distance and time. The relationship between these parameters, for the three-dimensional system, is given by the Fick's second Law:

$$\frac{\partial c}{\partial t} = -D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right)$$
(2.4)

#### 2.1. Thermodynamic Models.

The presence of an interface influences generally all thermodynamic parameters of the system. To consider the thermodynamics of a system with an interface, it is necessary to divide that system into three parts: the two bulk phases  $\alpha$  and  $\beta$ , and the interface  $\gamma$ . There are two main theoretical approaches describing divided system: (i) Gibbs and (ii) Guggenheim (Butt et al., 2003).

### 2.1.1. Gibbs Approach.

In this convention the two phases of volume  $V^{\alpha}$  and  $V^{\beta}$  are thought to be separated by an infinitesimal thin boundary layer, the Gibbs dividing plane, also called an ideal interface (Fig. 2.2) (Adamson and Gast, 1997; Butt et al., 2003). At this Gibbs dividing plane (surface) are "accumulated" adsorbed molecules and their "excessive concentration", in comparison to concentration in the bulk (see Fig. 2.2), called Gibbs surface excess ( $\Gamma_i$ ), is defined as:

$$\Gamma_{i} = \frac{n_{i}^{\gamma}}{A}$$
(2.5)

where  $n_i^{\gamma}$  is a number of these moles and *A* is the surface area. In the Gibbs model, the interface is ideally thin ( $V^{\gamma} = 0$ ) and the total volume is:

$$V = V^{\alpha} + V^{\beta} \tag{2.6}$$



Fig. 2.2. Schematic illustration of the Gibbs dividing surface.

The excess amount of the *i*-component adsorbed at the dividing surface is given as (Dukhin et al., 1995):

$$n_i^{\gamma} = n_i - \left(c_i^{\alpha} V^{\alpha} + c_i^{\beta} V^{\beta}\right)$$
(2.7)

where  $c_i^{\alpha}$  and  $c_i^{\beta}$  are the concentrations of the *i*-component in phases  $\alpha$  and  $\beta$ , respectively. All other extensive quantities, e.g. the internal energy (*U*), the entropy (*S*) or the Gibbs free energy (*G*) can be written as a sum of three components: one of bulk phase  $\alpha$ , one of bulk phase  $\beta$ , and one of the interfacial region  $\gamma$  (Dukhin et al., 1995; Butt et al., 2003):

$$U = U^{\alpha} + U^{\beta} + U^{\gamma}$$
(2.8)

$$S = S^{\alpha} + S^{\beta} + S^{\gamma} \tag{2.9}$$

$$G = G^{\alpha} + G^{\beta} + G^{\gamma}$$
(2.10)

For the constant *P* and *T*, the  $G^{\gamma}$  can be expressed by:

$$G^{\gamma} = \sum_{i} \mu_{i} n_{i}^{\gamma} \tag{2.11}$$

and the chemical potential of the *i*-component at the interface is:

$$\mu_{i}^{\gamma} = \left(\frac{\partial G^{\gamma}}{\partial n_{i}^{\gamma}}\right)_{\mathrm{T,p}}$$
(2.12)

For equilibrium condition, the following relation is fulfilled:

$$\mu_i^{\gamma} = \mu_i^{\alpha} = \mu_i^{\beta} \tag{2.13}$$

As the volume of the interface is equal to zero, thus, at the constant temperature it is possible to obtain that:

$$Ad\gamma + \sum_{i} n_{i}^{\gamma} d\mu_{i} = 0$$
(2.14)

The general form of the Gibbs adsorption equation therefore is:

$$-d\gamma = \sum_{i} \Gamma_{i} d\mu_{i}$$
(2.15)

The simplest application of the Gibbs adsorption isotherm is a system of two components, e.g. a solvent I and a solute 2. In this case, we have:

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \tag{2.16}$$

When at the Gibbs plane is conveniently located so that the solute surface excess  $\Gamma_I = 0$ , then we obtain:

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$$d\gamma = -\Gamma_2^{(1)} d\mu_2 \tag{2.17}$$

and the superscript "(1)" indicates that this is relative surface excess. The chemical potential of the solute is described by the equation:

$$\mu_2 = \mu_2^0 + RT \ln a_2 \tag{2.18}$$

where  $\mu_2$  is a standard chemical potential of the 2<sup>nd</sup> component in the solution and  $a_2$  its activity, *R* is the gas constant. For diluted solutions, one can assume, that  $a_2 \approx c_2$ , where  $c_2$  is the concentration of the 2<sup>nd</sup> component. Differentiation with respect to *c* at constant temperature leads to:

$$d\mu_2 = RT d \ln c_2 \tag{2.19}$$

Substituting this into Eq. (2.17) gives the Gibbs adsorption isotherm of the  $2^{nd}$  component:

$$\Gamma_2^{(1)} = -\frac{1}{\mathrm{RT}} \frac{\mathrm{d}\gamma}{\mathrm{d}\,\mathrm{lnc}_2} \tag{2.20}$$

#### 2.1.1. Guggenheim Approach.

The Guggenheim approach is closer to the real situation, i.e. takes into account that real interfacial region has a volume (Fig. 2.3) (Adamson and Gast, 1997). The system therefore consists homogenous  $\alpha$  and  $\beta$  phases and the interfacial layer  $\alpha\beta$ . All changes in properties from the phase  $\alpha$  to  $\beta$  occur inside  $\alpha\beta$  layer in a continuous way. The total surface concentration of components, *1* and *2*, in such interface are  $\Gamma_1^{\alpha\beta}$  and  $\Gamma_2^{\alpha\beta}$ ,



Fig. 2.3. Schematic illustration of the Guggenheim model of interface layer.

respectively. Thus, relationship for two component bulk solutions at the constant temperature can be written:

$$X_1 d\mu_1 = -X_2 d\mu_2$$
 (2.21)

where  $X_1$  and  $X_2$  are molar fractions of components *I* and 2. Applying Eq. (2.21) to Eq. (2.16) gives:

$$-d\gamma = \left[\Gamma_2^{\alpha\beta} - \frac{X_2}{X_1}\Gamma_1^{\alpha\beta}\right]d\mu_2$$
(2.22)

and after rearranging with Eq. (2.19):

$$\Gamma_2^{\alpha\beta} - \frac{X_2}{X_1} \Gamma_1^{\alpha\beta} = -\frac{1}{RT} \frac{d\gamma}{d \ln c_2}$$
(2.23)

after substituting from Eq. (2.20), we have that:

$$\Gamma_2^{(1)} = \Gamma_2^{\alpha\beta} - \frac{X_2}{X_1} \Gamma_1^{\alpha\beta}$$
(2.24)

Eq. (2.24) showed that in the case of dilute solutions of highly surface active substance, where  $X_1 \gg X_2$ , it can be assumed that values of the Gibbs surface excess are practically equal to the surface concentration, i.e.  $\Gamma_2^{(1)} \approx \Gamma_2^{\alpha\beta}$ .

#### 2.2. Surface Equations of State and Adsorption Isotherms.

The problem of interrelation between the chemical structure of a surfactant and its ability to be adsorbed at a liquid interface is one of the main questions in physical chemistry of surfactant solutions. Thus, an accurate description of the thermodynamics of adsorption layers at fluid/fluid interface gains large interest of the surface research. Adsorption equilibrium at interface can be described in two ways (Aksenenko, 2001; Chang and Franses, 1995; Fainerman and Miller, 2001):

• by applying the adsorption isotherm

$$Kc = f(K, c, \Gamma, \pi, T, \{\lambda_I\})$$

$$(2.25)$$

• using surface equation of state related to the changes in surface pressure  $(\pi)$ 

$$π = f(K, c, Γ, π, T, {λI})$$
(2.26)

where *K* is the adsorption equilibrium constant and  $\{\lambda_I\}$  is the sets of parameters specific for the isotherm, related to the thermodynamic and physical characteristic of the adsorption process. Surface pressure is defined as:

$$\pi = \gamma^0 - \gamma \tag{2.27}$$

where  $\gamma^{\theta}$  is the surface tension of a pure solvent. In the most cases of interest, the Eqs (2.25) and (2.26) express the thermodynamic quantities implicitly. From these equations, the surface tension (pressure) isotherm can be calculated and compared with experimental data.

#### 2.2.1. Nonionic Surface Active Substances.

**Henry isotherm** is the simplest isotherm and has rather historical significance than practical application (Chang and Franses, 1995). For a single component solution, this isotherm takes form:

$$\Gamma = K_{\rm H} c \tag{2.28}$$

Adsorption equilibrium constant  $K_H$  is parameter, which is used to estimate the surface activity of a surfactant. This isotherm can be applied to the systems of non-interacting molecules with low surfactant concentration, i.e. when the  $\Gamma$  is low in comparison to the maximum surface concentration ( $\Gamma_{\infty}$ ).

Langmuir adsorption model is based on a balance between adsorption and desorption kinetics at equilibrium (Dukhin et al., 1995; Chang and Franses, 1995). The Langmuir model assumes localized (immobile) and monolayer adsorption. In the molecules monolayer there are no lateral interactions. The Langmuir isotherm and the Langmuir-Szyszkowski equation of state are:

$$K_{\rm L}c = \frac{\Gamma\omega}{1 - \Gamma\omega} \tag{2.29}$$

$$-\frac{\pi\omega}{RT} = \ln(1 - \Gamma\omega) \tag{2.30}$$

where  $K_L$  is the adsorption equilibrium constant,  $\omega$  is a single parameter related to the area per molecule in the close-packed surface layer. The  $\Gamma \omega$  term can be replaced by the dimensionless surface coverage ( $\Theta$ ) defined as:

$$\Theta = \frac{\Gamma}{\Gamma_{\infty}} \tag{2.31}$$

and thus:

$$\omega = \frac{1}{\Gamma_{\infty}} \tag{2.32}$$

**Frumkin adsorption model** introduces an interaction between the molecules adsorbed at the surface (Aksenenko, 2001; Fainerman and Miller, 2001). The general forms of the isotherm and equation of state are:

$$K_{\rm F}c = \frac{\Gamma\omega}{1 - \Gamma\omega} \exp(-2a_{\rm F}\Gamma\omega)$$
(2.33)

$$-\frac{\pi\omega}{RT} = \ln(1 - \Gamma\omega) + a_F(\Gamma\omega)^2$$
(2.34)

where  $K_F$  is the adsorption constant and  $a_F$  is the parameter defined as:

$$a_F = \frac{H_S}{RT}$$
(2.35)

 $H_S$  is the parameter describing interactions between neighboring molecules adsorbed at the surface. The Frumkin model becomes identical to the Langmuir model for  $H_S = 0$ . Mathematical solution of the Frumkin isotherm, necessary to obtain the  $\Gamma$  vs. c dependence, is not so trivial in comparison with Langmuir model, and need to be calculated numerically.

#### 2.2.2. Ionic Surface Active Substances.

Theoretical description of the adsorption of ionic surfactants is relatively more complicated than in the case of nonionic ones, due to the interactions between surfactant chains, charged head-groups, and in addition strong screening of the counterions, always presented in ionic surfactant solutions. There can be found only a few models in literature describing adsorption of ionic surfactants (Lucassen-Reyners, 1966; Borwankar and Wasan, 1986; Kalinin and Radke, 1996; Fainerman et al., 1998; Warszynski et al., 2002), and two of them, presenting different approaches to the discussed problem, are described below.

In the two-dimensional solution model (Lucassen-Reyners, 1966; Fainerman et al., 1998; Aksenenko, 2001; Fainerman and Miller, 2001) it is assumed that the dividing surface is located at the external border of the electric double layer (EDL – see chapter 4.1.2). The distribution of surfactant between surface and solution is now obtained for electro-neutral combinations of ions. In the case of cationic surfactant RX (1:1, where  $R^+$  is the surface active cation and  $X^-$  is the counterion), the concentration *c* in the corresponding adsorption isotherm should be replaced by the mean ionic product concentration *c*\*:

$$c^* = f_{\pm} (c_{R^+} c_{X^-})^{1/2} \tag{2.36}$$

where  $f_{\pm}$  is the average coefficient of ions activity in the bulk solution,  $c_{R+}$  and  $c_{X-}$  are concentrations of cation and anion, respectively. The dissociation of the surfactant results in a variation in the number of adsorbed particles. The position of the dividing surface is chosen in the way that assured electro-neutrality of the surface layer:

$$\Gamma_{\rm R^+} = \Gamma_{\rm X^-} = \frac{\Gamma_{\rm RX}}{2}$$
 (2.37)

$$\Theta = \frac{\Gamma_{\text{RX}}}{\Gamma_{\text{RX}\infty}}$$
(2.38)

$$\omega_{\rm RX} = 2\omega \tag{2.39}$$

Therefore, for 1:1 ionic surfactants, Frumkin adsorption isotherm and equation of state are given by (Aksenenko, 2001):

$$K_{F}f_{\pm}(c_{R}+c_{X}-)^{1/2} = \frac{\Theta}{1-\Theta}\exp(-2a_{F}\Theta)$$
 (2.40)

$$-\frac{\pi\omega_{\text{RX}}}{2\text{RT}} = \ln(1-\Theta) + a_{\text{F}}(\Theta)^2$$
(2.41)

The Frumkin constant  $(a_F)$ , in addition to the van der Waals interaction, involves also the inter-ion interaction in the surface layer.

The better agreement of the theoretical approach with experimental data was achieved in the model proposed by Warszynski et al. (Warszynski et al., 1998a, 2002; Adamczyk et al., 1999; Para et al., 2003), which based on the previous finding of Kalinin and Radke (Kalinin and Radke, 1996). The main assumption of this model, called the **Surface Quasi Two-Dimensional Electrolyte (STDE) model**, is the lack of the electro-neutrality in the Stern layer. The model allows the penetration of counterions, which are fully mobile, into the interface, i.e. adsorption of counterions in the Stern layer, at the same Helmholtz plane as the surfactant head-groups. Moreover, in this model the finite size of surfactant head-groups and counterions was taken into account as well as their lateral electrostatic interactions. In the case of cationic surfactant adsorption, the surface concentration of surfactants and counterions adsorbed in the Stern layer is given by (Warszynski et al., 2002):

$$\frac{a_{+}}{\alpha_{s}}\exp\left(-\frac{Z_{s}e\Psi_{\delta}}{kT}\right)(1-\Theta_{s}-\Theta_{c}) = \Theta_{s}\exp(-2H_{s}\Theta_{s})\exp\left(\frac{\Phi_{s}}{kT}\right)$$
(2.42)

$$\frac{a_{-}}{\alpha_{c}}\exp\left(-\frac{Z_{c}e\Psi_{\delta}}{kT}\right)(1-\Theta_{s}-\Theta_{c}) = \Theta_{c}\exp\left(\frac{\Phi_{c}}{kT}\right)$$
(2.43)

where k is the Boltzmann constant,  $a_+$  and  $a_-$  are the activities of surfactant and counterion, respectively,  $\alpha_s$  is a "surface activity" of the surfactant ion,  $\alpha_c$  is the "surface activity" of the counterion,  $\Psi_{\delta}$  is the Stern potential, e is the elementary charge,  $Z_s$  and  $Z_c$  are the charges of surfactant and counterion, respectively,  $H_s$  is an interacting parameter of hydrophobic surfactant chains,  $\phi_s$  and  $\phi_c$  are the corrections related to the lateral interaction between ions,  $\Theta_s$  and  $\Theta_c$  are the relative surfactant and counterion, surface concentrations. The relative surfactant and counterion surface concentrations are expressed as:

$$\Theta_{\rm s} = \frac{\Gamma_{\rm s}}{\Gamma_{\rm s\infty}} \tag{2.44}$$

$$\Theta_{\rm c} = \frac{\Gamma_{\rm c}}{\Gamma_{\rm c\infty}} \tag{2.45}$$

where  $\Gamma_s$ ,  $\Gamma_c$  are the surfactant and counterion surface concentration, respectively,  $\Gamma_{s\infty}$  and  $\Gamma_{c\infty}$  are the limiting surfactant and counterion surface concentration of the closely packed monolayer, respectively. The total excess of the surfactant and all ions present in the system, taking into account adsorption in the diffuse part of the double layer and lateral interactions, is expressed as:

$$\Gamma_{i+} = \Gamma_{s} + \int_{0}^{\infty} (c_{i+}(x) - c_{i+b}) dx$$
(2.46)

$$\Gamma_{i-} = \Gamma_{c} + \int_{0}^{\infty} (c_{i-}(x) - c_{i-b}) dx$$
(2.47)

where  $\Gamma_{i+}$  are  $\Gamma_{i-}$  are the surface concentration of all cations and anions present in the solution,  $c_{i+}(x)$  and  $c_{i+b}$  are local concentration in double layer and concentration in the bulk of all cations, while  $c_{i-}(x)$  and  $c_{i-b}$  are local concentration in double layer and concentration in the bulk of all anions. The surface tension of the ionic surfactant solution can be calculated by integration of the Gibbs adsorption equation and is expressed in the form:

$$d\gamma = -RT \sum_{i} (\Gamma_{i+} dlna_{i+} + \Gamma_{i-} dlna_{i-})$$
(2.48)

#### 2.3. Adsorption Dynamics.

The surface active substances typical feature is ability to modify the properties of the interfaces, and due to that, they are applied in many technological processes. As most of the most of the technological processes are carried out under dynamic conditions, so knowledge about dynamic adsorption properties, rather than the equilibrium seems to be more appropriate. The present state of research allows describing the adsorption kinetics of surfactants at liquid interfaces quantitatively - in most cases. There are three groups of models describing the dynamics of adsorption at liquid interfaces (Dukhin et al., 1995; Chang and Franses, 1995; Miller et al., 2001): (i) the diffusion-controlled model, (ii) the kinetic-controlled model and (iii) the mixed diffusion-kinetics-controlled model. The diffusion-controlled model assumes that the diffusional transport of the SAS from the bulk to the interface is the rate-controlling process is the. Moreover, there is no activation barrier for the molecules transfer between the "subsurface" and the interface (Dukhin et al., 1995). This model was derived by Ward and Tordai (Ward and Tordai, 1946) and has following form:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}} \left( c_0 \sqrt{t} - \int_0^{\sqrt{\tau}} c_{ss}(0, t - \tau) d\sqrt{\tau} \right)$$
(2.49)

where *D* is the diffusion coefficient,  $c_0$  is a surfactant bulk concentration and  $c_{ss}$  concentration in the "subsurface" at the time *t*. The application of the Ward and Tordai equation to dynamic surface tension data  $\gamma(t)$  is not simple and often avoided due to numerical difficulties. When the second term of Eq. (2.49), describing desorption, on the right hand side is neglected, this relation is shortened to (Dukhin et al., 1995):

$$\Gamma(t) = c_0 \sqrt{\frac{Dt}{\pi}}$$
(2.50)

Eq. (2.50) describes the change of adsorption with time in very simple way and can be used only as a rather rough estimation of the adsorption coverage.

The kinetic-controlled model assumes that the transfer mechanism of the molecules from the "subsurface" to the interface is the rate limiting process. The most frequently used transfer mechanism is the rate equation of the Langmuir model (Chang and Franses, 1995; Miller et al., 2001):

$$\frac{d\Gamma}{dt} = k_{ad}c_0 \left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) - k_{des}\frac{\Gamma}{\Gamma_{\infty}}$$
(2.51)

where  $k_{ad}$  and  $k_{des}$  are the rate constants of adsorption and desorption processes, respectively.

For the Frumkin isotherm the following relation is obtained (MacLeod and Radke, 1994; Chang and Franses, 1995; Miller et al., 2001):

$$\frac{d\Gamma}{dt} = k_{ad}c_0 \left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) - k_{des}\frac{\Gamma}{\Gamma_{\infty}} \exp\left(a_F \frac{\Gamma}{\Gamma_{\infty}}\right)$$
(2.52)

The pure diffusion-controlled and kinetic-controlled models are the boundary cases and thus for many systems the mixed models are used for description of the adsorption dynamic. In **the diffusion-kinetic-controlled models**, it is considered that the rates of both processes controlling adsorption (the transport by diffusion in the bulk and the transfer of molecules from the "subsurface" to the adsorbed state and further desorption) are similar and therefore equally important. For such mixed adsorption models Eq. (2.51), fulfilling both conditions, can be rearranged by replacing the bulk concentration  $c_o$  by the "subsurface" concentration  $c_{ss}(0,t)$ . In the case of the Langmuir mechanism, it leads to (Dukhin et al., 1995; Miller et al., 2001):

$$\frac{d\Gamma}{dt} = k_{ad}c_{ss}(0,t)\left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) - k_{des}\frac{\Gamma}{\Gamma_{\infty}}$$
(2.53)

#### 2.3.1. Adsorption Kinetics at the Expanding Bubble Surface.

Adsorption kinetic over the expanding spherical surface, i.e. bubble growing on capillary orifice, is far more complicated problem and cannot be easily described by the models presented above, which are valid for the surface of constant area, only. Warszynski et al. (Warszynski et al., 1998b; Jachimska et al., 2001) developed model that allows to calculation of the adsorption coverage over the expanding bubble surface. This theoretical approach takes into account the rate of transport of surfactant molecules from the bubble solution to the neighborhood of the bubble surface, the rate of adsorption at the bubble solution interface, and the bubble expansion rate. If the first two processes are fast in comparison to the expansion of the bubble surface then the equilibrium surfactant coverage is reached at every stage of the bubble growth.

The transport of surfactant molecules to the interface of a growing bubble can be described with use of convective-diffusion equation, which can be expressed in spherical coordinates as (MacLeod and Radke, 1994; Warszynski et al., 1998b):

$$\frac{\partial c}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial c}{\partial r} - U_f \frac{\partial c}{\partial r}$$
(2.54)

where *c* is the surfactant concentration at given point, *r* is the distance of this point from the center of the bubble, and  $U_f$  is a fluid velocity. The fluid velocity can be found from:

$$U_{f} = U_{s}(t) \frac{r_{s}(t)^{2}}{r^{2}}$$
(2.55)

where  $r_s$  is the instantaneous radius of the bubble growing with the expansion velocity  $U_s$ . When Eq. (2.54) is expressed in terms of the coordinate relative ( $\beta$ ) to the instantaneous position of the bubble surface:

$$\beta = r - r_s(t) \tag{2.56}$$

then we obtain:

$$\frac{\partial c}{\partial t} = D \frac{1}{(\beta + r_s(t))^2} \frac{\partial}{\partial \beta} (\beta + r_s(t))^2 \frac{\partial c}{\partial \beta} - U_s(t) \left[ 1 - \frac{r_s(t)^2}{(\beta + r_s(t))^2} \right] \frac{\partial c}{\partial \beta}$$
(2.57)

Far from the bubble surface  $(r \to \infty)$ , where the surfactant concentration is equal to the bulk concentration  $(c \to c_b)$  the boundary conditions for Eq. (2.57) at the bubble interface, i.e. for  $\beta = 0$ , can be derived using the continuity equation flux:

$$\frac{1}{A_{b}}\frac{dn_{s}}{dt} = \frac{1}{A_{b}}\frac{d(\Gamma A_{b})}{dt} = \frac{d\Gamma}{dt} + \frac{2U_{s}}{r_{s}(t)}\Gamma = D\frac{\partial c}{\partial\beta_{I\beta\to0}}$$
(2.58)

where  $n_s$  is the number of moles of the surfactant adsorbed at the bubble surface  $A_b$ . Surfactant flux at the bubble interface can be also expressed as a balance between the adsorption  $(j_a)$  and desorption  $(j_d)$  fluxes, thus:

$$\frac{1}{A_{b}}\frac{dn_{s}}{dt} = D\frac{\partial c}{\partial\beta_{I\beta\to0}} = j_{a} - j_{d} = J(c_{\beta\to0},\Gamma)$$
(2.59)

The surfactant concentration in the "subsurface" and the adsorption coverage at the bubble surface affect the balance between adsorption and desorption fluxes. When the adsorption flux is balanced by the desorption one then the Eq. (2.59) describes adsorption isotherm. To solve Eq. (2.57) with the boundary conditions given by Eqs (2.58) and (2.59) the additional assumption describing an adsorption is needed, e.g. the Frumkin-Hinshelwood

adsorption kinetic model, which in equilibrium is consistent with the Frumkin adsorption isotherm (Jachimska et al., 2001).

### **3. Bubble Formation and Motion in Liquids.**

Formation of the gas bubbles in liquid can be realized on two ways: (i) as a result of nucleation in oversaturated liquids or (ii) in more common method - by gas dispersion (Malysa, 1992; Cho and Laskowski, 2002a). In dispersion methods, the bubbles are generated as a result of mixing together of liquid and gas phase with an energy input. Bubbles are commonly produced by sparging, that is, pumping gas through a capillary or frit into the bulk liquid. In this process, multi-body interactions between the bubbles causes that the bubbles generated can have various diameters. Addition of the surface active substances can prevent coalescence of the bubble, what leads to low scatter of bubble diameter in dispersion. With increasing SAS concentration, the degree of the bubble coalescence decreases and at a particular concentration (the Critical Coalescence Concentration - CCC), the coalescence of the bubbles is almost completely prevented (Cho and Laskowski, 2002a, 2002b; Grau et al., 2005). However, in the case of slow the bubble formation at a single capillary orifice, where no multi-body interactions are observed, the diameter of the formed bubble ( $d_b$ ) can be well controlled and is described by the Tate law (Tate, 1864):

$$d_{b} = \sqrt[3]{\frac{6d_{c}\gamma}{\Delta\rho g}}$$
(3.1)

where  $d_c$  is an inner diameter of capillary and  $\Delta \rho$  is a density difference between liquid and gas. As the bubble motion causes deformation of the bubble shape, sso the bubble equivalent diameter ( $d_e$ ) is often used in a size description of the rising bubble. The bubble equivalent diameter is defined as a diameter of the sphere with the same volume as rising bubble. The real shape of the rising bubble can be described with good approximation as the oblate spheroid of horizontal  $(d_h)$  and vertical  $(d_v)$  diameters, what gives formula for the equivalent diameter in form:

$$d_e = \sqrt[3]{d_h^2 d_v}$$
(3.2)

#### 3.1. Dynamic Adsorption Layer.

The terminal velocity of a fluid sphere is up to 50% higher than that of a rigid sphere of the same size and density. This effect is related to a smaller viscous drag exerted by liquid phase on the fluid gas/liquid interface and internal gas circulation induced inside the bubble (Fig. 3.1A). Presence of the surface active substances and their adsorption at the bubble surface affects (retards) fluidity of the surface, what leads to lowering of the bubble velocity (Levich, 1962; Clift et al., 1978; Dukhin et al., 1995; Sam et al., 1996; Krzan and Malysa, 2002). The mechanism responsible for this effect was for the first time described by Frumkin and Levich (Levich, 1962; Dukhin et al., 1995). They postulated, that the bubble detaching from capillary has uniform adsorption coverage of the SAS molecules over its surface but viscous drag exerted by liquid on the rising bubble surface induces uneven distribution of the SAS molecules. Depletion at the upstream bubble part and accumulation of the SAS molecules in the rear part means an inducement of the surface tension gradients and a tangential "Marangoni" stress opposing the flow shear stress (Fig. 3.1B) (Dukhin et al., 1995, 1998). Thus, formation of this dynamic adsorption layer



**Fig. 3.1.** Schematic view of A) internal circulation of air in the bubble B) inhomogeneous distribution of the SAS molecules at surface of the rising bubble.

(DAL) over the bubble interface is the reason of retardation of the bubble surface fluidity and internal circulation, what leads to an increase of the drag forces towards that of a rigid sphere (Krzan and Malysa, 2002; Krzan et al., 2007; Navarra et al., 2009; Rafiei et al., 2011; Tan et al., 2013). The bubble, detached from the capillary orifice, accelerates and attains its terminal velocity at a distance, which is highly dependent on type and concentration of the surface active substances (Fig. 3.2). Moreover, the existence of acceleration/deceleration stage for some concentrations of the SAS, before the establishment of the terminal velocity, can be addressed to the formation of the DAL architecture during the initial stage of the bubble motion (Krzan and Malysa, 2002, 2012; Krzan et al., 2007). There is also minimum degree of adsorption coverage (concentration), different for various SAS, which is sufficient for fully immobilization of the bubble surface(Zhang et al., 2001; Malysa et al., 2005; Rafiei et al., 2011). Further increase of the SAS coverage, above this "threshold" coverage, does not affect practically bubble terminal velocity (Fig. 3.2). Full retardation of the bubble surface mobility means that its motion is similar as for solid sphere of identical dimensions and density.



**Fig. 3.2.** Bubble terminal ( $d_b$ = 1.48mm) velocity as a function of the SAS (n-alcohols) concentration. Redrawn from (Krzan and Malysa, 2002; Krzan et al., 2007).
#### **3.2. Bubble Terminal Velocity.**

Motion (rising or falling) of the body in liquid, with its terminal velocity  $(U_T)$ , is described by the balance between the buoyancy  $(F_B)$  and the drag force  $(F_D)$ :

$$F_{\rm B} = \Delta \rho V_{\rm b} g \tag{3.3}$$

$$F_D = 0.5C_D \rho_L U_T^2 S_b \tag{3.4}$$

where  $C_D$  is a drag coefficient, g is a gravitational acceleration,  $\rho_L$  is a liquid density,  $V_b$ and  $S_b$  are volume and surface of projection on a horizontal plane of the body, respectively. Then, for spherical body of the diameter  $d_b$ , equation for the terminal velocity can be expressed as:

$$U_{\rm T} = \sqrt{\frac{4d_{\rm b}\Delta\rho g}{3C_{\rm D}\rho_{\rm L}}}$$
(3.5)

The main problem in the solving of Eq. (3.5) is determination of the drag coefficient. The  $C_D$  depends on the conditions of motion, often expressed as a function of dimensionless Reynolds number (*Re*):

$$Re = \frac{d_b U_T \rho_L}{\eta_L}$$
(3.6)

where  $\eta_L$  is a liquid viscosity. In fluid mechanics, the Reynolds number gives a measure of the ratio of inertial forces to viscous forces and often is used for description of flow conditions. It is assumed that bubble moves under creeping flow conditions when  $Re < 10^{-3}$ , laminar flow for Re < 1, transitional flow is observed for  $1 < Re < 10^2$  and turbulent flow for  $Re > 10^2$ . The Reynolds number, together with the Morton number (*Mo*) and the Eovots number (*Eo*), are used for characterization of the hydrodynamic conditions of the body motion in fluid. The Morton number and the Eovots number present the shape of bubbles or drops moving in a surrounding fluid:

$$Mo = \frac{\eta_L^4 g \Delta \rho}{\rho_L^2 \gamma^3}$$
(3.7)

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$$Eo = \frac{d_b^2 g \Delta \rho}{\gamma}$$
(3.8)

The other, often used, dimensional numbers are the Weber number (*We*), the Archimedes number (Ar) and the Lyshchenko number (Ly):

$$We = \frac{d_b U_T^2 \Delta \rho}{\gamma}$$
(3.9)

$$Ar = \frac{d_b^3 g \Delta \rho \rho_L}{\eta_L^2}$$
(3.10)

$$Ly = \frac{U_T^3 \rho_L^2}{g \Delta \rho \eta_L}$$
(3.11)

#### 3.2.1. Pure Liquids.

The very first model of the  $C_D$ , known as a Stokes Law, was obtained from solution of Navier-Stokes equation for symmetrical solid sphere falling in liquid under creeping flow conditions (Clift et al., 1978):

$$C_{\rm D} = \frac{24}{\rm Re} \tag{3.12}$$

what together with Eqs (3.5) and (3.6) gives:

0

0

$$U_{T} = \frac{d_{b}^{2}g\Delta\rho}{18\eta_{L}}$$
(3.13)

**Fig. 3.3.** Terminal velocity (creeping flow condition) as a function of diameter for solid sphere (red line) and air bubble (green line) of the same density difference.

Diameter [µm]

6

8

10

4

2

Later, Hadamard and Rybczynski assumed that for the pure interface an internal circulation is induced in a bubble and the equation for terminal velocity takes form (Clift et al., 1978):

$$U_{\rm T} = \frac{d_{\rm b}^2 g \Delta \rho}{6 \eta_{\rm L}} \cdot \frac{\eta_{\rm L} + \eta_{\rm G}}{2 \eta_{\rm L} + 3 \eta_{\rm G}} \tag{3.14}$$

where  $\eta_G$  is a gas viscosity. Comparison of terminal velocities in function of diameter calculated according to both models is presented in Fig. 3.3.

Levich (Levich, 1962) elaborated model for the potential flow of the spherical drops and bubbles in clean water, where the expression for the  $C_D$  for Re <50 and  $d_b < 0.5$  mm is given as:

$$C_{\rm D} = \frac{48}{\rm Re} \tag{3.15}$$

Bubbles of large diameter have non-spherical shapes, what influences the drag coefficient. For such an oblate, Moore (Moore, 1963, 1965) obtained, taking into account the dissipation of energy on the boundary layer, the following relation of the  $C_D$ :

$$C_{\rm D} = \frac{48}{\rm Re} G(\chi) \left[ 1 + \frac{\rm H(\chi)}{\sqrt{\rm Re}} + O\left(\frac{1}{\sqrt{\rm Re}}\right) \right]$$
(3.16)

where  $G(\chi)$  and  $H(\chi)$  are functions of the bubble deformation degree ( $\chi$ ):

$$G(\chi) = \frac{1}{3}\chi^{4/3}(\chi^2 - 1)^{3/2} \frac{\sqrt{\chi^2 - 1} - (2 - \chi^2) \sec \chi^{-1}}{\left(\chi^2 \sec \chi^{-1} - \sqrt{\chi^2 - 1}\right)^2}$$
(3.17)

$$H(\chi) = 0.0195\chi^4 - 0.2134\chi^3 + 1.7026\chi - 1.5732$$
(3.18)

The deformation can be found from the relation between the Weber number and  $\chi$ , for  $\chi < 2$ :

We = 
$$4\chi^{-4/3}(\chi^3 + \chi - 2)(\chi^2 \sec \chi^{-1} - \sqrt{\chi^2 - 1})^2(\chi^2 - 1)^{-3}$$
 (3.19)

Applicability of this model is said to be for wide range of the Reynolds numbers, 100 < Re < 10000, but comparison of the Moore model prediction with experimental data (Clift et al., 1978; Duineveld, 1995) showed that this model underestimates values of the bubble terminal velocities for bubbles of  $d_b > 1.2$  mm. Clift et al. (Clift et al., 1978) reviewed in their monograph most of the known models and compared with experimental data. They emphasized influence of the bubble deformation on the drag coefficient for bubbles rising in clean water, what resulted in presentation of two relations, according to the Reynolds number:

$$C_{\rm D} = 14.9 {\rm Re}^{-0.78} \tag{3.20}$$

for *Re* <150, and for *Re* >565:

$$U_{\rm T} = \left(\frac{2.14\gamma}{d_{\rm b}\rho_{\rm L}} + 0.505d_{\rm b}g\right)^{1/2}$$
(3.21)

The other semi-analytical relation of the  $C_D$ , which fit with experimental data for Re < 130 in clean water, was proposed by Masliyah et al. (Masliyah et al., 1994):

$$C_{\rm D} = \frac{16}{\rm Re} \left(1 + 0.077 \rm Re^{0.65}\right) \tag{3.22}$$

Karamanev (Karamanev, 1994, 1996) after analysis of available in the literature experimental data and the correlations for rising gas bubbles motion, proposed a semi-analytical equation linking the bubble rising velocity and its geometry. Moreover, the drag coefficient was described in more convenient way - in the term of the Archimedes number (Ar). Using these considerations, the terminal velocity of the bubbles can be calculated as follow:

$$U_{\rm T} = 40.3 \frac{d_{\rm e}}{d_{\rm h}} \sqrt{\frac{V_{\rm b}^{1/3}}{C_{\rm D}}}$$
(3.23)

where  $V_b$  is a volume of the bubble, and the drag coefficient is expressed as:

$$C_{\rm D} = \frac{432}{\rm Ar} \left( 1 + 0.047 {\rm Ar}^{2/3} \right) + \frac{0.517}{1 + 154 {\rm Ar}^{-1/3}}$$
(3.24)

for Ar < 13000, and  $C_D = 0.95$  for Ar > 13000. The term  $d_e/d_h$  is calculated using the correlation proposed by Clift et al. (Clift et al., 1978):

$$\frac{d_e}{d_h} = (1 + 0.163Eo^{0.757})^{-1/3}$$
(3.25)

for *Eo* <40, and  $d_e/d_h = 0.62$  for *Eo* >40.



**Fig. 3.4.** Comparison of terminal velocity, calculated for few different models and experimental data (Zawala, 2008), as a function of bubble diameter for clean water.

Rodrigue (Rodrigue, 2001a, 2001b) proposed another generalized correlation, which uses the flow number (*Fl*) and the velocity number (*Ve*) introduced earlier by Abou-El-Hassan (Abou-El-Hassan, 1983):

$$Ve = U_T \left(\frac{\rho_L^2 d_b^2}{\gamma \eta_L}\right)^{1/3}$$
(3.26)

$$Fl = g \left(\frac{\rho_L^5 d_b^8}{\gamma \eta_L^4}\right)^{1/3}$$
(3.27)

Based on the experimental data available and after several iterations, Rodrigue found the following relation (Rodrigue, 2004):

$$Ve = \frac{Fl}{12} \left[ \frac{\left(1 + 1.31 \cdot 10^{-5} \cdot Mo^{11/20} Fl^{73/33}\right)^{21/176}}{(1 + 0.020 Fl^{10/11})^{10/11}} \right]$$
(3.28)

Figure 3.4 presents a comparison between predictions of some models and experimental data (Zawala, 2008; Malysa et al., 2011) and as seen there are quite significant discrepancies. This comparison illustrates clearly that there does not exist any universal theory describing the bubble motion outside the creeping flow conditions.

# 3.2.2. Solution of Surface Active Substances.

The terminal velocity of the bubble in solutions of surface active substances, called often "contaminated" liquids, was a topic of many research studies, mainly focused on the bubbles with fully immobilized surfaces, which motion showed some similarities to the falling of the rigid spheres. In the case of rise in the laminar flow conditions, drag coefficient can be described using the Stokes equation (Eq. 3.12), but even for such small velocities some deviations, first noted by Oseen (Clift et al., 1978), were observed. Ossen, after simplifying of the Navier-Stokes equation by linearization, showed that the drag coefficient becomes larger comparing to Eq. (3.12) and for Re < 0.1 can be calculated from:

$$C_{\rm D} = \frac{24}{\rm Re} \left( 1 + \frac{3}{16} {\rm Re} \right)$$
(3.29)

In the case of the higher Reynolds number (for *Re* <800), Schiller and Naumann proposed the following formula (Clift et al., 1978):

$$C_{\rm D} = \frac{24}{\rm Re} \left(1 + 0.15 {\rm Re}^{0.687}\right) \tag{3.30}$$

Clift et al. (Clift et al., 1978) collected and analyzed data for contaminated liquids, similarly as for the bubbles motion in pure liquids, and presented following relationship for bubble terminal velocities:

$$U_{\rm T} = \frac{\eta_{\rm L}}{\rho_{\rm L} d_{\rm b}} \,\mathrm{Mo^{-0.149}}(J_{\rm C} - 0.857) \tag{3.31}$$

where:

 $J_{\rm C} = 0.94 {\rm H_{\rm C}}^{0.757} \tag{3.32}$ 

for  $2 < H_C < 59.3$ , and

 $J_{\rm C} = 3.42 {\rm H}_{\rm C}^{0.441} \tag{3.33}$ 

for  $H_C$  >59.3, and  $H_C$  is described as:

$$H_{\rm C} = \frac{4}{3} {\rm EoMo^{-0.149}} \tag{3.34}$$

Karamanev (Karamanev, 1996) assumed, that the Eq. (3.24), used for the clean water system, can be used for estimation of the  $C_D$  in the case of free rising sphere contaminated liquid. If the bubble in contaminated liquid has spherical shaped then there is no need to add geometrical term in formula for bubble terminal velocity. Thus, terminal velocity of free rising sphere should be calculated from Eq. (3.5) and Eq. (3.24), which is valid for  $Ar < 1.18 \cdot 10^6 d_b^2$ , and  $C_D = 0.95$  for  $Ar > 1.18 \cdot 10^6 d_b^2$ .

Nguyen et al. (Nguyen et al., 1997a) also showed that the terminal velocity of failing solid sphere can be directly predicted on the basis of the Archimedes number and the Lyaschenko number, but in more straightforward way than proposed by Karamanev. Later using similar derivation (Nguyen, 1998), the formulas for bubble terminal velocity in contaminated system was presented. Nguyen assumed, that for Re < 130, the bubbles shape is spherical and the bubble drag coefficient is equal to that of solid particle.

The following correlation for bubble terminal velocity was proposed:

$$U_{\rm T} = \frac{d_b^2 g \Delta \rho}{18 \eta_{\rm L}} \left[ 1 + \frac{{\rm Ar}/96}{(1+0.079 {\rm Ar}^{0.749})^{0.755}} \right]^{-1}$$
(3.35)

For Re > 130, Nguyen proposed, similarly as Karamanev, that  $C_D = 0.95$ , but additionally in formula for bubble terminal velocity he applied numerical parameters (*a*,*b*) describing shape of the rising bubble:

$$U_{\rm T} = \sqrt[3]{\frac{g\eta_{\rm L}}{\gamma}} \left(\frac{4a^2 M o^{0.46b}}{2.85}\right)^{1/(2-2b)} Ar^{\frac{2b+1}{6-6b}}$$
(3.36)

The values of *a* and *b* depend on the Archimedes number and they are collected in work of Nguyen (Nguyen, 1998).

Ng et al. (Ng et al., 1999, 2000) predicted the  $C_D$  with use of the solution of the Oseen law, and for 0.2 < Re < 20000 following formula was derived:

$$C_{\rm D} = \frac{24}{\rm Re} \left( \frac{7}{6} {\rm Re}^{0.15} + 0.02 {\rm Re} \right)$$
(3.37)

This model was validated by Krzan et al. (Krzan and Malysa, 2002), where the experimentally determined values of terminal velocities were in a very good agreement with data predicted with use of Eq. (3.37).



**Fig. 3.5.** Comparison of terminal velocity, calculated for few different models, as a function of bubble diameter for "contaminated" water ( $\gamma = 50 \text{ mN/m}$ ).

All these models can somehow approximate terminal velocity for the bubble with fully immobilized surface, but none of them is capable to make of proper prediction for the  $U_T$  in the case of partial immobilization of the bubble surface. To this problem was addressed work of Tomiyama et al. (Tomiyama et al., 1998, 2002; Myint et al., 2006). Based on the previous works, they proposed the formulas of the  $C_D$  for three "contamination" regimes:

a) for a clean system

$$C_{\rm D} = \max\left\{\min\left[\frac{16}{\rm Re}(1+0.15{\rm Re}^{0.687}), \frac{48}{\rm Re}\right], \frac{8}{\rm S}\frac{\rm Eo}{\rm Eo+4}\right\}$$
(3.38)

b) for a slightly contaminated system

$$C_{\rm D} = \max\left\{\min\left[\frac{24}{\rm Re}(1+0.15{\rm Re}^{0.687}), \frac{72}{\rm Re}\right], \frac{8}{3}\frac{\rm Eo}{\rm Eo+4}\right\}$$
(3.39)

c) for fully contaminated system

$$C_{\rm D} = \max\left\{ \left[ \frac{24}{\rm Re} (1 + 0.15 {\rm Re}^{0.687}) \right], \frac{8}{3} \frac{\rm Eo}{\rm Eo + 4} \right\}$$
(3.40)

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# 4. Thin Liquid Films.

Thin liquid films (TLF) are important elements of every dispersed system under dynamic and static conditions. The TLF can be described as a liquid layer separating two interfaces, where the specific additional interactions - DLVO theory (Derjaguin-Landau-Verwey-Overbeek) - start to play an essential role for their stability (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). Thus, the main difference of the TLF from the bulk phase is the presence of these specific interactions, which occur for liquid films thinner than ca. 100 nm. Due to type of the interfaces and interrelated specific DLVO forces, thin liquid films can be divided into two groups (Scheludko, 1967):

- symmetrical films (Fig. 4.1A), which possess two identical interfaces (e.g. foam films, emulsion films) interactions are homogenous
- asymmetrical films (Fig. 4.1B), formed between two different interfaces (e.g. wetting films) heterogeneous interactions.

As the TLF are the fundamental elements of all dispersed systems, investigation of the properties of each of these single films could lead to a better understanding of the behavior of the entire macroscopic systems, such as its stability. This is the reason why so much effort is put into determination of the TLF properties, mainly by analysis of the surface forces acting across thin liquid films separating particles or macroscopic bodies.



Fig. 4.1. Thin liquid films A) symmetrical film – foam film, B) asymmetrical film – wetting film.

### 4.1. Disjoining Pressure.

For two surfaces in a fluid phase, separated by an interlayer with sufficient large thickness h (Fig. 4.2A), that is, with such thickness that the middle parts of the layer retains

the bulk phase properties, changes in the interlayer do not change the system free energy. Therefore, in the absence of external forces, the two interfaces will be in a neutral position to each other, where no additional interactions, across the TLF, are observed. The situation is different at some sufficiently small h (Fig. 4.2B), where the surface zones, close to the interfaces, begin to overlap and then, the properties of liquid interlayer become different from those of the bulk phase. In general, to maintain thermodynamic equilibrium, opposing forces (named "disjoining pressure" -  $\Pi$ ), proportional to the interlayer area must be applied to the interfaces. Thus, the equilibrium is fulfilled for the following condition (Scheludko, 1967):

$$\Pi(\mathbf{h}) = \mathbf{P}_{\mathbf{f}}(\mathbf{h}) - \mathbf{P}_{\mathbf{0}} = \Delta \mathbf{P}_{\mathbf{f}}$$
(4.1)

where  $P_f$  is a pressure exerted by the dispersed phases on the interlayer, an  $P_0$  is a pressure in the bulk liquid phase.



Fig. 4.2. Surface layers A) thick film - layers do not overlap, B) thin film - layers overlap.

On the other hand, the overlap of the transition regions results in the appearance of excess Gibbs free energy of the interlayer induced by this overlapping, and in the term of the Gibbs free energy can be presented as (Scheludko et al., 1965; Derjaguin, 1989):

$$\Pi(\mathbf{h}) = -\frac{1}{A} \left( \frac{\partial \mathbf{G}}{\partial \mathbf{h}} \right)_{\mathbf{T}, \mathbf{P}, \boldsymbol{\mu}_{\mathbf{i}}}$$
(4.2)

According to established tradition, the total disjoining pressure in thin film is considered as an additive sum of different components of disjoining pressure, each defined by mechanisms of different physical nature (Derjaguin, 1989; Israelachvili, 1991):

$$\Pi = \Pi_{\rm vW} + \Pi_{\rm el} + \Pi_{\rm non-DLVO} \tag{4.3}$$

Subscripts in Eq. (4.3) indicate the following contributions: vW for van der Waals forces, el for electrostatic forces, and *non-DLVO* is components not accounted in the classical DLVO theory. In generally, if the  $\Pi > 0$ , then  $\Pi$  acts towards disjoining of interfaces, and for  $\Pi < 0$  film becomes thinner.



Fig. 4.3. Schematic illustration of the interactions in symmetrical TLF.

#### 4.1.1. Van der Waals Forces.

The van der Waals forces are the sum of attractive forces, of the same distance dependence ( $\sim d^6$ ), between molecules, which are (Israelachvili, 1991; Adamson and Gast, 1997):

- Keesom forces: permanent dipole permanent dipole interactions
- Debye forces: permanent dipole induced dipole interactions
- London or dispersion forces: instantaneous dipole induced dipole interactions.

These interactions are dominant for distances smaller than 10 nm in aqueous phase, as for longer distances the dispersion force decays ten times faster due to so-called electromagnetic retardation. There are, essentially, two approaches to the prediction of van der Waals interaction between two bodies as a function of their separation distance: the microscopic approach - developed by Hamaker (Hamaker, 1937), and the continuum - macroscopic approach developed by Lifshitz (Lifshitz, 1955; Dzyaloshinsky et al., 1961).

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In the Hamaker approach, the interaction energy is calculated by a pair-wise summation of all the relevant microscopic interactions, which are assumed as non-retarded and additive. Thus, for two plane-parallel interfaces the  $\Pi_{vdW}$  can be calculated from (Hamaker, 1937; Israelachvili, 1991):

$$\Pi_{\rm vw} = -\frac{A^{\rm H}}{6\pi h^3} \tag{4.4}$$

 $A^{H}$  represents the Hamaker constant which accounts for the material properties and is defined as (Israelachvili, 1991):

$$A^{\rm H} = \pi^2 C \varphi_1 \varphi_2 \tag{4.5}$$

where  $\varphi_1$  and  $\varphi_2$  are the number of atoms per unit volume in the two bodies and *C* is the coefficient in the atom-atom pair interaction. This theory allows to make an approximate calculations of the  $A^H$  for more complex system, e.g. phase *I* and phase *2* divided by phase *3*, using data for two-phases interactions (Derjaguin, 1989):

$$A_{132}^{\rm H} = A_{12}^{\rm H} - A_{13}^{\rm H} - A_{23}^{\rm H} + A_{33}^{\rm H}$$
(4.6)

where subscripts indicate the Hamaker constant of mentioned bodies measured in vacuum.  $A^{H}_{132}$  can be approximated with use of  $A^{H}_{11}$ ,  $A^{H}_{22}$  and  $A^{H}_{22}$  (Israelachvili, 1991):

$$A_{132}^{\rm H} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right) \left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \tag{4.7}$$

The assumptions of simple pairwise additivity inherent in Eq. (4.5) ignore the influence of neighboring atoms on the interactions between any pair of atoms. Further, the additivity approach cannot be readily extended to bodies interacting in medium. The problem of additivity is completely avoided in the Lifshitz theory (Dzyaloshinsky et al., 1961), where the atomic structure is ignored and the forces between large bodies, now treated as continuous media, are derived in terms of such bulk properties as their dielectric constants and refractive indices. The Eq. (4.4) is still valid, even within the framework of the Lifshitz theory, the only change is the way of the Hamaker constant calculation. Israelachvili (Horn and Israelachvili, 1981; Israelachvili, 1991) derived a simply formula

for the case of two macroscopic bodies: 1 and 2 interacting across a medium 3, when the all three media have the same single absorption frequency (v):

$$A^{H} \cong \frac{3kT}{4} \left(\frac{\epsilon_{1} - \epsilon_{3}}{\epsilon_{1} + \epsilon_{3}}\right) \left(\frac{\epsilon_{2} - \epsilon_{3}}{\epsilon_{2} + \epsilon_{3}}\right) + \frac{3h_{P}\nu}{8\sqrt{2}} \frac{(n_{1}^{2} - n_{3}^{2})(n_{2}^{2} - n_{3}^{2})}{\left(\sqrt{n_{1}^{2} + n_{3}^{2}} + \sqrt{n_{2}^{2} + n_{3}^{2}}\right)\sqrt{(n_{1}^{2} + n_{3}^{2})(n_{2}^{2} + n_{3}^{2})}$$

$$(4.8)$$

where  $\varepsilon$  is the static dielectric constant, *n* is the refractive index of the medium in the visible light, *h*<sub>P</sub> is the Planck constant. The first term in Eq. (4.8) includes the Keesom and the Debye dipolar contributions, where the second term gives the London energy contribution.

In the symmetrical films, the  $\Pi_{vW}$  is always negative (i.e. there are attraction between the similar film interfaces). In asymmetrical films (for instance wetting films),  $\Pi_{vW}$  can become either negative or positive (i.e. there are attraction or repulsion between the film interfaces). It is worth mentioning that in the case of wetting films, where the repulsion is observed, e.g. silica-water-air ( $A^H = -1.0 \cdot 10^{-20}$  J) (Israelachvili, 1991), in fact silica attracts both phases, but its attraction of the "denser" material (i.e. water) is stronger, what results in a negative value of the  $A^H$  for whole considered system. Thus, the  $\Pi_{vW}$ becomes positive (i.e. forces are repulsive) (Israelachvili, 1991; Lyklema, 1991).

#### 4.1.2. Electrostatic Forces.

When two phases are placed in contact, it causes a difference in potential between them. If one of the phases is polar liquid, like water, its dipolar molecules will tend to be oriented in particular direction at the interface and this will generate a potential difference. If there are ions or excess electrons in one or both phases, there will be tendency for the electric charges to distribute themselves in a non-uniform way at the interface (Hunter, 1981; Lyklema, 1991). The region between two adjoining phases is always marked by a separation of electric charges so that near to or on the surface of phase *I* there is an excess of charge of one sign and the balancing charge is distributed in some way through the adjoining surface regions of phase 2. The most important mechanisms which gives rise to the spontaneous separation of charge between two phases in contact are (Hunter, 1981):

- differences in the affinity of the two phases for electrons responsible, in generally, for the development of the contact potential difference between dissimilar metals and/or semiconductors;
- differences in the affinity of the two phases for ions of one charge including: the distributions of anions and cations between two immiscible phases, the differential adsorption of ions from an electrolyte solution onto a solid surface;
- ionization of surface groups is commonly observed for surfaces with carboxylic acid, amine and oxide groups;
- physical entrapment of non-mobile charge in one phase commonly in solids,
   where *n* and *p* type defects in the crystals may occur.

In the case of the liquid/gas or liquid/solid interfaces, the electrical state of a charged surface is usually determined by the spatial distribution of ions in liquid phases. Such distribution of charges has traditionally been called "electrical double layer" (EDL). The simplest picture of the EDL was introduced by Helmholzt (Hunter, 1981). In this model, both layers of charge are fixed in parallel planes to form a molecular capacitor and the potential at the surface decreases linearly. For most purposes, a more elaborated model is necessary. Classic theory, developed independently by Gouy and by Chapman (Chapman, 1913; Hunter, 1981; Delgado et al., 2005), presents the EDL as a physical model in which one layer of the EDL is envisaged as a fixed charge, bound to the interface, while the other layer is distributed more or less diffusely within the solution in contact with the surface. Diffusion layer contains an excess of counterions (ions opposite in sign to the fixed charge), and has a deficit of co-ions (ions of the same sign as the fixed charge).

The fundamental electrostatic equation, used for description of the EDL's phenomenon, is the Poisson equation, which for the plane-parallel surfaces takes form (Hunter, 1981):

$$\frac{d^2\Psi}{dx^2} = -\frac{1}{\varepsilon_0\varepsilon_r}\rho \tag{4.9}$$

where  $\Psi$  is an electrostatic potential, x is a distance from the interface,  $\varepsilon_0$  and  $\varepsilon_r$  are the vacuum permittivity and the relative permittivity, respectively, and  $\rho$  is a charge density defined as:

$$\rho = \sum_{i} n_i Z_i e \tag{4.10}$$

where  $n_i$  is an amount of the *i*-component,  $Z_i$  is a charge of the *i*-component, *e* is the elementary charge. The local concentration of each type of ion in the EDL is described by the Boltzmann equation, which for the plane-parallel surfaces and in the presence of symmetric electrolyte (Z:Z) can be presented as:

$$n_{i} = n_{i}^{0} \exp\left(-\frac{Z_{i} e\Psi}{kT}\right)$$
(4.11)

Eqs (4.9)-(4.11), together, give Poisson-Boltzmann (P-B) equation:

$$\frac{d^2\Psi}{dx^2} = -\frac{1}{\varepsilon_0\varepsilon_r}\sum_i Z_i e n_i^0 exp\left(-\frac{Z_i e\Psi}{kT}\right)$$
(4.12)

In the Debye-Huckel linear approximation, valid for small values of potential ( $\Psi$ < 25 mV), the exponential term is expanded, what finally gives (Hunter, 1981; Lyklema, 1991):

$$\Psi = \Psi_0 e^{-\kappa x} \tag{4.13}$$

where  $\Psi_0$  is the surface potential and  $\kappa$  is the Debye-Huckel parameter defined as:

$$\kappa = \sqrt{\frac{e^2 \sum_i n_i Z_i^2}{\epsilon_0 \epsilon_r k T}}$$
(4.14)

In addition, the Debye length  $(l_D)$ , describing thickness of the diffusion layer, is defined with use of the Debye-Huckel parameter:

$$l_{\rm D} = \frac{1}{\kappa} \tag{4.15}$$

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In most cases, Eq. (4.13) is not valid, and then it is necessary to use the nonlinear solution of the Poison-Boltzmann eq., which can be presented as:

$$\frac{d^2\Psi}{dx^2} = \frac{2n_i^0 Z_i e}{\varepsilon_0 \varepsilon_r} \sinh\left(\frac{Z_i e\Psi}{kT}\right)$$
(4.16)

Additionally, the total charge ( $\sigma$ ) of the EDL is calculated from (Butt et al., 2003):

$$\sigma = -\int_0^\infty \rho dx = \varepsilon_0 \varepsilon_r \left(\frac{d\Psi}{dx}\right)$$
(4.17)

Integration of Eq. (4.12) once gives:

$$\frac{d\Psi}{dx} = -\frac{2\kappa kT}{Z_i e} \sinh\left(\frac{Z_i e\Psi}{2kT}\right)$$
(4.18)

what, together with Eq. (4.17), leads to:

$$\sigma = -\frac{4n_i^0 Z_i e}{\kappa} \sinh\left(\frac{Z_i e\Psi}{2kT}\right)$$
(4.19)

It is worth mentioning that the P-B equation is used with few assumptions (Butt et al., 2003):

- the electrolyte ions could be regarded as point charges
- the solvent could be treated as a structureless dielectric of constant permittivity
- ions in solution were considered as a continuous charge distribution
- surface is flat on the molecular scale.

Stern (Hunter, 1981; Delgado et al., 2005) showed that the ions in the solution have finite sizes and cannot approach to the surface closer than the Stern distance  $(x_{\delta})$ , which can be attributed to the ion effective radius. The region between the surface and the locus of hydrated counterions is called the Stern layer, whereas ions beyond it form the Gouy layer (diffuse layer). Later, Grahame (Grahame, 1947; Hunter, 1981) assumed that in some cases, the Stern layer should be subdivided into an inner Helmholtz layer (IHL), bounded by the surface and the inner Helmholtz plane (IHP) and an outer Helmholtz layer (OHL), located between the IHP and the outer Helmholtz plane (OHP) (see Fig. 4.4). The necessity

of this subdivision may occur when some ion types are specifically adsorbed on the surface while the hydrated ions can be adsorbed only at larger distance from the surface, due to the water molecules surrounding them.



Fig. 4.4. Schematic illustration of the Graham model of electric double layer.

Under dynamic conditions, the existence of a surface charge is related to a fluid motion with respect to the interface. The good examples are electrokinetic phenomena (Hunter, 1981; Delgado et al., 2005), i.e. electrophoresis, electroosmosis, streaming potential and sedimentation potential, or even air bubble rising in a liquid (Li and Somasundaran, 1991, 1992; Graciaa et al., 1995; Yang et al., 2001; Elmahdy et al., 2008). As the surface binds one, two, or several layers of liquid molecules and possibly ions more or less tightly, then the shear plane is often located not directly at the interface, but at a distance  $x_{\zeta}$  away from the surface (Fig. 4.4). The potential at this distance is called the zeta potential  $\zeta$ .

When two charged surfaces approach each other on sufficiently small distance h so that their electrostatic double layers (EDLs) overlap, then additional interactions between them occur. The range of this interactions can be even 100 nm (Scheludko, 1967), what makes, these long-range forces, important component of the DLVO theory. These interactions can be repulsive, for the interfaces of the same charges, or additive, in the case of opposite charges on the film interfaces. For simplicity, the below presented considerations are performed for the symmetrical film (see Fig. 4.5), but similar derivation can be also conducted for the asymmetrical films.

For the plane-parallel surfaces and in the presence of symmetric electrolyte (Z:Z) of concentration  $c_{el}$ , Eq. (4.16) in 1-dimension, can be rearranged to (Derjaguin, 1989; Israelachvili, 1991):

$$\frac{d^2\Psi}{dx^2} = \frac{2c_{el}ZF}{\varepsilon_0\varepsilon_r}\sinh\left(\frac{ZF\Psi}{RT}\right)$$
(4.20)

where F is the Faraday constant. After rearrangement and integration of the P-B Eq., we obtain:

$$2c_{el}RT\cosh\left(\frac{ZF\Psi}{RT}\right) - \frac{\varepsilon_0\varepsilon_r}{2}\left(\frac{d\Psi}{dx}\right)^2 = P_m$$
(4.21)

where  $P_m$  is an integration constant. It turns out that this constant  $P_m$  is equal to the osmotic pressure due to the ion concentration at the mid-plane (x = h/2) of the liquid film, where  $d\Psi/dx = 0$  and  $\Psi = \Psi_m$ :

$$P_{\rm m} = 2c_{\rm el}RT\cosh\left(\frac{ZF\Psi_{\rm m}}{RT}\right)$$

$$= RT\left[c_{\rm el}\exp\left(\frac{ZF\Psi_{\rm m}}{RT}\right) + c_{\rm el}\exp\left(-\frac{ZF\Psi_{\rm m}}{RT}\right)\right] = RT(c_{\rm el}^{+} + c_{\rm el}^{-})_{\rm m}$$

$$(4.22)$$

Thus, disjoining pressure can be given by the difference in pressure between the interfaces and the osmotic pressure due to ions outside the plates (Langmuir, 1938; Israelachvili, 1991):

$$\Pi_{el} = RT(c_{el}^{+} + c_{el}^{-})_{m} - 2RTc_{el} = 2c_{el}RT\left(\cosh\frac{ZF\Psi_{m}}{RT} - 1\right)$$
(4.23)

Although, calculation of the electrostatic potential of the mid-plane ( $\Psi_m$ ) directly from the P-B eq. is not easy, then some assumptions for simplifications can be made. After second integration of Eq. (4.20) we obtain:

$$\tanh\left(\frac{ZF\Psi}{4RT}\right) = \tanh\left(\frac{ZF\Psi_0}{4RT}\right)\exp(-\kappa x)$$
(4.24)

For small  $\Psi$ , using  $tanh(a) \approx a$ , Eq. (4.24) gives:

$$\Psi \approx \frac{4RT}{ZF} \tanh\left(\frac{ZF\Psi_0}{4RT}\right) \exp(-\kappa x)$$
(4.25)

In the "weak overlap approximation",  $\Psi_m$  at a surface separation *h* is simply given by adding the potential arising from the two surfaces:

$$\Psi_{\rm m} \approx 2\Psi\left({\rm x}=\frac{{\rm h}}{2}\right) = \frac{8{\rm RT}}{{\rm ZF}} \tanh\left(\frac{{\rm ZF}\Psi_0}{4{\rm RT}}\right) \exp\left(-\kappa\frac{{\rm h}}{2}\right)$$
(4.26)

The *cosh* term in the expression for  $P_m$  (Eq. 4.23) can also be simplified for small  $\Psi_m$ , leading to:

$$\Pi_{\rm el} = \frac{F^2 c_{\rm el}}{RT} \Psi_{\rm m}^2 \tag{4.27}$$

what, after including Eq. (4.26), gives the following formula for electrostatic component of the disjoinning pressure of symmetrical films of given *h* and  $\Psi_0$  (Verwey and Overbeek, 1948; Scheludko, 1967; Israelachvili, 1991):

$$\Pi_{\rm el} = 64c_{\rm el}RT \tanh^2 \left(\frac{ZF\Psi_0}{RT}\right) e^{-\kappa h}$$
(4.28)

Further derivation of this model leads to formula for asymmetrical films, with the different surface potentials  $\Psi_1$  and  $\Psi_2$  (Kar et al., 1973; Derjaguin et al., 1987; McCormack et al., 1995; Slavchov et al., 2005):

$$\Pi_{\rm el} = 64c_{\rm el}RT \tanh\left(\frac{ZF\Psi_1}{RT}\right) \tanh\left(\frac{ZF\Psi_2}{RT}\right) e^{-\kappa h}$$
(4.29)

From the Eq. (4.28), it easily can be assumed that for two interfaces of the same surface charge the  $\Pi_{el}$  becomes positive, what means that this forces are repulsive. In the case of Eq. (4.29), where two interfaces are of the opposite charges, then  $\Pi_{el} < 0$ , what leads to attractive interactions – thin liquid film becomes unstable.



**Fig. 4.5.** Potential distribution of the symmetrical thin liquid film (red line) and of the isolated interfaces (blue dash-lines).

# 4.1.3. Non-DLVO Forces.

Since the time, when DLVO theory was formulated, many studies have found that this theory was unable to describe colloidal behavior in some particular cases. Thus, some additional interactions have to be included into theory of disjoining pressure, and these extra forces can be repulsive, attractive or even can be of the oscillatory feature.

The good example of non-DLVO forces is solvation forces (Israelachvili, 1991; Adamson and Gast, 1997), which can be also repulsive or attractive. These forces depend not only on the properties of the intervening medium but also on the chemical and physical properties of the surfaces. A surface having surface groups that interact very strongly with water will have a net repulsion with another like surface, due to energetic coast of removing the bounded water layer - this is termed hydration force (Pashley, 1982). For opposite situation, when the surface repels water, there will be an energetic gain in removing water layers from between two surfaces producing the hydrophobic force.

The group of the non-DLVO components includes also: structural component (Derjaguin, 1989) or steric component (Exerowa and Kruglyakow, 1998). Although the DLVO theory is still expanded, the basic elements, i.e. van der Waals and electrostatic components, are still of the main importance for describing of the stability of the thin liquid layers.

#### 4.2. Foam Films.

Foams are complicated physicochemical systems and like other dispersed systems, are formed under dynamic conditions. There is no doubt on the importance of the foams for many technological processes, e.g. flotation, fire-fighting, washing, water treatment etc., and because of that, they are in the scientific spotlight of many research groups. The most essential foam properties, like gas bubble expansion, lifetime, and structure rupture and/or gas bubble expansion are determined by properties of the thin liquid film.

# 4.2.1. DLVO Interactions in Foam Films.

As mentioned above, foam film is the film with two liquid/gas interfaces, thus the surface forces acting across liquid core are symmetrical. It is also well known that the liquid/gas interface acquire a surface charge. The charging mechanism involves a combination of orientation of the water molecule dipole at the gas/liquid interface (Paluch, 2000) or adsorption of ions, dissociation of ionic groups, and charge separation (Hunter, 1981; Karraker and Radke, 2002; Gray-Weale and Beattie, 2009; Leroy et al., 2012). Regardless of the fact which mechanism is responsible for the presence of charge at the liquid /gas interface, the foam film surfaces are similarly charged, what causes that the electrostatic interactions are always repulsive (Exerowa and Kruglyakow, 1998; von Klitzing, 2005; Malysa and Lunkenheimer, 2008). In contradiction, the van der Waals Literature review

force are always attractive, destabilizing the foam films (Exerowa and Kruglyakow, 1998; Malysa and Lunkenheimer, 2008). Similar behaviors of DLVO interactions are also observed in the case of emulsion films, which are the other example of symmetrical liquid films (Exerowa and Kruglyakow, 1998; Karakashev et al., 2008; Gotchev et al., 2010, 2011). The one of the most accurate method to study of the DLVO interactions in thin liquid films is the microinterferometric method.

## 4.2.2. Microscopic Foam Films.

The intensive studies on the foams led to development of many different methods of characterization of the foams properties (Exerowa and Kruglyakow, 1998; Pugh, 2005) but for the studies of thin liquid films, the microscopic foam film techniques (Scheludko, 1967; Exerowa and Kruglyakow, 1998) seems to be the most proper method. This method has been developed and successfully applied for the more than 40 years, what makes it trustable way of foam films studies. The measurement technique bases on formation of the thin liquid film in controlled way under quasi-static conditions, in the special cell developed by Scheludko and Exerowa. The foam film is "opened" in the middle of biconcave drop situated in a glass tube of given radii or in the hole of porous plate (Fig. 4.6). This procedure allows us to observe the stability of foam films, but more important is that using Scheludko-Exerowa cell and interferometry it is possible to measure thickness of the TLF. Moreover, data obtained in this method, e.g. film thickness, can be used for calculation of the DLVO interactions in foam films (Chan et al., 1980; Sedev and Exerowa, 1999).

The microscopic foam film techniques has undeniable contribution into studies of influence of the surface active substances on stability of thin liquid films, and helped explain processes occurring during film drainage. With use of this method, nonhomogeneous thinning of the foam films was confirmed (Manev et al., 1974) and defined more precisely the stable regions of foam films, called common black film (CBF)

and Newton black film (NBF) (Exerowa et al., 1981, 1987; Kolarov et al., 1989). The CBF consists of two surfactant monolayers with a water core between them and is stabilized due to electrostatic forces - thickness c.a. 30 nm (see Fig. 4.6). Addition of the electrolyte causes screening of the electrostatic interactions, what affects in further thinning of the foam film until the NBF is formed – thickness 5-10 nm. The NBF consists of two surfactant monolayers, which are in contact to each other, and there is no liquid core between them. In the case of the NBF, screening of the electrostatic interactions leads to assumption that other mechanism, not accounted in DLVO theory, has to be responsible for the film stability. Mainly, occurrence and stability of the NBF is explained on the basis of the steric and hydration forces (Sedev and Exerowa, 1999; Cohen et al., 2003).



**Fig. 4.6.** Photos presenting microscopic foam films: A) thick film ( $h \ge 100$  nm), B) thin film ( $h \le 100$  nm), C) common black film ( $h \approx 30$  nm).

It is worth mentioning here that the same measurement technique was developed and adapted for studying of the emulsion films (Exerowa and Kruglyakow, 1998; Karakashev et al., 2007; Panchev et al., 2008) and the wetting films (Platikanov, 1964; Diakova et al., 2002; Nedylakow et al., 2010).

### 4.3. Wetting Films.

The wetting film can be described as the thin liquid film that separates two different, solid and gas, phases. This system consists gas/liquid and solid/liquid interfaces, and therefore the wetting film is called also the asymmetrical film. Film asymmetry is revealed in DLVO forces, which main components, van der Waals and electrostatic, can be either repulsive or attractive. Wetting, i.e. ability of liquid to spread over the solid surface, is directly interrelated to hydrophilic/hydrophobic properties of the solid surface. Hydrophilic surface is the solid surface of good wettability by water, and hydrophobic means that surface prefers contact with gas phase. Difference in hydrophilicity and hydrophobicity of the solids is the principle attribute applied in many technological processes, e.g. flotation of ores is based on the selective wetting properties (Gaudin, 1957).

# 4.3.1. Contact Angle.

The hydrophilic/hydrophobic properties of the solid surface can be determined by the contact angle measurement. If a drop of liquid is placed on a solid surface, then there are two possibilities: the liquid spreads on the surface completely (contact angle  $\theta = 0^{\circ}$ ) or a finite contact angle is established. In general, it is arbitrary denoted and rather commonly considered that the solid surface is hydrophilic (partially of fully wetted) for  $\theta < 90^{\circ}$  and for  $\theta > 90^{\circ}$  it is hydrophobic. However, it needs to be added here that as flotation of a mineral can proceed at any contact angle higher than zero (Leja, 1982; Drzymala, 2007), so the surfaces having contact angles below 90° are also termed as weakly hydrophobic (Leja, 1982), while that of  $\theta > 90^{\circ}$  are called strongly hydrophobic. The magnitude of the contact angle is related to the interfacial tensions working in the line of contact between the solid, the liquid and the gas phase (Fig. 4.7). The first quantitative description of interrelation between contact angle and wetting was introduced by Young (Young, 1805). Young equation relates the contact angle ( $\theta_Y$ ) to the interfacial tensions  $\gamma_{SY}$ ,  $\gamma_{SL}$ , and  $\gamma_{LV}$  on ideal (smooth, homogeneous, rigid and insoluble) solid surface:

$$\gamma_{\rm LV}\cos\theta_{\rm Y} = \gamma_{\rm SV} - \gamma_{\rm SL} \tag{4.30}$$

Subscripts in Eq. (4.30) indicate: L stands for liquid, V for vapor (or gas), and S for solid.

For liquid which is not originally in contact with the solid substrate but makes contact and adheres to it, the work of adhesion ( $W_A$ ) can be expressed as (Adamson and Gast, 1997):

$$W_{A} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \tag{4.31}$$

what together with Eq. (4.30) gives:

$$W_{A} = \gamma_{LV} (1 + \cos \theta) \tag{4.32}$$

Since work of cohesion  $(W_C)$  is given by:

$$W_{\rm C} = 2\gamma_{\rm LV} \tag{4.33}$$

Spreading of the liquid over the solid surface can be described in form of:

$$S_{\rm C} = W_{\rm A} - W_{\rm C} \tag{4.34}$$

what after rearrangement gives:

$$S_{\rm C} = \gamma_{\rm LV}(\cos\theta - 1) \tag{4.35}$$

The spreading coefficient ( $S_C$ ) is used for description how strongly a liquid can spread on a surface, i.e. for  $S_C > 0$  fully spreading is observed, where for  $S_C < 0$  a finite contact angle is formed.



Fig. 4.7. Liquid drop with circular contact area on a planar solid surface.

In order to apply Young's equation, the solid should be ideal: chemically homogeneous, rigid, and flat and smooth at an atomic scale and not perturbed by chemical interaction or by vapor or liquid adsorption. If such an ideal solid surface were present, then there would be a single, unique contact angle, but on real surfaces we have to face the complexity of hysteresis (*H*) (Butt et al., 2003; Erbil, 2006). Measurement of the contact angle, while the volume of the drop is increasing, just before the wetting line starts to advance give us so-called advancing contact angle ( $\theta_{adv}$ ). If afterwards the volume of the drop is decreased and the contact angle is determine just before the wetting line is receding, then it is measured the so-called receding contact angle ( $\theta_{rec}$ ). The hysteresis is defined then as (Butt et al., 2003; Erbil, 2006):

$$H = \theta_{adv} - \theta_{rec} \tag{4.36}$$

The H is equal typically 5-20° but can also be significantly higher. Hysteresis complicates the mathematical approach considerably because it is not known which situation refers to thermodynamic equilibrium.



Fig. 4.8. Schematic illustration of A) homogeneous wetting B) heterogeneous wetting.

As the Young equation does not take into account roughness of the solid surfaces, which affects strongly values of the contact angle, so other models were derived. Wetting on rough surfaces may occur at two regimes either: homogeneous wetting, where the liquid completely penetrates the roughness grooves (Fig. 4.8A), or heterogeneous wetting, where air (or another fluid) is trapped underneath the liquid inside the roughness grooves (Fig. 4.8B). The apparent contact angle on a rough surface in the homogeneous regime  $(\theta_W)$ , is given by the Wenzel equation (Wenzel, 1936):

$$\cos \theta_{\rm W} = r_{\rm w} \cdot \cos \theta_{\rm Y} \tag{4.37}$$

where  $r_w$  is the roughness ratio and is defined as:

$$r_{\rm w} = \frac{A_{\rm R}}{A_{\rm G}} \tag{4.38}$$

 $A_R$  and  $A_G$  are the geometrical and the real areas of the surface. It is clearly seen that, for hydrophobic surfaces, i.e.  $\theta_Y > 90^\circ$ , roughness (r >1) makes  $\theta_W$  higher than  $\theta_Y$ . The apparent contact angle in the heterogeneous regime, ( $\theta_{CB}$ ), is described by the Cassie-Baxter (CB) equation (Cassie and Baxter, 1944):

$$\cos \theta_{\rm CB} = r_{\rm f} \cdot \cos \theta_{\rm Y} + f - 1 \tag{4.39}$$

where *f* is the fraction of the projected area that is wet and  $r_f$  is the roughness ratio of the wet area. When *f*=1 then  $r_f$  is equal to  $r_w$  and CB equation simplifies to Wenzel equation.

The great surface roughness is also the characteristic properties of the superhydrophobic surfaces (Shirtcliffe et al., 2010), e.g. lotus effects - rolling away of the droplets from the surface (Barthlott and Neihuis, 1997) or bursting of the air bubble on a lotus leaf surface immersed in liquid (Wang et al., 2009). Generally, the superhydrophobic surfaces are the surfaces of high roughness ratio that keep the water surface as close as possible to the tops of the roughness asperities (Marmur, 2006).

#### 4.3.2. DLVO Interactions in Wetting Films.

As the wetting film has two different interfaces, thus DLVO interactions can vary due to different conditions. Eq. (4.29) shows that electrostatic interactions depend on surfaces potentials of both surfaces, and can by either attractive or repulsive. Electrostatic component of disjoining pressure depends on the charge of the solid surface and on the charge of the liquid/gas interface. Presence of the ionic surfactants is the main reason of the changes of surface charge (Exerowa et al., 2001, 2003; Krasowska et al., 2007a). As the air/water (clean water) interface is negatively charged (Graciaa et al., 1995; Exerowa and Kruglyakow, 1998; Ciunel et al., 2005), then for negatively charged solid surface the electrostatic forces are repulsive. This effect, for weakly hydrophobic surfaces, can stabilize wetting film. Opposite situation, i.e. positively charged solid surface, leads to the film destabilization and its immediately rupturing (Diakova et al., 2002; Ciunel et al., 2005; von Klitzing, 2005). It was also showed that addition of the ionic surfactants influences the film stability. Preferential adsorption of the cationic surfactant on the liquid/gas interfaces causes changing of the sign of surface potential and in the case of the negative charge of the solid surface provides to destabilizations of the liquid film, due to reverse in electrostatic interactions from repulsive into attractive (Niecikowska et al., 2010, 2011). It is important to remember here that cationic surfactants can also adsorb on the negatively charged solid surface, what for high concentrated solutions of cationic surfactants induce formation of stable wetting films (Exerowa et al., 2001, 2003; Niecikowska et al., 2011). Similar reasoning can be carried out for the anionic surfactant and positively charged solid surface. The strength and range of these forces can varied with changes of electrolyte concentration and pH of the liquid solution, especially in the case of hydrophilic and weakly hydrophobic surfaces (Zawala et al., 2008; Jiang et al., 2010; Krasowska et al., 2011a; Niecikowska et al., 2012). Jiang et al. (Jiang et al., 2010) studied wetting film on hydrophilic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles. In all experiments, the bubbles were negatively charged while the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles either were negatively (above pH of the isoelectric point, pH<sub>IEP</sub>) or positively (below pH<sub>IEP</sub>) charged. The stability of wetting film was found to be strongly influenced by the surface charge of the particles. The film destabilization occurred when the bubble and particle were oppositely charged (at low pH values) and at low salt concentration, i.e. when a long-range attractive electrostatic interaction is present. In the case where both bubble and particle were of the same charge, the TLF remained stable. Similar behaviors of the wetting film were observed in the case of the titania surfaces (Krasowska et al., 2011a), where stability of the TLF was controlled by the changes of the pH.

The state of the electrostatic interactions is not the only factor responsible for wetting film properties - the other ones are the van der Waals forces. The van der Waals contribution may be either positive or negative, depending on the dielectric properties of the three phases. A positive contribution exists when the dielectric properties of the liquid are intermediate between those of the two limiting media (Israelachvili, 1991; Lyklema, 1991). This is the case for aqueous solutions between glass and nitrogen (Saramago, 2010). Generally, in the case of hydrophilic solid surface the repulsive van der Waals forces between solid and gas phases are observed (Schulze and Birzer, 1987; Hewitt et al., 1993; Krasowska et al., 2011a). Moreover, the adsorption of silane at solid surface and/or the adsorption of a surfactant layer at the air/liquid interface change slightly the Hamaker constant (Laskowski and Kitchener, 1969; Mahnke et al., 1997; Diakova et al., 2002; von

Klitzing, 2005), since the Hamaker constant reflects rather the properties of the bulk than of the surface. In the case of the originally hydrophobic surfaces, it is possible to obtain attractive interactions (Preuss and Butt, 1999; Nguyen et al., 2001), however, they are only of range of 10-20 nm, thus their influence on film stability should be rather slight (von Klitzing, 2005).

#### 4.3.3. Nanobubbles.

Characteristic attribute of the highly hydrophobic surfaces is occurrence of some deviations from DLVO theory. At first, it was observed that two hydrophobic bodies immersed in water relieve some additional, even up to several hundred nanometers, attractive interactions, not accounted in DLVO theory (Israelachvili and Ninham, 1977). The other interesting phenomenon is rupturing of the wetting film in thickness much higher than predicted by the theory (Padday, 1970; Blake and Kitchener, 1972). These unusual findings led to introduction of "long range hydrophobic forces" (LRHF) concept (Israelachvili and Pashley, 1982, 1984). The origins of those additional attractions were not know, but the concept was popular and widespread (Herder, 1990; Rabinovich, 1994; Yoon and Ravishankar, 1996; Yoon, 2000; Adler et al., 2001). The first reasonably explanation of the LRHF origin was presented in work of Parker et al. (Parker et al., 1994). They were using a highly sensitive surface force apparatus (SFA) to measure the attractive force between two hydrophobic surfaces in water and found that the force exhibited clear steps, which can be interpreted as arising attraction from the presence of nanobubbles on the surfaces. This finding, that the LRHF was actually a capillary force resulting from the gaseous bridge formed from the coalescence of nanobubbles, was immediately confirmed by the many other research groups (Gong et al., 1999; Miller et al., 1999; Attard, 2000; Ederth and Liedberg, 2000). The most direct argument, that proved the existence of nanobubbles on hydrophobic surfaces, was obtained with use of the atomic force measurement (AFM) working in "tapping mode" (Ishida et al., 2000; Lou et al., 2000). It was found that diameter and height of nanobubbles are of ca. 700 nm and ca. 50 nm, respectively. Further studies, with use of the solvent exchange technique (Zhang et al., 2008; Hampton et al., 2008) demonstrated that the presence, or absence, of nanobubbles is strongly dependent upon the history of the sample. It is now rather commonly accepted that the additional attraction observed for hydrophobic bodies immersed in water occur due to the presence of gaseous domains at the liquid-hydrophobic solid interface (Tyrrell and Attard, 2002; Mishchuk, 2005; Hampton et al., 2009; Palmer et al., 2011). Nevertheless, some aspects, e.g. nanobubbles existence (Poynor et al., 2006) and methods of their studies (Mao et al., 2004; Doshi et al., 2005), are still questionable. The most controversial topic is stability of nanobubbles at a hydrophobic surface immersed in aqueous phase, which can be from hours to few days even (Zhang et al., 2006, 2008). As the the pressure inside the bubble ( $\Delta P$ ) of the curvature radius  $R_c$ , attached to the solid surface can be calculated by the Young-Laplace equation:

$$\Delta P = \frac{2\gamma_{LV}}{R_{cur}} \tag{4.40}$$

then pressure inside the nanobubble is much greater than outside, what should result in a quick dissolving of the nanobubbles into solution. Recently, it was reported that the contact angle of nanobubbles is significantly higher than the macroscopic contact angle (Zhang et al., 2008; Ducker, 2009), and because of that, the radius of curvature of the bubbles is much larger than the contact radius. As the mentioned deviation of the contact angle has significant implication for explanation of the nanobubbles stability - driving force for dissolution is greatly reduced, it is not clear why the contact angle is so high. There are two suggested explanations: (i) the line tension at the three-phase line is significant, what for such small volumes can have a crucial effect on the contact angle (Yang et al., 2003), (ii) small scale roughness can lead to pinning of the interface and result in a contact angle that is far from the equilibrium value (Zhang et al., 2007). After almost 20 years, nanobubbles

are still of interest to many research groups (Craig et al., 2012), what was recently concluded by Hampton and Nguyen (Hampton and Nguyen, 2010) with sentence that: "...experimental evidence is sound but a theoretical understanding is still lacking".

Presence of the air on the hydrophobic surfaces can be important in many practical applications. The accumulation of gas at the liquid-hydrophobic solid interface has influence on the stability of the wetting films and their critical thickness of rupturing (Stockelhuber et al., 2001, 2004; Snoswell et al., 2003; Belova et al., 2013), is crucial for superhydrophobicity (Shirtcliffe et al., 2010), and can lead to changes in hydrodynamic boundary slip conditions (Vinogradova, 1999; Fan and Vinogradova, 2005). The presence of gas phase at the interface can be even important for stability of the emulsion films (Ruckenstein, 2013) and also, what is essential, can affect kinetics of technological processes, e.g. flotation (Schubert, 2005; Krasowska and Malysa, 2007a; Fan et al., 2010; Hampton and Nguyen, 2009; Kosior et al., 2013).

### 4.4. Three-Phase Contact Formation.

The three-phase contact (TPC), solid-liquid-gas, can be formed either by liquid spreading over the solid surfaces or due to thinning and rupturing of the wetting film. The mechanism of the rupture process can be described by two theoretical approaches: (i) growing capillary wave mechanism (Vrij, 1966; Scheludko, 1967; Scheludko et al., 1976) (ii) the nucleation mechanism (Derjaguin and Gutop, 1962). The former theory is based on liquid surface instability against thermal fluctuation in presence of any kind of an attractive force, which amplifies the amplitude of fluctuation; this instability leads to the rupture of the film during its drainage. In the nucleation mechanism, no attractive forces are necessary. The film rupture occurs due to density fluctuations inside the film near hydrophobic spots or tiny gas bubbles. It was showed (Letocart et al., 1999; Schulze et al., 2001; Stockelhuber, 2003) that both mechanisms, nucleation and the capillary wave

mechanism, are possible to occur during the TPC formation, depending on the acting surface forces and the condition (hydrophobicity, heterogeneity etc.) of the surface.

As the froth flotation is one of the largest applications of surface chemistry, thus interactions between three different phases: gas, liquid, and solid, are of the interest of many researches. In flotation systems, the three-phase contact is formed in so-called elementary flotation act, that is, formation of stable bubble-grain aggregates as a result of mutual collisions between the bubbles and the grains (Gaudin, 1957). Process of formation of the stable bubble-grain aggregate can be divided into three steps (Nguyen et al., 1997b): (i) thinning of the liquid film formed by the colliding bubble to a critical thickness, (ii) the film rupture and formation of a three-phase contact nucleus, and (iii) expansion of three-phase contact line. The collision time in flotation systems is very short, of the order of milliseconds, only. Thus, properties and kinetics of rupture of the liquid film, separating the colliding bubble and solid surface, can be of crucial importance for the process efficiency and yield, especially when the film drainage and rupture are the slowest steps, that is, the steps determining kinetics and outcome of the entire process (Ralston et al., 2002).

The kinetics of the thin liquid film drainage depends on so many factors, that prediction of the time-scale of TPC formation becomes difficult problem for flotation process design. The hydrophilic/hydrophobic property of the solid surface is probably the one of the most important factor that determines stability of the wetting films. Generally, the more hydrophobic the surface, the less stable is the wetting film (Laskowski and Kitchener, 1969; Blake and Kitchener, 1972). In the flotation processes. hydrophilic/hydrophobic properties of the ore components are modified selectively with use of chemical reagents, named collectors. These reagents adsorb on particle surfaces via physical and/or chemical adsorption and affect the bubble-particle interaction, hence attachment time (Gaudin, 1957). Laskowski and Kitchener (Laskowski and Kitchener,

1969) assumed that the instability of water films on hydrophobic solids is fundamentally due to a deficiency of hydrogen bonding in these films as compared with liquid water. This proximity to any nonpolar surface imposes on neighboring water molecules an "unfavorable" configuration, causing the TLF destabilization. Sharma and Ruckenstein (Sharma and Ruckenstein, 1990) evaluated energetic criteria for the breakup of wetting films on solid surfaces. They calculated changes in the free energy during the process of the film thinning and a hole formation, and showed that instability of the wetting films increased nonlinearly with the increase in the degree of hydrophobicity. The properties of the mixed hydrophilic/hydrophobic solid surfaces were studied by Karakashev et al. (Karakashev et al., 2011). The glass surfaces were patterned with grid of hydrophilic squares and hydrophobic bars of different sizes. It was showed that wetting film ruptured on that solid surface, forming droplets on the hydrophilic domains.

Surface roughness is the other important property of the solid surface that undoubtedly affects the stability of the wetting film. The solid surfaces of the same chemical and physical properties but of different roughness show different wetting behaviors. It is well known that increase of the surface roughness causes increase of the contact angle (Sedev et al., 2004; Marmur, 2008; Krasowska et al., 2006; Nilsson et al., 2010). More interesting is the influence of surface roughness on stability of the liquid film formed during collision of the rising bubble and solid surface. Anfruns and Kitchener (Anfruns and Kitchener, 1977) published data about flotation efficiency of highly hydrophobic (via surface methylation) spherical glass and irregular quartz grains, and they found that the flotation efficiency was much greater in the case of irregular (rough) quartz grains. Similar findings were obtained in the model system, where rising bubble collided with solid plate immersed horizontally in liquid (Krasowska and Malysa, 2007a; Kosior et al., 2013), what confirmed that the greater surface roughness leads to shortening of the time of bubble attachment to the solid surface. Krasowska et al. (Krasowska and Malysa,

2007a; Krasowska et al., 2009) attributed the effect of Teflon roughness on the kinetics of the bubble attachment to: (i) the radius of the local liquid film formed at irregularities of the solid surface of different roughness; and (ii) the presence of air entrapped in the scratches, grooves and irregularities of the hydrophobic surface. According to the former mechanism, the local aqueous films are of significantly smaller radius than the radius of the entire 'global' liquid film formed between the colliding bubble and the solid surface. Such local films of much smaller tangential dimension need much shorter time to drain to their critical thickness of rupture. The latter mechanism attributes shortening of the time of TPC formation to the presence of previously de-wetted areas - sub-microscopic air bubbles entrapped in scratches upon the hydrophobic surface during its immersion into aqueous phase. It was showed (Krasowska et al., 2007b, 2009), that the amount of air entrapped depended on the roughness of the Teflon surface, and it was larger when the roughness was increased. The importance of air presence on solid surfaces on kinetic of TPC formation was also studied by Stockelhuber et al. (Stockelhuber, 2003; Stockelhuber et al., 2004; Slavchov et al., 2005). They explained the destabilizing effect of nanobubbles at the collision of hydrophobic particles with air bubbles. When nanobubbles exist in the contact region, the liquid film is no more considered as the wetting film only, but there are also locally formed foam films (Fig. 4.9). Stockelhuber et al. (Stockelhuber et al., 2004) stated: "Nanobubbles in wetting films can be the cause of rupture of wetting films, especially when all acting surface forces are repulsive. An introduction of "long-range hydrophobic interaction forces" is neither necessary nor appropriate."





As the flotation is the process where many different reagents are used, thus it is important to determine their influence on kinetic of the TPC formation. Besides, above-mentioned collectors, other important surface active substances presented in froth flotation are frothers. The frothers are responsible for a better dispersion (smaller bubbles) of the gas phase to assure formation of a froth layer of a desirable stability (Gaudin, 1957; Leja and Schulman, 1954; Malysa, 1992). They also help to facilitate the three-phase contact formation (Leja and Schulman, 1954; Leja, 1982) and prevent coalescence of the bubbles formed in the flotation cell (Cho and Laskowski, 2002a, 2002b). Moreover, the smaller bubble size and the presence of an adsorption layer at the air/liquid interface results in a significant decrease of the bubbles rise velocity (Clift et al., 1978; Levich, 1962; Malysa et al., 2005, 2011). This is an important factor resulting in the prolongation of the contact time during the bubble and mineral grain collision, and consequently, the probability that during the collision the liquid intervening film will drain to its critical thickness of rupture so a bubble-mineral grains aggregate can be formed, is increased. It was showed also, that too high concentrations of the surface active substances could be counterproductive for flotation effectiveness (Krasowska et al., 2009, 2011b; Kosior et al., 2013). This rather unexpected effect of the prolongation of time of attachment at high concentrations of the SAS was related to presence of air at highly hydrophobic surfaces. When air is entrapped in irregularities of hydrophobic surface then foam films are formed locally between the micro- and/or nano-bubbles and the colliding macro-bubble. These foam films exhibit higher stability in the presence of SAS, what can significantly affect kinetics of the TPC formation.

# 4.5. Velocity of the Film Drainage.

The outflow of the liquid from the thin films plays an essential role for the lifetime of dispersed systems. Thinning of the film occurs under the influence of gravity and/or suction at the Plateau-borders (capillary pressure). Generally, velocity  $(V_f)$  can be described as:

$$V_{\rm f} = -\frac{{\rm d} h}{{\rm d} t} \tag{4.41}$$

where h is a film thickness and t is a time. For the first time, the film drainage was theoretically described by Stefan and Reynolds (Reynolds, 1886). In their model of the film thinning, the lubrication approximation was applied to the Navier–Stokes equation (Landau and Lifshitz, 1987). This model assumes that fluid is incompressible and drains between two plane-parallel, tangentially immobile surface, where the space between the surfaces is relatively small to the radius of the film. With these assumptions, the following expression for the rate of the film thinning was derived:

$$V_{\rm Re} = \frac{2h^3 \Delta P}{3\eta R_{\rm f}^2} \tag{4.42}$$

where  $\Delta P$  is a pressure difference between the film and surrounding fluid,  $\eta$  is a fluid viscosity and  $R_f$  is a film radius. Later, it has been showed that thin liquid films generally exhibit faster thinning velocities, than that predicted by the Reynolds equation (Scheludko and Manev, 1967; Manev et al., 1974). The discrepancy has been attributed to a number of factors including finite tangential mobility (Lee and Hodgson, 1968; Radoev et al., 1974, 1983), the non-parallel nature and geometry of the flexible interfaces (Vrij, 1966; Ivanov et al., 1970; Manev et al., 1997), and dynamic surface waves (Ruckenstein and Sharma, 1987). Thus, modification of Eq. (4.42) by Scheludko (Scheludko, 1967), made it applicable not only for two tangentially immobile interfaces, but also in the case where one of them is fully mobile:

$$\frac{d\left(\frac{1}{h^2}\right)}{dt} = \frac{4n\Delta P}{3\eta R_f^2}$$
(4.43)

In this equation, factor n depends on the interface mobility and is equal to 4, when the film is created between the interface with no-slip condition and a completely mobile liquid/gas
interface, and n = 1 for two tangentially immobile interfaces, what affects in reduction of Eq. (4.43) to Reynolds equation. Moreover,  $\Delta P$  can be expanded, due to DLVO theory, to formula:

$$\Delta P = \Delta P_{\rm f} - \Pi(h) \tag{4.44}$$

where  $\Delta P_f$  is the "total" pressure causing film squeezing (capillary pressure, buoyancy force) and  $\Pi$  is a disjoining pressure. For film thicker than ca. 100 nm influence of disjoining pressure is negligible and therefore can be neglected.

The other significant deviations the film thinning rate from the classical Stefan-Reynolds equation is related to the film thickness non-homogeneity which strongly increases with the increase in film size and persists during the film evolution up to its rupture at the critical thickness. According to work of Levich (Levich, 1962) this fluctuations of the film thickness can be addressed to surface waves in thin liquid films (Vrij, 1966; Lucassen-Reyners and Lucassen, 1969; Ivanov et al., 1970). Experimental works (Manev et al., 1974; Maldarelli et al., 1980) assumed that corrugation of the film surface channels exists in the large film, dividing it into several smaller films (centers) with increased thinning rate, i.e. the complete symmetry of thinning is destroyed. This approach to the quantitative description of the film thickness non-homogeneity as a function of film size was resulted in developing a model (Manev et al., 1997; Tsekov, 1998; Coons et al., 2005; Manev and Angarska, 2005), which will be called below as the MTsR (Manev-Tsekov-Radoev) model:

$$V_{\rm MTsR} = V_{\rm Re} l^{3/2} \tag{4.45}$$

where l is the number of domains or rings in the film and is given by the following theoretical expression:

$$l = \left[\frac{\Delta P R_f^2}{16h\gamma}\right]^{2/5}$$
(4.46)

From Eqs (4.42), (4.45) and (4.46) we obtain:

$$V_{\rm MTsR} = \frac{1}{6\eta} \sqrt[5]{\frac{h^{12} \Delta P^8}{4\gamma^3 R_{\rm f}^4}}$$
(4.47)

Previous models do not take into account influence of adsorption layer on velocity of the flow on the film surface. In the presence of surface active substances assumption about slip conditions on liquid/gas interface may not be realized, and because of that more precious models, valid in the case of SAS presence, were developed in following works: Radoev et al., 1974; Ivanov and Dimitrov, 1974; Ivanov, 1980; Ivanov et al., 1985. This theory of the film thinning, called Radoev-Dimitrov-Ivanov (RDI) model, introduces the correction for the Marangoni-Gibbs effect accounting incomplete retardation of the foam film surfaces and dependency on the surfactant surface concentration gradient:

$$V_{\rm RDI} = V_{\rm Re}(1+\alpha) \tag{4.48}$$

where  $\alpha$  is expressed in term of:

$$\alpha = b + \frac{h_s}{h} \tag{4.49}$$

with:

$$b = -\frac{3\eta D}{\Gamma_{eq}\frac{\partial\gamma_{eq}}{\partial C}}$$
(4.50)

$$h_{\rm S} = -\frac{6\eta D_{\rm S}}{\Gamma_{\rm eq} \frac{\partial \gamma_{\rm eq}}{\partial \Gamma_{\rm eq}}} \tag{4.51}$$

D is a diffusion coefficient and  $D_S$  is a surface diffusion coefficient. The same RDI model, after rearranging, can be used for calculations of the thinning velocity of the foam film with two interfaces of different surfactant coverage (Ivanov et al., 1985), e.g. between bubble and free surface (Warszynski et al., 1996):

$$b^{A,B} = \frac{4\Gamma^{A}\Gamma^{B}b^{A}b^{B} + (\Gamma^{A} - \Gamma^{B})(\Gamma^{B}b^{B} - \Gamma^{A}b^{A})}{(\Gamma^{A} + \Gamma^{B})(\Gamma^{A}b^{A} + \Gamma^{B}b^{B})}$$
(4.52)

$$h_{\rm S}^{\rm A,B} = \frac{2\Gamma^{\rm A}\Gamma^{\rm B} \left(h_{\rm S}^{\rm A}b^{\rm B} + h_{\rm S}^{\rm B}b^{\rm A}\right)}{(\Gamma^{\rm A} + \Gamma^{\rm B})(\Gamma^{\rm A}b^{\rm A} + \Gamma^{\rm B}b^{\rm B})}$$
(4.53)

where *A* and *B* denotes two different interfaces. In the cause when one of the surface is fully mobile ( $\Gamma \approx 0$ ), the  $\alpha$  can be described as (Jachimska et al., 1998, 2001):

$$\alpha = 3 + 4b + \frac{h_s}{h} \tag{4.54}$$

Finally, similar theoretical considerations were performed for wetting film by Ivanov et al. (Ivanov, 1980; Ivanov et al., 1985), resulted in the following equation:

$$V = V_{Re} \frac{3 + b + \frac{h_S}{2h}}{3 + 4b + 2h_S}$$
(4.55)

This study covered also other important factor – deformation of the film interfaces, and assumed that  $V_{Re}$  in Eq. (4.48) and (4.55) should be replaced by formula (Dimitrov and Ivanov, 1978; Ivanov, 1980; Ivanov et al., 1985):

$$V_0 = \frac{h^3 \Delta P}{2\eta R_f^2} \tag{4.56}$$

The drainage models presented so far were developed under the assumption that hydrodynamic corrugations are static waves superimposed onto a plane parallel interface. Ruckenstein and Sharma hypothesized that hydrodynamic corrugations traverse the film laterally and induce an extra pumping action (Ruckenstein and Sharma, 1987; Sharma and Ruckenstein, 1987a, 1987b). Thus, the total velocity of film thinning for a thin liquid film is composed of Reynolds velocity and an additional velocity component that arises due to the pumping action of the traveling interfacial waves. Their final model of thinning velocity contains correction for the Marangoni-Gibbs effect for incomplete retardation of the film surfaces and the correction for the surface waves contribution to the film thinning (Sharma and Ruckenstein, 1988):

$$V_{\rm ShR} = V_{\rm Re} \left[ 1 + 13.33 \left( \frac{R_{\rm f}}{\lambda} \right) \left( \frac{\xi}{h} \right) [1 - f(\alpha)] \right]$$
(4.57)

where  $\lambda$ ,  $\xi$  are a wavelength and an amplitude of the typical interfacial wave, and  $f(\alpha)$  is a function accounting effect of surface elasticity and surface viscosity, which detailed form is given in (Dimitrov and Ivanov, 1978; Sharma and Ruckenstein, 1988).

The other important factor affecting the thinning rate for all presented models, despites the discrepancies between them, is the film size. It is well experimentally established, that the time of the film drainage to a given thickness is longer for the films with larger radii (Scheludko, 1967; Manev et al., 1984; Malhotra and Wasan, 1987; Kumar et al., 2002). Thus, for the films formed under dynamic conditions, e.g. during collisions of bubbles, droplets or particles with different interfaces, the film diameter ( $d_f$ ) has to be estimated from the colliding objects geometry. Table (4.1) presents mostly considered types of the films formed under dynamic conditions.

Ivanov et al. (Ivanov et al., 1985) derived the following general expression for the film radius for all systems presented in Table (4.1):

$$R_f^2 = \frac{F_T \overline{R}_b}{2\pi \overline{\gamma}}$$
(4.58)

where  $F_T$  is a driving force, and:

$$\overline{R}_{b} = \frac{R_{b}^{A} \cdot R_{b}^{B}}{R_{b}^{A} + R_{b}^{B}}$$
(4.59)

$$\bar{\gamma} = \frac{\gamma^{A} \cdot \gamma^{B}}{\gamma^{A} + \gamma^{B}} \tag{4.60}$$

Table 4.1. Models of the films formed under dynamic conditions (Ivanov et al., 1985).



GAS SOLID LIQUID	Allan et al., 1961; Princen, 1969		
GAS d <sub>r</sub> GAS LIQUID	Princen, 1963; Lee and Hodgson, 1968		
GAS LIQUID GAS	Charles and Mason, 1960; Chappelear, 1961; Princen, 1969		
LIQUID SOLID dr GAS	Ivanov et al., 1985		

**II. AIM OF THE THESIS** 

The Thesis aims at determining and evaluating importance of nanostructures of adsorption layers and hydrophobic solids surfaces on properties and stability of thin liquid films (TLF), formed at the liquid/gas and liquid/solid interfaces by the colliding bubble. Bubble motion in solutions of surface active substances (SAS) leads to formation over the bubble surface a dynamic architecture of the adsorption layer (DAL). Presence of air (nano- and micro-bubbles) at hydrophobic solid surfaces, immersed into aqueous phase, and the solid surface roughness can affect significantly the kinetics and mechanism of the three-phase contact (TPC) formation.

Rapid phenomena occurring during the bubble collisions with liquid/air and solid/air interfaces, namely the bubble bouncing, the liquid films formation, drainage and rupture, and the TPC formation were studied and described. Properties of thin liquid films formed, in distilled water and solutions of non-ionic and ionic surface active substances, under dynamic and static conditions, and their influence on kinetics of the TPC formation and bubble coalescence were investigated. Presence of surface active substances and the DAL formation over the bubble surface lowers significantly velocity of the rising bubbles and affects drainage velocity of the liquid films formed at the interfaces. Influence of the DAL formation on kinetics of the bubble bouncing, coalescence and the TPC formation was studied, by placement the liquid/gas and liquid/solid interfaces at two different locations (L=3 and L=250 mm), in respect to the point of the bubble formation. Sizes, lifetimes, drainage velocities and rupture thicknesses of the foam films formed by the bubble colliding with free surfaces were determined. Properties of the films formed under dynamic conditions were compared and analyzed in relation to properties of the microscopic static foam films. Problem of the air presence at hydrophobic solid surfaces and its importance in kinetics and mechanism of the TPC formation at hydrophobic solid surfaces was investigated and analyzed. Significant prolongation of the TPC formation at high concentrations of non-ionic and ionic SAS observed was attributed to air presence at the hydrophobic solid surfaces immersed into aqueous phase. When air, in a form of nanoand micro- bubbles, is present then the three-phase contact is formed as a result of rupture of the foam films, formed locally between the colliding macro-bubble and micro-bubbles already attached to hydrophobic solid surfaces.

# III. EXPERIMENTAL METHODS AND PROCEDURES

# 5. Methods.

#### 5.1. Bubble Collision.



**Fig. 5.1.** Experimental set-ups for monitoring the bubble collision with liquid/gas (A) and liquid/solid (B) interfaces.

Fig. 5.1 presents schematically set-ups used for studies of the bubble collision with the free surface (Fig. 5.1A) and solid surface (Fig. 5.1B). The experiments were carried out in a square borosilicate glass column (50 mm x 50 mm) with a capillary of inner diameter of 0.075 mm mounted at the column bottom. The capillary was connected with a gas-tight syringe (Hamilton, 5 ml) of a precise syringe pump. The equivalent diameter of the bubble  $(d_{eq})$  detaching from the capillary was 1.48 ±0.03 mm in Milli-Q water. A high-speed camera (SpeedCam MacroVis, 1040 frames per second), used for monitoring the bubble collision, bouncing and coalescence/attachment was mounted in two configurations: (i) side-view (free surface and all solid plates) (SpeedCam A), and/or (ii) top-view (free surface and transparent glass plates only) (SpeedCam B). To get absolute dimensions, the image of nylon sphere of 3.89 mm diameter, inserted inside the column after each experiment, was recorded. In series of experiments the free surface was located at the distances L equal either L= 3 or L= 250 mm from the capillary orifice. Similarly, the solid plate was positioned horizontally beneath the solution surface at a distances L= 3 or L= 250 mm from the capillary orifice. The variations of the bubble velocity during collisions and bouncing were determined from the measurements of the positions of the bubble bottom pole on subsequent frames of the recorded movies. The local velocity of the bubble  $(U_b)$  at a given position was calculated as:

$$U_{b} = \frac{\sqrt{(x_{i+1} - x_{i})^{2} - (y_{i+1} - y_{i})^{2}}}{\Delta t}$$
(5.1)

where (x,y) are coordinates of the subsequent positions of the bubble, and  $\Delta t$  is the time interval between subsequent frames of the camera. The bubble terminal velocity was calculated as the mean value of the local velocities for the distances at which the  $U_b$ became constant. The experiments were carried out in room temperature, ca. 21 ±1°C. Each experiment was repeated 20–40 times to get reliable data. The recorded movies were analyzed using the VirtualDub Video Analyze Software, the SigmaScan Pro Image Analyze Software, the ImageJ Software, and the WinAnalyze Motion Analyze Software.

#### 5.2. Microscopic Thin Liquid Films.

Properties of the equilibrium foam films were studied by the microinterferometric method, using the Scheludko-Exerowa glass cell (Fig. 5.3) (Scheludko, 1967; Exerowa and Kruglyakow, 1998). The completely experimental set-up used in studies of microscopic thin liquid films is presented schematically in Fig. 5.2. The measurements were carried out in a thermostated chamber ( $21 \pm 1^{\circ}$ C). The set-up was positioned on anti-vibration table, in room with regulated humidity to prevent film evaporation. The foam film was formed in the middle of a biconcave drop situated (i) in a film holder (Fig. 5.2A) (glass tube of radius *R*) by withdrawing liquid from it, or (ii) in a porous plate (Fig. 5.2B) by pressure increase



Fig. 5.2. Experimental set-up for the study of microscopic foam films.

in the vessel. The glass tubes of inner radius ( $R_{cell}$ ) of 1 mm and 2 mm were used, and radiuses of formed foam films ( $R_f$ ) were of 100 µm and 200 µm, respectively. The solution surface tension ( $\gamma$ ) and  $R_{cell}$  determined magnitude of the capillary pressure ( $P_\gamma$ ):

$$P_{\gamma} = \frac{2\gamma}{R_{cell}}$$
(5.2)

One of the important advantages of the contemporary set-up is the possibility to record and document the process of the microscopic foam film formation. Video files are subjected to video processing to render data about film lifetime. The film thickness (h) is monitored using the microinterferometric method (Exerowa and Kruglyakow, 1998).



Fig. 5.3. Schematic view of the Scheludko Exerowa cell with film holder (A) and porous plate (B).

Experimental methods and procedures

The microinterferometric technique is based on a measurements and comparison of intensities of monochromatic light ( $\lambda$ = 546 nm) incident at the film interfaces and reflected from it. The course of the interference can be registered as a curve photocurrent vs. time in which the maxima and minima correspond to maxima and minima of the interference. The film thickness (between a maximum and a minimum) is calculated from the ratio between the intensities measured of the reflected monochromatic light *I*, corresponding to a certain thickness, and *I<sub>max</sub>*, corresponding to the interference maximum, according to the formula (Exerowa and Kruglyakow, 1998):

$$h = \frac{\lambda}{2\pi n_{\lambda}} \left( k_{\lambda} \pi \pm \arcsin \sqrt{\frac{I/I_{max}}{1 + \left[ \left( n_{\lambda}^2 - 1 \right)/2n_{\lambda} \right]^2 (1 - I/I_{max})}} \right)$$
(5.3)

where  $n_{\lambda}$  is the refractive index of the solution, and  $k_{\lambda}$  is the interference order. The accuracy of the so determined microscopic thin liquid film thickness is  $\pm 0.2$  nm.

#### 5.3. Drop and Bubble Micro Manipulator.

The drop and bubble micro manipulator SINTERFACE DBMM-1 was used to measure the lifetime of thin films which were created between two bubbles in liquid (Loglio et al., 2011; Won et al., 2013) (Fig. 5.4). The DBMM consists of: (i) two closed measurement-cell blocks, made of stainless steel, with the active devices, i.e. the piezo-excitation actuator and the pressure sensor, connected with (ii) capillaries immersed together into (iii) the liquid in open to atmosphere optical cell. The inner and outer diameter of the stainless steel capillaries were 0.67 mm and 0.90 mm, respectively.



**Fig. 5.4.** Photos presenting two air bubbles in water before establishing contact (A), at contact (B) and after coalescence (C).

Diameter of the studied bubbles was  $1\pm0.1$  mm. The standard CCD camera allowed video recording with sampling rate 20 fps. Software dedicated enable to determine the radii of the two bubbles at both sides and simultaneously, the corresponding capillary pressure. The experiments were carried out in room temperature, ca.  $21 \pm 1^{\circ}$ C.

#### 5.4. Surface Tension Measurements.

The surface tension measurements were performed using KRUSS Drop Shape Analysis System DSA100 by pendant drop technique (Adamson and Gast, 1997). The surface tension values were calculated from profile of the pendant drop, which was recorded using the CCD camera. The images of the drop were transferred to the computer, where Gauss-Laplace equation was fitted to the experimental drop shape coordinates using KRUSS Software for Drop Shape Analysis DSA3. The measurements were carried out with constant drop volume in room temperature, ca.  $21 \pm 1^{\circ}$ C.

Values of dynamic surface tension were obtained using maximum bubble pressure technique (Fainerman and Miller, 1998). The SINTERFACE BPA-1S tensiometer with automatic control of the capillary immersion depth was used. The method is based on the measurement of the maximum pressure ( $P_{max}$ ) in a bubble growing at the tip of a capillary immersed into the liquid under study. The surface tension is calculated via the Laplace equation taking the capillary radius ( $R_c$ ) as radius of curvature and with addition of the respective hydrostatic pressure:

$$P_{\max} = \frac{2\gamma}{R_c} + \Delta \rho g l_{im}$$
(5.4)

where  $l_{im}$  is the capillary immersion depth and  $\Delta \rho$  is the density difference. The capillary radius and immersion depth were 0.170 mm and 5 mm, respectively. The experiments were carried out with decreasing airflow rate, i.e. with decreasing frequency of the bubble detachment from 0.0001 to 100 s.

Adsorption isotherms were fitted using Isotherm Fitting Program IsoFit, and adsorption kinetic was analyzed using Ward&Tordai Equation Solution Software (Aksenenko, 2001). The mentioned softwares used are distributed on a non-profit basis on the following website: http://www.thomascat.info/Scientific/AdSo/AdSo.htm.

#### 5.5. Contact Angle.

The contact angles on the studied solid surfaces were measured by (i) a sessile drop and (ii) captive bubble techniques. The values of the contact angle were determined using KRUSS Software for Drop Shape Analysis DSA3 by tangent method, i.e. fitting of polynomial function at the contact point where the liquid and the solid intersect.

The static advancing contact angles were measured by a sessile drop technique. A single drop of liquid of constant volume (ca. 5  $\mu$ l) was deposited at the solid surface

The dynamic contact angles measurement consisted of two steps: determination of advancing and receding contact angle. At first step, a single drop of volume ca. 2  $\mu$ l was formed at the solid surface and then the volume was slowly increased to ca. 14  $\mu$ l. To obtain receding contact angle, the volume of the drop formed in previous step was slowly decreased from ca. 14  $\mu$ l to ca. 4  $\mu$ l.

The static and dynamic contact angles measurement were carried out using the Kruss DSA100 apparatus. Measurement was repeated at least 10 times in different localizations on each solid plate and each experiment was recorded using CCD camera for further analysis.

The captive bubble technique allowed measuring the receding contact angle. The static receding contact angle was studied using the set-up for monitoring bubble collision with solid surface (see chapter 5.1). The videos recorded after the bubble attachments were analyzed by KRUSS DSA3 Software and the values of receding contact angle were determined.

#### 5.6. Streaming Potential.

Streaming potential measurements were conducted to determine the zeta potential of a Teflon surface. The measurements were carried out using a home-made cell, the main part of which was a parallel plate channel. The streaming potential ( $E_s$ ) was measured using a pair of Ag/AgCl electrodes as a function of the hydrostatic pressure difference ( $\Delta P_h$ ), which was driven by the electrolyte flow through the channel. The overall cell electric conductivity ( $K_e$ ) was determined using a pair of Pt electrodes. Knowing the slope of the  $E_s$  vs.  $\Delta P_h$  dependence, the apparent zeta potential of substrate surface ( $\zeta_i$ ) was calculated from the Smoluchowski relationship:

$$\zeta_{i} = \frac{\eta L_{c}}{4\varepsilon b_{c}c_{c}R_{c}} \left(\frac{\Delta E_{s}}{\Delta P_{h}}\right) = \frac{\eta K_{e}}{4} \left(\frac{\Delta E_{s}}{\Delta P_{h}}\right)$$
(5.5)

where  $\eta$  is the dynamic viscosity of the solution,  $\varepsilon$  is the dielectric permittivity, and  $R_e$  is the net electric resistance of the cell being the sum of the bulk and surface resistances,  $b_c$ ,  $c_c$  and  $L_c$  are dimensions of the parallel plate channel. A detailed description of the experimental set-up and the determination of the zeta potential were published in works of Zembala et al. (Zembala and Adamczyk, 1999; Zembala et al., 2001).

# 6. Materials.

#### 6.1. Reagents.

The conductivity and the surface tension of the Milli-Q water used in experiments and for the solutions preparation were <0.05  $\mu$ S/cm and 72.4 mN/m, respectively.

N-octanol and a-terpineol were used as the non-ionic surfactants while cetyltrimethylammonium bromide (CTABr) as the ionic one. All SAS used in the experiments were commercially available reagents of the highest available purity: n-octanol, Fluka  $\geq$ 99.5%;  $\alpha$ -terpineol, SAFC  $\geq$ 96%; and CTABr, Sigma  $\geq$ 98%. The solubility of n-octanol,  $\alpha$ -terpineol, and CTABr is  $3.8 \cdot 10^{-3}$  M,  $2.4 \cdot 10^{-3}$  M, and  $1 \cdot 10^{-1}$  M, respectively.



Fig. 6.1. Chemical structure of Rhamnolipids: R1 and R2.

Rhamnolipids (biosurfactants), used in our studies, are produced by Pseudomonas aeruginosa and usually obtained as a mixture of two or four species - at the natural pH, these biosurfactants are of the anionic type (Muller et al., 2012). Rhamnolipids of microbial origin, of purity greater than 99%, was donated by Jeneil Biosurfactant Company to research group of Bulgarian Academy of Sciences, Sofia. The author is grateful to prof. Dotchi Exerowa for sharing the mentioned reagent. Biosurfactant was donated as a mixture of R2:R1 at a ratio of 1.2 (effective molecular weight of 584 g/mol) (Fig. 6.1). Whereas R1 has the chemical formula of α-L-rhamnopyranosyl-β-hydroxydecanoate with a single rhamnose group and molecular weight of 504 g/mol, and R2 has two rhamnose groups with an ether bridge of oxygen with the chemical formula of 2-*O*-α-L-rhamnopyranosyl-β-hydroxydecanoate and molecular weight of 550 g/mol (Cohen et al., 2003). The biosurfactant has been neutralized and supplied in the form of 15% aqueous solution. Rhamnolipid solutions of studied concentrations were prepared on the day of the investigation from stock solutions of concentration 2·10<sup>-3</sup> M.

NaCl (Merck, Suprapur) was used as an electrolyte. To remove possible organic impurities, NaCl was roasted at 550°C for 2 h.

(Tridecafluoro-1,1,2,2-tetrahydrooctyl) trimetoxysilan (Fig. 6.2), Gelest Inc.  $\geq$ 95%, was used for modification of glass surface.

#### 6.2. Solid Surfaces.

Microscope glass slides (Paul Marienfield GmbH&Co.KG) were used as a model hydrophilic solid. Prior to the use, the glass plates were treated according to standardized cleaning procedure. At first, the glass slides were immersed in chromic acid mixture overnight and then rinsed with large quantity of bi-fold distilled water. Next, the plates were immersed in diluted "Mucasol" for two hours, rinsed with Milli-Q water, and then dried in 110°C. To check the purity of the glass surface, the advancing contact angle was measured. It was always below 4°.



Fig. 6.2. Schematic view of the reaction between organosilanes and a glass surface in an ideal case.

The hydrophobized glass surface was obtained using a standard silanization procedure (Newcombe and Ralston, 1994; Huang et al., 1995) (Fig. 6.2). First, the glass slides were cleaned (procedure described above). Just before the silanization, the plates were dried in 110°C for one hour and then immersed in 4% (v/v) solution of (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimetoxysilan in ethanol for three hours in room temperature. Next, the glass plates were rinsed with methanol and ethanol, rinsed again with huge quantity of Milli-Q and dried in 100°C. Afterward, they were stored in a closed vessel in room temperature. To get a rough hydrophobic glass plate (SG600), the surface of the microscope glass slide was roughened with abrasive paper of grid number No. 600, before cleaning and silanization procedure. 
 Table 6.1. Characteristic of the studied solid plates.

Plate name	Material	Modification procedure	Microscopic photo	Roughness
T2500	PTFE	Abrasive paper No.2500	100µm	1-5 µm
T1200	PTFE	Abrasive paper No.1200	<u>100µт</u>	10-20 µm
Т600	PTFE	Abrasive paper No.600	100µm	40-60 µm
T100	PTFE	Abrasive paper No.100	то/ 1 <u>00µm</u>	80-100 µm
P00	PVC	No modification	<u>100µт</u>	1-5 µm
SG00	Glass	Silanization	100µm	1-5 µm
SG600	Glass	Abrasive paper No.600 + Silanization	100µm	10-20 µm

The Teflon plates used in the experiments were cut from the same piece of the commercially available polytetrafluoroethylene (PTFE) block. Surface roughness of the Teflon plates was mechanically modified using abrasive paper of different grid numbers,

from No. 2500 down to No. 100. Teflon2500 denotes the smoothest Teflon surface, while Teflon100 the roughest one. The polyvinyl chloride (PVC) samples were cut from the commercially available Anwidur® sheet (Anwil S.A.). Roughness of the polymer surfaces was evaluated from the image analysis of the photos taken using the optical microscope Nikon Epiphot 200 (Table 6.1). The hydrophobic properties of the studied solid surfaces were determined by measuring of the contact angle. Figure 6.3 presents values of the static advancing contact angles for the solid surfaces used in this work.



Fig. 6.3. Static advancing contact angles of the solid plates used in experiments.

# **IV. RESULTS AND DISCUSSION**

# 7. Bubble Properties.

#### 7.1. Bubble Adsorption Coverage.

As the most of the experiments were carried out in presence of surface active substances, so the influence of the SAS studied on the bubble formation, size, motion parameters and degree of the adsorption coverage over the bubble surface was determined and analyzed in details. Fig. 7.1 presents dependencies of the surface tension on concentration of n-octanol,  $\alpha$ -terpineol and CTABr solutions. Points of Fig. 7.1 present the experimental data, while the lines show the best fit of the Frumkin isotherm. The fitting was performed using Isotherm Fitting Program IsoFit. Parameters of the fitted Frumkin isotherms for mentioned SAS are gathered in Table 7.1.



**Fig. 7.1.** Equilibrium surface tension vs. concentration of n-octanol,  $\alpha$ -terpineol and CTABr solutions. Points are the experimental data, lines present the best fit of the Frumkin isotherm.

Solute	K <sub>F</sub> [dm <sup>3</sup> /mmol]	ω [m²/mol]	a <sub>F</sub>
n-octanol	1.34	$1.60 \cdot 10^5$	1.00
α-terpineol	1.01	$2.40 \cdot 10^5$	0.50
CTABr	8.23	$1.80 \cdot 10^5$	0.40

**Table 7.1.** Parameters of the fitted Frumkin isotherms.



**Fig. 7.2.** Adsorption coverage at surface of the detaching bubble (grey circles) and the equilibrium coverage (white circles) as a function of n-octanol (A),  $\alpha$ -terpineol (B), and CTABr (C) concentration.

In solutions of surface active substances the bubble formation at the capillary orifice is accompanied by the SAS adsorption and formation of adsorption layer over the growing bubble surfaces. The adsorption coverage is uniform but the equilibrium coverage at surface of the detaching bubble is obtained only in the cases when the adsorption kinetics is much faster than velocity of the bubble surface expansion. The convective-diffusion adsorption model for the adsorption kinetics at the growing spherical surface (presented in Chapter 2.3.1) was used for calculation the degree of adsorption coverage ( $\Theta$ ) at the expanding surface of the bubble growing at the capillary orifice. The calculations

were performed using software developed by prof. Warszynski. In our experiments, the time of the bubble growth at the capillary orifice was 1.6 s, so this value was used in calculations to get coverage at interface of the detaching bubble. Results of these calculations for n-octanol,  $\alpha$ -terpineol and CTABr solutions are presented in Figs 7.2 A-C. For the comparison's sake there are also presented the equilibrium adsorption coverage's for each SAS, which were calculated under the assumption  $t_{ads} = infinity$ .

## 7.2. Bubble Diameter.

Diameter of the bubble formed at the capillary orifice of known diameter  $(d_c = 0.075 \text{ mm})$  depends on solution surface tension and can be calculated, using the Tate's Law (Eq. 3.1) and adsorption isotherms. Sizes of the bubbles were also determined experimentally for studied concentrations of n-octanol,  $\alpha$ -terpineol and CTABr solutions. Fig. 7.3 presents a comparison of the experimental results and the calculated values.



**Fig. 7.3.** Diameter of the bubble as a function of n-octanol,  $\alpha$ -terpineol and CTABr solutions. Points present the experimental data, lines – values calculated according to Eq. 3.1.

Gu and Li (Gu and Li, 2000) assumed that the point of zeta reversal (PZR) for glass in CTABr solution occurs at a concentration between  $10^{-4}$  and  $10^{-3}$  M. Thus, to avoid capillary hydrophobization caused by adsorption of the cationic surfactant on the

negatively charged surface, the highest studied concentration of the CTABr solution was  $c=2\cdot10^{-5}$  M. In the case of n-octanol and  $\alpha$ -terpineol, a good agreement between experimental and calculated diameters was observed, even for high solutions concentrations. As seen in Fig. 7.3 with increasing solution concentration the bubbles diameters were decreasing, but the changes, at the range of studied concentrations were relatively small (ca. 10%).

#### 7.3. Bubble Impact Velocity.

Two methods were applied to modify the bubble impact velocity ( $U_{imp}$ ), that is, the bubble velocity at the moment of its collision with liquid/gas and liquid/solid interfaces, namely: (i) via variations of the distance between the capillary orifice and the interface, and (ii) via addition of the surface active substances. As it was mentioned in Chapter 5.1, solid/liquid or air/liquid interfaces were located in distances "far" (L= 250 mm) or "close" (L= 3 mm). The bubble impact velocity, for interface located "far" was equal to the bubble terminal velocity ( $U_T$ ), while at L= 3 mm the bubble was still at the acceleration stage (Malysa et al., 2011).



**Fig. 7.4.** Bubble terminal velocity in function of (A) SAS concentration (B) bubble coverage. The lines are drawn to guide the eye.

As can be seen in Fig. 3.2 and Fig. 7.4 the bubble terminal velocity variations depend on the type of the surface active substance but, in general, the most drastic velocity decrease always takes place at the lowest solutions concentrations. In distilled water, the bubble terminal velocity was  $34.7 \pm 0.3$  cm/s and decreased rapidly down to 15-16 cm/s at very low n-octanol ( $3 \cdot 10^{-5}$  M),  $\alpha$ -terpineol ( $5 \cdot 10^{-5}$  M) and CTABr ( $5 \cdot 10^{-6}$  M) concentrations - see Fig. 7.4A. These concentrations are the minimum ("threshold") concentrations assuring a complete retardation of the bubble surface mobility. The bubble velocity stayed practically constant for higher concentration values. Figure 7.4B presents the bubble velocity as a function of the adsorption coverage over detaching bubble surface. As seen, the adsorption coverages at the "threshold" concentrations of the solutions studied were as small as ca. 2.6% (n-octanol), 3.9% ( $\alpha$ -terpineol) and 0.8% (CTABr). These adsorption coverages were sufficient for a complete immobilization of the rising bubble surface.

Figs 7.5 A-D present the bubble impact velocities, for the interface locations at the distance L= 3 mm and L= 250 mm, as a function of n-octanol (Fig. 7.5A),  $\alpha$ -terpineol (Fig. 7.5B), CTABr (Fig. 7.5C) and Rh1.2 (Fig. 7.5D) solutions concentrations. As it was mentioned above, the bubble impact velocities for location "far" was equal  $U_T$ , but there was a concentration range, where bubble impact velocity for L= "close" was higher than its terminal velocity. This phenomenon was related to the time-scale of the DAL architecture formation (see Chapter 3.1). In these concentration ranges the detached bubbles reached, after acceleration stage, a maximum velocity value, higher than the terminal one. Appearance of the maximum on the local velocity profiles is an indication that the dynamic steady state architecture of the adsorption layer over the rising bubble surface was not established during the acceleration stage. In such cases, a deceleration stage was observed until bubble slowed down to its terminal velocity (Krzan and Malysa, 2002; Krzan et al., 2007; Malysa et al., 2011).



**Fig. 7.5.** Bubble impact velocity as a function of n-octanol (A),  $\alpha$ -terpineol (B), CTABr (C) and Rh1.2 (D) concentration for the interface located "far" (grey circles) and "close" (white circles) from the capillary. The lines are drawn to guide the eye.

# 8. Foam Films.

#### 8.1. Bubble Bouncing at Liquid/Gas Interface.

## 8.1.1. Water/Air Interface.

Figure 8.1 presents phenomena occurring during the rising bubble collisions with surface of distilled water located at distance L= 250 mm and 3 mm. The sequences of photos show the bubble bouncing and coalescence on liquid/air interface and illustrate dynamics of the bubble shape and velocity variations. As seen in the case when the water/air surface located at L= 250 mm (location "far") the bubble bounced back three



times and the coalescence took place during the fourth collision coalescence, while for L=3 mm (location "close") the bubble coalescence occurred during the third collision.

Fig. 8.1. Sequences of photos of the bubble colliding with water/air interface located at the distances L= 250 and 3 mm.

Quantitative data on variations of the bubble velocity and shape deformation during the bubble collisions with water/air interface located at distances L= 3 mm ("close") and L= 250 mm ("far") are presented in Fig. 8.2. For the water surface located at L= 250 mm the bubble approached the surface with constant velocity equal to the bubble terminal velocity,  $U_t$ = 34.8 ± 0.2 cm/s, while for the "close" location, the bubble was still in acceleration stage and its velocity at the moment of collision (impact velocity) was significantly lower -  $U_{imp}$ = 19.4 cm/s (see Fig. 7.5). After the first collision, the bubble bounced backwards, that is, started to move in the direction opposite to the buoyancy force.

After dissipation of the energy related to backward motion, the bubble started again to rise towards and collided second time with the water surface but with lower impact



**Fig. 8.2.** Variation of (A) the bubble velocity and (B) shape deformation during collisions with water surface located at distance L= 250 mm (white circles) and L= 3 mm (grey circles) from the capillary orifice. velocity and bounced again. As can be observed in Fig. 8.2A the amplitude of each subsequent "approach-bounce" cycle was diminishing due to the energy dissipation. Finally, the colliding bubble ruptured and it happened during the 4<sup>th</sup> collision with water surface located at L= 250 mm, and during the 3<sup>rd</sup> one at L= 3 mm. During each collision, the bubble shape was changing rapidly, especially during the 1<sup>st</sup> collision (Fig. 8.2B). The deformation degree, that is the ratio of the bubble horizontal and vertical diameters, was

smaller and smaller during each subsequent collision due to the decreasing impact velocity (Sunol and Gonzales-Cinca, 2010; Zawala and Malysa, 2011).

Comparing the bubble coalescence time, i.e. the time interval form the moment of the 1<sup>st</sup> collision until the bubble rupture (coalescence), it is clearly seen in Fig. 8.2 that impact velocity is the parameter strongly affecting the bubble coalescence time ( $t_c$ ) at surface of the distilled water. Generally, time of the bubble coalescence can be considered as a sum of the time of the bubble bouncing ( $t_{bouncing}$ ) and lifetime ( $t_{film}$ ) of the liquid film formed at the interface by the colliding bubble:

$$t_{\rm C} = t_{\rm bouncing} + t_{\rm film} \tag{8.1}$$

For the  $U_{imp}$ = 34.8 cm/s (L= 250 mm) the bubble coalescence time was 73 ±1 ms, while for  $U_{imp}$ = 19.4 cm/s (L= 3 mm) the  $t_c$  was only 42 ±1 ms. As can be noted in Fig. 8.2A, this prolongation of the coalescence time was due to higher number of the bubble "approach-bounce" cycles. Thus, in the case of clean water surface, the  $t_c$  value is determined by the bubble bouncing time because lifetime of the water film formed prior to the bubble rupture is only of order 1-3 ms (see Fig. 7.8A).

Prolongation of the bubble coalescence time at water surface at higher bubble impact velocity is related to size of the liquid film formed during the bubble collision. The bubble bounces when the thinning water film between the bubble and air/water interface does not reach its rupture thickness during the collision time. Higher impact velocity means larger deformation of the bubble shape and larger radius of the liquid film formed, i.e. longer time is needed for the film drainage. Radius of the thin liquid film ( $R_f$ ), formed by the bubble at various interfaces, can be estimated using Eq. 4.58, called often Princen equation, which in the case of the liquid/air interface is as follows (Princen, 1969; Ivanov et al., 1985):

$$R_{f}^{2} = \frac{F_{T}R_{b}}{\pi\gamma}$$
(8.2)

where  $F_T$  is a driving force,  $R_b$  is the bubble radius and  $\gamma$  is a surface tension. In the case of the bubble stopped at the interface (static conditions), the force  $F_T$  is equal to the buoyancy force, but under dynamic conditions, the radius of the intervening liquid film is determined by a temporary force ( $F_{dyn}$ ) related to the kinetic energy associated with the motion of the bubble ( $E_k$ ). The  $F_{dyn}$  is responsible for the bubble deformation and water squeezing out from the water film separating the colliding bubble from air phase. The physical meaning of this temporary force is that it is the work of the bubble shape deformations, carried out at the distance of the bubble deformation (Zawala and Malysa, 2011; Zawala et al., 2011):

$$F_{dyn} = \frac{E_k}{\Delta d_v}$$
(8.3)

where  $\Delta d_v$  is a difference in vertical diameter  $(d_v)$  of the bubble just before collision and at the moment of the bubble maximum deformation. The kinetic energy associated with the motion of the bubble is equal to (Levich, 1962):

$$E_{k} = 0.5C_{m}\Delta\rho V_{b}U_{imp}^{2}$$
(8.4)

The added mass coefficient ( $C_m$ ) is a function of the bubble-deformation ratio, i.e., the ratio between the horizontal and vertical diameters ( $\chi$ ) (Tsao and Koch, 1995; Klaseboer et al., 2001):

$$C_{\rm m} = \frac{f(\chi)}{2 - f(\chi)} \tag{8.5}$$

where:

$$f(\chi) = \frac{2\chi^2}{\chi^2 - 1} \left( 1 - \frac{1}{\sqrt{\chi^2 - 1}} \cos^{-1}\left(\frac{1}{\chi}\right) \right)$$
(8.6)

After linearization of Eq. 8.5, for  $1 \le \chi \le 2.5$ :

$$C_{\rm m} = 0.62\chi - 0.12 \tag{8.7}$$

Assuming that  $d_h/2$  is the radius of the deformed bubble at the moment of the collision we obtain from Eqs 8.2-8.4:

$$R_{f}^{2} = \frac{E_{k}d_{h}}{2\pi\gamma\Delta d_{v}}$$
(8.8)
Collision	d <sub>h-collision</sub>	U <sub>imp</sub>	E <sub>k</sub> •10 <sup>-9</sup>	$F_{dyn} \cdot 10^{-4}$	R <sub>f</sub>					
no.	[mm]	[cm/s]	[J]	[N]	[mm]					
L = 250 mm										
1.	$1.86 \pm 0.02$	$34.7\pm0.2$	92.4	4.4	$1.34 \pm 0.09$					
2.	$1.64 \pm 0.01$	$19.0 \pm 0.3$	17.9	1.0	$0.61 \pm 0.04$					
3.	$1.59 \pm 0.01$	$12.8 \pm 0.1$	7.7	0.5	$0.41 \pm 0.04$					
4.	$1.55 \pm 0.02$	$8.4 \pm 0.2$	3.2	0.2	$0.26\pm\!\!0.02$					
L = 3 mm										
1.	$1.63 \pm 0.02$	$19.4 \pm 0.2$	19.6	2.0	$0.84\pm\!\!0.07$					
2.	$1.58 \pm 0.02$	$12.0 \pm 0.3$	6.7	0.7	$0.51 \pm 0.03$					
3.	$1.51 \pm 0.01$	$6.5 \pm 0.1$	1.9	0.2	$0.27\pm\!\!0.03$					

**Table 8.1.** Values of the dynamic radius of the liquid film formed by the bubble colliding with the water/air interface.

The experimental ( $U_{imp}$ ,  $d_{h-collision}$ ) and the calculated ( $E_k$ ,  $F_{dyn}$ ,  $R_f$ ) values, for each collisions of the bubble with the interfaces locations at L= 250 and 3 mm, are presented in the Table 8.1. As seen, the radius of the liquid film formed was the largest at the first collision and substantially smaller in the subsequent collisions. Note please, that at the moment of bubble coalescence the film radius was practically identical for the distances "close" and "far". As the Princen equation, relating the film size to bubble radius was elaborated for small deformations of the bubble shape, thus, its application to dynamic conditions is rather a crude approximation, and therefore, the numerical values obtained should be treated with caution. Nevertheless, data obtained and presented in Table 8.1 illustrate an influence of the film size on kinetics of the bubble coalescence.

## 8.1.2. Solutions of Surface Active Substances.

Presence of a surface active substance affects significantly profiles of the bubble local velocity and can lower the terminal velocity even by over 50% (see Chapter 3.1). Simultaneously, stability of the foam films increases rapidly with SAS concentration and the film equilibrium thickness depends on the SAS type and solution concentration (Exerowa and Kruglyakow, 1998). As showed in Fig. 8.2 lowering of the bubble impact velocity caused shortening the bouncing time so it can be expected that with increasing

n-octanol concentration the  $t_{bouncing}$  values should be decreasing while the  $t_{film}$  values should be increasing. Fig. 8.3 presents sequences of photos illustrating influence of n-octanol concentration on the bubble bouncing on liquid/air interface located at distance L= 250 mm. For  $4 \cdot 10^{-6}$  M n-octanol solution, there are presented 1<sup>st</sup> and 4<sup>th</sup> collisions only. As can be observed in Fig. 8.3 the bubble coalescence took place during 4<sup>th</sup> collision, that is, similarly as in the case of distilled water (See Fig. 8.1). At  $c= 5 \cdot 10^{-6}$  M, bubble did not rupture during the 4<sup>th</sup> collision but bounced two times more and after that stayed practically motionless beneath the surface, till the moment when thin liquid film ruptured. Also at  $c= 1 \cdot 10^{-4}$  M, bubble did not rupture during the coalescence.



**Fig. 8.3.** Sequences of photos of the bubble colliding with liquid/air interface located at L= 250 mm in n-octanol solutions of different concentrations.

Figures 8.4 A-B present the bubble velocity variations during collision with the liquid/air interfaces. There are presented results for distilled water and n-octanol solutions

of low concentrations. As seen at these low n-octanol concentrations the foam film formed during collision between rising bubble and a free surface were not stable enough to prevent the bubble coalescence during the "approach-bounce" cycles – the bubble ruptured during the 3<sup>rd</sup> and the 4<sup>th</sup> collision, for interface located L= "close" and "far", respectively, similarly like in distilled water. However, in the case of L= 250 mm, the bubble coalescence time for  $4 \cdot 10^{-6}$  M n-octanol solution was only 58 ±3 ms, i.e. was by 15 ms shorter than in distilled water (Fig. 8.4B). This shortening of the coalescence time was a consequence of lower impact velocity, smaller bouncing amplitudes and shorter bouncing time. If the case of the interface location at L=3 mm this effect was unnoticeable because the bubble impact velocities were very similar - 19.4 cm/s and 18.8 cm/s, for water and 4.10<sup>-6</sup> M n-octanol solution, respectively (Fig. 8.4A). In this case, the bubbles detached from the capillary were at the acceleration stage and therefore their impact velocities were lower and did not decrease so rapidly with n-octanol concentration.



Fig. 8.4. The bubble velocity variations during collisions with free surface located at L=3 mm(A) and L= 250 mm (B), in water and n-octanol solutions of different concentration.

Effect of a further increase of n-octanol concentration of the bubble bouncing and coalescence time at the solution/air interfaces located "close" and "far" is presented in Figs 8.5 A and B, respectively. It was found that, that there was a "threshold" concentration ( $c=5\cdot10^{-6}$  M) at which the liquid (foam) film formed at n-octanol solution Results and discussion

surface started to be stable enough to prevent rupture of the colliding bubble during the bouncing stage. After the bouncing stage, the bubble stayed practically motionless beneath the solution surface and its rupture occurred after ca. 1200 ms, i.e. the bubble coalescence time was by over an order of magnitude longer than its bouncing time ( $t_{bouncing}$ = 80 ms). Thus, 5·10<sup>-6</sup> M n-octanol concentration can be considered as the "threshold", that is, minimum concentration for obtaining the foam films, stable enough to survive the disturbances caused by the colliding bubble. At higher n-octanol concentrations the bubble bouncing time was decreasing rapidly to ca. 15 ms and started be constant for  $c \ge 1 \cdot 10^{-4}$  M. At these high n-octanol concentrations the kinetic energy associated with the bubble motion was practically completely dissipated after the bubble first collision and the bubble shape pulsation were also damped rapidly, as can be noted in Fig. 8.5, for  $c = 1 \cdot 10^{-3}$  M. It is seen there that already after ca. 15 ms from the first collision the bubble stayed motionless beneath the solution surface, but its coalescence time was very long (a few seconds, at least).



**Fig. 8.5.** The bubble velocity variations during collisions with free surface located at L= 3 mm(A) and L= 250 mm(B), in n-octanol solutions of different concentration.

Figure 8.6 presents a comparison of influence of n-octanol concentration on the bubble impact velocity and the bouncing time at the solution/air interface location at

L= 3 mm (Fig. 8.6A) and L= 250 mm (Fig. 8.6B), respectively. Analyzing influence of n-octanol concentration on the bubble bouncing and coalescence time, for both distances, it was found that there exists a concentration (c= 5·10<sup>-6</sup> M) at which the liquid (foam) film formed at n-octanol solution surface starts to be stable enough to survive disturbances caused by the colliding bubble. For n-octanol concentrations lower than 5·10<sup>-6</sup> M the bubble bouncing amplitude and the bouncing time was decreasing due to decreasing the bubble impact velocity and the bubble ruptured quicker. At 5·10<sup>-6</sup> M and higher n-octanol concentrations the outcome of the bubble collisions with solution surfaces starts to be quite different. The bubble bouncing time increased drastically at 5·10<sup>-6</sup> M n-octanol. This rapid increase of the bubble coalescence time at 5·10<sup>-6</sup> M n-octanol is clearly seen in Fig. 8.6. After end of the bouncing period, the bubble stayed motionless until the coalescence occurred, what confirms an increased stability of the foam film formed between the colliding bubble and the solution surfaces.



**Fig. 8.6.** The time of the bubble bouncing (black circles) and the bubble impact velocity (white circles) during collisions with surface located at L=3 mm (A) and L=250 mm (B) as a function of n-octanol concentration.

The  $t_{bouncing}$  values are determined as a period from the bubble first collision until the moment when either the bubble ruptured or no gap between the bubble and the solution surface could be detected at the recorded movies. Determination of the end moment of the bubble bouncing was quite simple and precise when applied for water surface and lowest n-octanol concentrations. However, when the solution concentration increased  $(c \ge 5 \cdot 10^{-6} \text{ M})$  it became more difficult and not precise enough. Therefore, in these cases the end moment of the bouncing was determined from comparison of the photos acquired using the SpeedCam A and SpeedCam B (see Fig. 5.1). The *t*<sub>bouncing</sub> values were measured as the time interval form the first collision until the moment when the SpeedCam A photos (top-view) showed that there was a permanent contact between the bubble and solution surface. This moment was an indication that the bouncing period was over.



**Fig. 8.7.** Sequences of the top-view (upper rows) and side-view photos of the bubble colliding with liquid/air interface located at L= 250 mm in  $6 \cdot 10^{-6}$  M n-octanol solution.

Figure 8.7 presents sequences of photos, recorded using top-view and side-view camera, which show the bubble bouncing in  $6 \cdot 10^{-6}$  M n-octanol solution at the liquid/air interface located at distance L= 250 mm. There are presented  $1^{\text{st}}$ ,  $2^{\text{nd}}$ ,  $3^{\text{rd}}$  and  $6^{\text{th}}$  collisions only. It can be observed there, that bubble bounced of the free surface after each of the first three collisions, and using top-view observation it can be recognized that liquid film

between bubble and surface disappeared then. Similar observations were made for the 4<sup>th</sup> and 5<sup>th</sup> collisions. After 6<sup>th</sup> collision, the bubble stayed motionless under the free surface, and liquid film was formed permanently until the moment of the bubble coalescence.



**Fig. 8.8.** Variation of (A) the bubble velocity and (B) film radius during collisions with  $6 \cdot 10^{-6}$  M n-octanol solution surface located at distance L= 250 mm from the capillary orifice.

Note please, that even after the establishment of the bubble-surface permanent contact some residual bubble shape pulsations were still having place. As the bubble velocity was determined on the basis of the bubble bottom pole positions, so there were also measured some residual velocity variations of an order 1-3 cm/s (Kosior et al., 2013). Similarly, slight changes of the liquid film radius were noted after the moment of establishment of the bubble-surface permanent contact. The both effects, for  $6 \cdot 10^{-6}$  M n-octanol solution, are showed on Fig. 8.8, where after 6<sup>th</sup> collision some residual variation of the bubble velocity (Fig. 8.8A) and the film radius (Fig. 8.8B) are still seen. It needs to be underlined here that as explained above, these residual variations at *t* >84.6 ms of the bubble velocity and the film radius are related to the bubble shape pulsations – shape pulsations means variation of the bubble diameters and bottom pole positions.



**Fig. 8.9.** Radius of the foam film formed between bubble and free surface as a function of n-octanol concentration. Points present the experimental data, lines – values calculated according to Eq. 8.9.

As the bubble shape pulsations were quickly diminished with time, so these residual variations of the bubble velocity and the film radius ( $R_f$ ) were quickly approaching the constant values (zero in the case of the velocity). Using Eq. (8.2) and taking into account, that for the motionless bubble the buoyant force is the driving force of the film thinning, we obtain:

$$R_{\rm f}^2 = \frac{4\Delta\rho g R_{\rm b}^4}{3\gamma} \tag{8.9}$$

Radius of the bubble formed on the capillary orifice of known diameter ( $d_c$ = 0.075 mm) depends on solution surface tension and can be calculated, using the Tate's Law (Eq. 3.1) and the Frumkin isotherm (Table 7.1). Sizes of the liquid films formed at surface of n-octanol solutions were also determined experimentally for these n-octanol concentrations, where the colliding bubbles survived the bouncing stage. Figure 8.9 presents a comparison of the experimental results and the calculated values. As can be observed the agreement between the experimental and theoretical values is very good. For example, in the case of the  $R_f$  the values calculated for n-octanol solution of concentration  $1 \cdot 10^{-3}$  M ( $R_b$ = 0.66 mm and  $\gamma$ = 51 mN/m) was equal  $R_{f(theoretical)}$ = 0.22 mm, while the experimentally determined equal to  $R_{f(measured)}$ = 0.21 ±0.01 mm.

**Table 8.2.** Theoretical and experimental values of the dynamic radius of the liquid film formed by the bubble colliding with the n-octanol solution/air interface.

Collision	R <sub>f(theoretical)</sub> R <sub>f(measured)</sub>		Relative					
по.	լՠՠյ	լՠՠյ	error [%]					
$c = 6 \cdot 10^{-6} M$								
1.	1.15	$0.67 \pm 0.03$	72.02					
2.	0.43	$0.47\pm\!\!0.04$	8.43					
3.	0.36	$0.38\pm\!\!0.03$	5.42					
4.	0.34	$0.35\pm\!\!0.02$	2.46					
5.	0.31	$0.32\pm0.01$	4.36					
6.	0.26	$0.26\pm0.01$	1.60					
$c = 1 \cdot 10^{-3} M$								
1.	0.50	0.37 ±0.06	34.55					
2.	0.24	$0.25 \pm 0.02$	4.33					

The same method that was applied for calculations of the film radius in clean water (Eq. 8.8) was used for determination of the film radius formed between rising bubble and liquid/air interface in n-octanol solutions during each collision. Table 8.2 presents the theoretical - Eq. (8.8), and the experimental (data obtained from the top-view recordings) values of the foam film radius for  $6 \cdot 10^{-6}$  M and  $1 \cdot 10^{-3}$  M n-octanol solutions. It needs to be added here, that the film radius during collision changed constantly (see Fig. 8.8B). The experimental values given in Table 8.2 are the maximum  $R_f$  values measured during each

of the collision. The greatest discrepancies of the theoretical and the measured values are observed for the first collision, but for the further collisions, the relative error was significantly diminished. In other words, the discrepancies are biggest for largest deformations of the colliding bubble shape. As the Princen equation was elaborated for small deformations of the bubble shape, therefore we have these discrepancies for the initial collisions, that is, when the colliding bubble shape was deformed in a great extent, and a pretty good agreement in the case of the last collisions.



Fig. 8.10. Time of the bubble coalescence as a function of n-octanol concentration.

Figure 8.10 presents the bubble coalescence time ( $t_c$ ) as a function of n-octanol concentration for L= 3 mm and L= 250 mm. As already discussed above, in the case of low n-octanol concentrations (c< 5·10<sup>-6</sup> M) the coalescence time was shorter than 100 ms (see insert - Fig. 8.10B) and its value was determined by the bubble bouncing time, which in turn depends on the bubble impact velocity. Higher was the impact velocity larger was the bubble bouncing amplitude and longer the bouncing time (see Figs 8.4-8.6). Therefore, at low n-octanol concentrations the bubble coalescence time was longer at L= 250 mm than at L= 3 mm. At n octanol concentration of 5·10<sup>-6</sup> M the  $t_c$  values increase rapidly and starting

from this concentration the bubble bouncing (time) stops to determine its coalescence time. Therefore, this n-octanol concentration can be considered as a threshold concentration above which the bubble coalescence time is determined by properties of the liquid film formed between the n-octanol solution surface and surface of the bubble captured beneath the solution surface. Further increase of n-octanol concentration caused significantly prolongation of the bubble coalescence time and for  $1 \cdot 10^{-3}$  M n-octanol concentration the  $t_c$  value was above 30 s.

### 8.2. Microscopic Foam Films.

Figure 8.11 shows example photos of formation and drainage of the foam film formed in Scheludko-Exerowa cell. The microinterferometric method (Scheludko-Exerowa cell) enables observation of formation of the microscopic foam films (quasi-static conditions), their stability and precise measurements of their equilibrium thicknesses (static conditions). Nowadays it is accepted that the stability of the thicker foam films, typically of thickness  $h \sim 20\text{-}100$  nm, is determined mainly by the balance between the long-range repulsive electrostatic and the molecular (van der Waals) attractive surface forces. Moreover, using data obtained in this method, especially the film thickness, we are able to calculation of the DLVO forces acting in studied foam films studied.



**Fig. 8.11.** Photos of formation of the microscopic foam film ( $R_{cell} = 1 \text{ mm}$ ,  $R_f = 100 \text{ }\mu\text{m}$ ) of  $6 \cdot 10^{-4}$  n-octanol solution in presence of  $1 \cdot 10^{-2}$  M NaCl.

Figure 8.12 presents photos of the microscopic foam films formed from n-octanol solutions of different concentrations, without any electrolyte added (Fig. 8.12A) and in presence of  $5 \cdot 10^{-4}$  M NaCl (Fig. 8.12B). At n-octanol concentrations  $c < 1 \cdot 10^{-4}$  M the films were unstable, that is, they ruptured before uniform equilibrium thickness was reached (see



**Fig. 8.12.** Photos of the microscopic foam films ( $R_{cell} = 1 \text{ mm}$ ,  $R_f = 100 \text{ }\mu\text{m}$ ) of n-octanol solutions without (A) and in presence (B) of  $5 \cdot 10^{-4} \text{ M}$  NaCl.

photos). The average lifetime of these unstable foam films was from ca. 7  $\pm 2$  to 22  $\pm 5$  s (see Fig. 8.13). At concentrations  $c \ge 1 \cdot 10^{-4}$  M the formed films were stable (the lifetime longer than 5 minutes) and they drained to their equilibrium thicknesses. The equilibrium adsorption coverage for 1.10<sup>-4</sup> M n-octanol concentration was ca. 15.4%. It is worth mentioning here that in the case of the foam films formed under dynamic conditions (bubble colliding with free surface), the foam films were treated as an unstable film if the coalescence took place during the bubble bouncing stage, i.e. the  $t_c$  was within millisecond scale. Data in Fig. 8.13, showing influence of NaCl concentration on the stability of the foam films formed from  $3 \cdot 10^{-5}$  M and  $6 \cdot 10^{-4}$  M n-octanol, and  $1 \cdot 10^{-3}$  M  $\alpha$ -terpineol solutions, confirm essential role of the SAS concentration for the foam film stability. As described above the foam films with lifetime longer than 5 min. were considered as the stable films. In the case of  $3 \cdot 10^{-5}$  M n-octanol solution, the film ruptured before reaching its equilibrium thickness in whole range of NaCl concentrations, because in this n-octanol concentration the surfactant coverage in adsorption layer was not dense enough (ca. 4.2%) to stabilize thin liquid film and to prevent its rupture. For  $6 \cdot 10^{-4}$  M n-octanol and  $1 \cdot 10^{-3}$  M  $\alpha$ -terpineol solutions, the equilibrium adsorption coverages were ca. 79.4% and 66.1%, respectively. At those SAS concentrations, films drained to its equilibrium thickness and then stayed stable, i.e. neither ruptured nor changed its thickness. However, increase of the NaCl concentration caused sudden decrease of the foam film lifetime. This effect indicates that electrostatic surface forces play a major role in mechanism of the foam films stabilization – screening of the repulsive electrostatic surface forces (shortening a range of their interactions) led to the film destabilization.



**Fig. 8.13.** Stability of the microscopic foam films as a function of NaCl concentration for n-octanol  $3 \cdot 10^{-5}$  M (red circles) and  $6 \cdot 10^{-4}$  M (green circles), and  $\alpha$ -terpineol  $1 \cdot 10^{-3}$  M (blue triangles) solutions.

The obtained films, without electrolyte, were thick, h > 100 nm and therefore it was not possible to determine the thickness values with a high precision. In presence of NaCl the *h* values were below 100 nm and varied with electrolyte concentration. Figure 8.14 presents the dependence of thickness of foam films formed from  $6 \cdot 10^{-4}$  M n-octanol solution on NaCl concentration. With increasing electrolyte concentration the films became thinner (see Fig. 8.14), but were stable up to NaCl concentration of  $5 \cdot 10^{-2}$  M (see Fig. 8.13), at which the foam films ruptured. The decrease of the thickness with the increase of NaCl concentrations evidences the action of long-range electrostatic surface forces. Microscopic films formed in the cell of smaller diameter ( $R_{cell}$ = 1 mm) were thinner due to the higher capillary pressure ( $P_{\gamma}$ ). In presence of  $5 \cdot 10^{-4}$  M NaCl the *h* values were below 100 nm (see Fig. 8.14), i.e. it was possible to measure thicknesses of these films with high precision.



**Fig. 8.14.** Thickness of the microscopic foam films formed from  $6 \cdot 10^{-4}$  M n-octanol solution as a function of NaCl concentration.



**Fig. 8.15.** Thickness of the microscopic foam films in presence of NaCl ( $c = 5 \cdot 10^{-4}$  M) as a function of n-octanol (white circles) and  $\alpha$ -terpineol (grey circles) concentration.

Fig. 8.15 presents the dependencies of the film thickness on concentration of n-octanol and  $\alpha$ -terpineol solutions, containing 5.10<sup>-4</sup> M NaCl. It needs to be added here

that the *h* values, for  $3 \cdot 10^{-5}$  M n-octanol and for  $1 \cdot 10^{-5}$  M  $\alpha$ -terpineol concentrations, are not the equilibrium ones, as at these SAS concentrations the films ruptured before equilibrium thicknesses were reached. Increase of the film thickness in high SAS concentrations is due to the lowering of the external forces acting on the foam film - the increase of the SAS concentration caused reducing the surface tension, thus, for the  $R_{cell}$ = constant, the capillary pressure decreased (see - Eq. 5.2).

Precise determination of the film thickness *h* makes possible the theoretical estimation of DLVO forces acting in the thin liquid films. The DLVO forces in foam films can be calculated according to the following algorithm proposed by Chan et al. (Chan et al., 1980; Exerowa et al., 1987). For the stable foam film, external forces ( $P_{\gamma}$ ) and disjoining pressure acting in thin liquid film are in the equilibrium:

$$\Pi = P_{\gamma} \tag{8.10}$$

The value of the  $\Pi_{\nu w}$  for measured thickness can be calculated using Eq. (4.4). The Hamaker constant for foam films formed from water solutions is  $A^{H}=3.7\cdot10^{-20}$  J (Israelachvili, 1991; Lyklema, 1991). Knowing values of the  $P_{\gamma}$  and the  $\Pi_{\nu w}$ , the  $\Pi_{el}$  for measured film thickness is obtained from:

$$\Pi_{\rm el} = P_{\gamma} - \Pi_{\rm vw} \tag{8.11}$$

For the fixed  $\Pi_{el}$ , Eq. (4.23) gives the electrostatic potential of the mid-plane ( $\Psi_m$ ).

Finally, the surface potential can be obtained from solution of the Poisson-Boltzmann equation:

$$\frac{d^2\Psi}{dx^2} = \frac{\kappa^2 RT}{FZ} \sinh\left(\frac{ZF\Psi}{RT}\right)$$
(8.12)

using numerical technique - Runge-Kutta method, with following boundary conditions:

for 
$$x = 0$$
  
 $\Psi = \Psi_{\rm m}$ 
(8.13)

$$\frac{\mathrm{d}\Psi}{\mathrm{d}x} = 0 \tag{8.14}$$

for 
$$x = h/2$$

$$\Psi = \Psi_0 \tag{8.15}$$

$$\frac{\mathrm{d}\Psi}{\mathrm{d}x} = \frac{1}{\varepsilon_0 \varepsilon_\mathrm{r}} \sigma_0 \tag{8.16}$$

Figures 8.16 A and B presents distribution of electrostatic potential ( $\Psi$ ), calculated via method described above, for foam films formed from n-octanol (Fig. 8.16A) and  $\alpha$ -terpineol (Fig. 8.16B) solutions. It is seen that increase of n-octanol and  $\alpha$ -terpineol concentrations caused increase of the surface potential ( $\Psi_0$ ). The calculated DLVO parameters for n-octanol and  $\alpha$ -terpineol solutions are gathered in Table 8.3. For comparison sake, the surface potential of the clean water/air interface is ca. -30 mV (Exerowa and Kruglyakow, 1998), and in presence of 5·10<sup>-4</sup> M NaCl, the  $\Psi_0$  is reduced to ca. -15 mV (Exerowa and Kruglyakow, 1998; Exerowa et al., 2001).



**Fig. 8.16.** Distribution of the electrostatic potential in symmetric (foam) films obtained from n-octanol (A) and  $\alpha$ -terpineol (B) solutions of different concentrations.

As it is seen in Table 8.3, addition of the non-ionic SAS caused generally increase of the equilibrium thickness of foam films, what is related to the rise (toward more negatively values) of the  $\Psi_0$ . For the symmetrical foam films, increase of the surface potential means greater repulsion between interfaces, due to increase of the repulsive electrostatic interactions.

C <sub>SAS</sub> [mole/L]	h [nm]	Ρ <sub>γ</sub> [Pa]	П <sub>el</sub> [Pa]	Ψ <sub>m</sub> [mV]	Ψ <sub>0</sub> [mV]	σ <sub>0</sub> [mC/m <sup>2</sup> ]			
n-octanol; C <sub>NaCl</sub> = 5·10 <sup>-4</sup> M; R <sub>cell</sub> = 1 mm									
$1 \cdot 10^{-4}$	55 ±6	140.7	152.5	-8.97	-35.58	-1.99			
$6 \cdot 10^{-4}$	63 ±4	115.3	123.1	-8.07	-43.21	-2.50			
$1 \cdot 10^{-3}$	65 ±3	101.8	109.0	-7.59	-43.70	-2.54			
$\alpha$ -terpineol; $C_{NaCl} = 5 \cdot 10^{-4} \text{ M}$ ; $R_{cell} = 1 \text{ mm}$									
3.10-5	$49\pm 6$	144.6	161.3	-9.22	-29.28	-1.59			
5.10-5	49 ±2	144.2	160.8	-9.21	-29.24	-1.59			
$3 \cdot 10^{-4}$	47 ±2	139.0	157.9	-9.12	-26.93	-1.45			
$1 \cdot 10^{-3}$	$69\pm3$	127.3	133.3	-8.39	-58.32	-3.70			

**Table 8.3.** Equilibrium thickness measured and the surface electrostatic parameters computed from the DLVO theory for foam films obtained from n-octanol and  $\alpha$ -terpineol solutions.

The calculated values of the surface potential can be used for obtaining disjoining pressure dependence on film thickness. Under the condition of constant surface potential and using Eqs (4.4) and (4.28), the  $\Pi(h)$  function is expressed in a form:

$$\Pi(\mathbf{h}) = -\frac{\mathbf{A}^{\mathrm{H}}}{6\pi\mathbf{h}^{3}} + 64c_{\mathrm{el}}\mathrm{R}\mathrm{T}\mathrm{tanh}^{2}\left(\frac{\mathrm{ZF}\Psi_{0}}{\mathrm{RT}}\right)\mathrm{e}^{-\kappa\mathbf{h}}$$
(8.17)

where the first term on the right side is the van der Walls ( $\Pi_{vW}$ ) and the second term is the electrostatic ( $\Pi_{el}$ ) contributions of the disjoining pressure. Figure 8.17 presents the  $\Pi_{vW_i}$  the  $\Pi_{el}$ , and the summary interaction,  $\Pi$ , for the foam film formed from  $6 \cdot 10^{-4}$  M n-octanol solution in function of the film thickness. The grey points on Fig 8.17 are the experimental data,  $\Pi(h)$  isotherm, obtained using the "porous plate" technique (see Chapter 5.2). For the studied system, the experimental and calculated values of the disjoining pressure are in a good agreement (see Fig. 8.17). In the "porous plate" method, the foam film ruptured under pressure ca. 2.3 kPa, what correspond to thickness ca. 25 nm. Similar thickness was observed for foam films formed from  $6 \cdot 10^{-4}$  M n-octanol solution in presence of  $5 \cdot 10^{-2}$  M NaCl, in the "equilibrium film" technique i.e. the thickness was 21 ±1 nm and 31 ±6 nm for the  $R_f$  equal to 1 mm and 2 mm, respectively. Thus, thickness of the foam film formed from n-octanol solution, in range of ca. 20-30 nm, can be treated as the critical thickness of the film rupture ( $h_{cr}$ ).



**Fig. 8.17.** Disjoining pressure and its components in foam film formed from  $6 \cdot 10^{-4}$  M n-octanol solution in function of film thickness.

## 8.3. Influence of Electrolyte.





Influence of electrolyte concentration on equilibrium thicknesses of microscopic films, as observed also for the n-octanol films studied (Fig. 8.13), is the phenomenon well-known and thoroughly described (Exerowa and Kruglyakow, 1998; Exerowa et al., 1987; Kolarov et al., 1989). Moreover, it has been reported that some electrolytes, at

sufficiently high concentrations can inhibit bubble coalescence whereas others have no influence on bubble coalescence (Craig et al., 1993a, 1993b; Craig, 2004). As the measurement of the film thickness and determinations of the DLVO forces using microinterferometric method required addition of electrolyte, thus it was necessary to check influence of NaCl on bubble motion, bouncing and coalescence.



**Fig. 8.19.** Time of the bubble bouncing in function of NaCl concentration for water (white circles) and  $1 \cdot 10^{-3}$  M n-octanol (grey circles) solutions for L= 3 mm.

Figure 8.18 presents profiles of the local velocities for the bubble rising in distilled water and in 0.15 M NaCl solution. As it is seen, there is no difference between the bubble velocities profiles in distilled water and NaCl solution. Similar lack of changes of profile of the local velocities in wide range of NaCl concentrations was reported earlier by Zawala (Zawala, 2008). Thus it can be stated, that NaCl has no influence on bubble surface fluidity. However, so far there is no information about influence of electrolyte concentration on the bubble bouncing. Therefore, two series of the experiments were carried out and their results are presented in Fig. 8.19 as dependences of the bubble bouncing. It is clearly seen there that within scatter of the experimental results there is no influence of

NaCl concentration on the bubble bouncing time. Thus, contribution of the bubble bouncing time to the coalescence time of the colliding bubble does not depend on electrolyte concentration.



**Fig. 8.20.** Sequences of photos presenting coalescence of two air bubbles in distilled water. The time interval between subsequent photos is 0.05 s.

The influence of NaCl on the bubble coalescence time was studied using the Drop & Bubble Micro Manipulator (DBMM) apparatus. This method allowed observation of the interacting bubbles for a long time (even for hours), what was not possible using SpeedCam in the colliding bubble method. Figure 8.20 presents sequences of photos of two air bubbles in water. The t= 0.0 s is the moment, when the contact between two bubbles is established. The apparatus detected this moment automatically. The bubble coalescence was clearly seen on the computer monitor (see photo for t= 1.35 s). Moreover,



Fig. 8.21. Time of the bubble coalescence as a function of n-octanol concentration.

changes of the capillary pressure allowed the DBMM apparatus registration of the moment of the bubble coalescence. Fig. 8.21 presents time of the bubble coalescence in a function of n-octanol concentration for solutions with (white circles) and without (grey triangles) presence of  $5 \cdot 10^{-4}$  M NaCl. As it is seen, the  $t_c$  increased with increasing of n-octanol concentration. For  $1 \cdot 10^{-3}$  M n-octanol solution, the bubble lifetime was not determined – bubbles were stable even after 60 minutes. The more important is, that the addition of  $5 \cdot 10^{-4}$  M NaCl practically did not affect the  $t_c$ .

#### 8.4. Velocity of the Foam Film Drainage.

Thicknesses of the films at the moment of their rupture can be evaluated on the basis of the bubble coalescence times measured and sizes of the films, formed by the colliding bubble. Model of the film thinning rate developed by Radoev et al. (Radoev et al., 1974) was used, because it takes into account that fluidity of the liquid/gas interface (slipping conditions) depends on the surfactant surface concentration ( $\Gamma$ ). According to this model (called further the RDI model), the film thinning velocity (V) in the case of inhomogeneous film drainage, i.e. formation of the dimple, is given as (Dimitrov and Ivanov, 1978; Ivanov et al., 1985):

$$V = \frac{h^3 \Delta P}{2\eta R_f^2} (1 + \alpha) \tag{8.18}$$

where,  $\Delta P$  is a st the "total" pressure causing the film squeezing. The  $\alpha$ -parameter takes into account the interface mobility and depends on the state of the adsorption layers. The thinning velocity can be calculated for two boundary conditions:

(i) for symmetrical foam films (Fig. 8.22A), that is, the films having identical and equilibrium adsorption coverage at both surfaces:  $\Gamma_{surface} = \Gamma_{bubble} = \Gamma_{eq}$ , using Eqs (4.49)-(4.51):

$$V = \frac{h^3 \Delta P}{2\eta R_f^2} \left( 1 + b + \frac{h_s}{h} \right)$$
(8.19)

(ii) in the case when one of the surface is fully mobile (fully unsymmetrical foam film) (Fig. 8.22B):  $\Gamma_{surface} = \Gamma_{eq}$  and  $\Gamma_{bubble} = 0$ , using Eqs (4.54) and (4.50)-(4.51):

$$V = \frac{h^3 \Delta P}{2\eta R_f^2} \left( 4 + 4b + \frac{h_s}{h} \right)$$
(8.20)

However, bubble detaches from the capillary with non-equilibrium adsorption coverage (see Chapter 7.1), what results in following conditions for film thinning:  $\Gamma_{surface} = \Gamma_{eq}$  and  $\Gamma_{bubble} < \Gamma_{eq}$  (Fig. 8.22C). For that type of unsymmetrical foam film, Ivanov et al. (Ivanov et al., 1985) proposed extended RDI model - Eqs (4.49)-(4.53):

$$V = \frac{h^{3} \Delta P}{2\eta R_{f}^{2}} \left( 1 + b^{A,B} + \frac{h_{s}^{A,B}}{h} \right)$$
(8.21)

Note please, that in the case of the both models, presented on Figs 8.22 A and C, the molecules in adsorption layers are uniformly distributed over the bubble surfaces.



**Fig. 8.22.** The state of adsorption layers for the bubbles colliding with solution/air interfaces in the case of formation of the symmetrical (A), fully unsymmetrical (B), and partially unsymmetrical (C) foam films.

For calculations of the correction for the Marangoni-Gibbs effect ( $\alpha$ ) it is necessary to know adsorption isotherm (Table. 7.1) and values of the surfactant diffusion coefficient in bulk (D) and the surface diffusion coefficient (Ds), The following literature values of the diffusion coefficients were used:  $D = 6 \cdot 10^{-6}$  cm<sup>2</sup>/s and  $D_s = 5 \cdot 10^{-5}$  cm<sup>2</sup>/s (Ivanov et al., 1985; Valkovska and Danov, 2000; Jachimska et al., 2001). The "total" pressure causing drainage of the film formed between bubble and liquid/gas interface is given as:

$$\Delta P = \frac{2\gamma}{R_b} - \Pi(h)$$
(8.22)

For the film thickness greater than 100 nm, the disjoining pressure term is negligible. Thus, Eq. (8.17) together with Princen eq. (Eq. 8.9) and Eq. (8.18) gives:

$$V = \frac{3h^3\gamma^2}{4\eta g\Delta\rho R_b^5} (1+\alpha)$$
(8.23)

The theoretical lifetime  $(t_{film})$  of the foam film can be determined as:

$$t_{\rm film} = \int_{h_{\rm f}}^{h_{\rm i}} \frac{1}{V} dh \tag{8.24}$$

where  $h_i$  is an initial thickness and  $h_f$  is a final thickness when the film ruptures. For  $h_i \gg h_f$ , initial thickness has practically of no importance for the foam film lifetime. The lifetime calculations were performed for various critical thickness of rupturing in function of n-octanol concentration.



**Fig. 8.23.** Dependence of the bubble lifetime on n-octanol solution concentration calculated from the RDI model for symmetrical (red line), fully unsymmetrical (green line) and partially unsymmetrical (blue line) foam film for  $h_f$ = 100 nm (A) and  $h_f$ = 60 nm (B).

Figures 8.23 A and B presents the dependences obtained for  $h_j$ = 100 nm and  $h_j$ = 60 nm, respectively. It is clearly seen, that the state of adsorption layer over the bubble surface play important role for the film lifetime. Increase of the n-octanol concentration causes immobilization of the solution/air interfaces what results in slower film drainage velocity for all calculated models. However, for the fully unsymmetrical foam film, the velocity of

the film drainage is much higher due to the slip-conditions over the bubble surface. The real situation is more complicated due to (i) non-equilibrium coverage of the bubble departing capillary, and (ii) changes of the architecture of adsorption layer during the bubble motion. As it was showed previously, for the entire range of n-octanol concentration, the adsorption equilibrium coverage was not established at the surface and thus the partially nonsymmetrical film during collision can be formed. This situation is presented by blue lines on Figs 8.23 A and B. Despite that the RDI model allows for carrying calculations for unsymmetrical foam films, there is still lack of a precise theory describing the non-uniform architecture of the adsorption layer over the rising bubble. From data obtained in "colliding bubble" experiments, it is possible to evaluate values of the film rupture thickness. Figure 8.24 presents dependence of thickness of the film, at the moment of the bubble coalescence (rupture) at free surface, on n-octanol concentration, calculated from the RDI model for two limiting cases: symmetrical and fully unsymmetrical foam films formed by the colliding bubbles. Note please, a few interesting points. At n-octanol concentrations  $c < 5 \cdot 10^{-6}$  M the film rupture thickness is of an order a few µm, ca. 8 and 6 µm for symmetrical and unsymmetrical films, respectively. Certainly, it is as one should expected, it is as in the case of the unsymmetrical foam films the fluidity of one of its interface is as in the case of clean water so the thinning velocity is higher and therefore, after a definite thinning time the film thickness is smaller. For  $c = 5 \cdot 10^{-6}$  M, the film thickness at the moment of the bubble rupture drops by over an order of magnitude, down to ca. 400 nm for symmetrical film. At n-octanol concentrations of 3.10<sup>-5</sup> M the thickness reached by the draining symmetrical film is ca. 170 nm, that is, of the same order as thicknesses of microscopic equilibrium foam films without electrolyte added (ca. 100 nm). At higher n-octanol concentration ( $c \ge 1 \cdot 10^{-4}$  M) the values of the film thicknesses calculated from the RDI model tends to the thicknesses of the equilibrium foam films (Scheludko-Exerowa cell data). Thus, these evaluation show that when

n-octanol concentration was high enough the single foam films formed by the colliding bubble captured beneath the solution surface can approach (reach), before their rupture, the thicknesses similar as the microscopic equilibrium foam films.



**Fig. 8.24.** Thickness of the foam films at the moment of the bubble rupture at n-octanol solutions surface (L=250 mm), calculated from the RDI model.

# 9. Three-Phase Contact Formation.

### 9.1. Bubble Bouncing and the TPC Formation in Distilled Water.

### 9.1.1. Effect of the Solid Surface Hydrophobicity.

When the bubble collides with a solid surface, a liquid film between the bubble and solid surface is formed. In pure water, depending on hydrophilic/hydrophobic properties of the solid surface, the liquid film either (i) ruptures and three-phase contact (TPC) - gas/liquid/solid - is formed or (ii) a stable wetting film prevents bubble from attachment to solid surface. The former case is typical for hydrophobic surfaces, while the latter for hydrophilic ones. Sequences of photos illustrating phenomena occurring during the bubble collisions with hydrophilic and hydrophobised (silanized) glass surfaces are presented in

Fig. 9.1. There are presented photos from top-view and side-view camera recordings. The subsequent photos of each sequence show phenomena occurring, within time interval of 0.96 ms. The top-view photos (upper rows of the sequences) show clearly variations of radius of the film formed at the subsequent collisions, while the side-view photos show variations of the bubble shape and position.



**Fig. 9.1.** Sequences of photos, from the top-view (upper rows) and side-view movies, recorded during the bubble collisions with hydrophilic and hydrophobic (silanized) glass surfaces located at distance L= 250 mm from the capillary orifice.

Generally, as can be noted, the bubble shape deformations and simultaneously the dimensions of the liquid film formed (top-view photos) are diminishing with time, that is, with decreasing the bubble impact velocity. After the energy dissipation the bubble stayed captured motionless, as can be observed in Fig. 9.1 (bottom sequences), and in the case of silanized glass the TPC was formed at  $t_{TPC}$  = 102 ms, while the TPC was not formed at the hydrophilic glass surface – wetting film, separating the interacting surfaces, was stable. It needs to be explained here that the time of TPC formation ( $t_{TPC}$ ) is defined as the time

interval from the moment of the first collision to the moment of the film rupture. Thus, the  $t_{TPC}$  is given as:

$$t_{\rm TPC} = t_{\rm bouncing} + t_{\rm D} \tag{9.1}$$

where  $t_{Bouncing}$  is the time of the bubble bouncing and  $t_D$  is the drainage time of the liquid film formed. Time of the bubble bouncing ( $t_{Bouncing}$ ) is the time period needed for dissipation of the kinetic energy ( $E_k$ ) associated with the bubble motion, that is, the  $t_{Bouncing}$ is the entire time of all "approach-bounce" cycles. The  $t_D$  is determined as the time interval from the moment when after the kinetic energy dissipation, the bubble stays captured (motionless) beneath the solid surface, until the moment of the TPC formation. Moment of the bubble permanent contact with solid surface (no bouncing gap observed – see Chapter 8.1.2) is used as the film drainage starting point.

Figure 9.2 presents quantitative data on the bubble velocity variations (Fig. 9.2A) and shape deformations (Fig. 9.2B) during collisions with hydrophilic glass and silanized glass (SG00). In Fig. 9.2 there are clearly seen four distinct "approach-bounce" cycles. Note also, that the amplitude and frequency of these "approach-bounce" cycles were practically identical for the surfaces studied – similarly as the bubble shapes variations (see Fig. 9.2B). It needs to be added here that the velocity variations during the bubble collisions and bouncing were determined from the measurements of the positions of the bubble bottom pole on subsequent frames of the recorded movies. Therefore, even after the 5<sup>th</sup> collision, when the kinetic energy was dissipated in degree assuring that there was no bouncing (lack of the bubble separation from the solid surface) there can still be noted some minor velocity variations related to the residual oscillations of the bubble bottom pole clearly shows the moment of the TPC formation. As seen in the case of silanized glass surfaces the TPC was not formed and the bubble stays captured motionless – velocity equal zero.



**Fig. 9.2.** Bubble velocity variation (A) and bubble shape deformation (B) during collisions with hydrophilic glass and silanized glass (SG00) located at distance L= 250 mm from the capillary orifice.

### 9.1.2. Effect of the Surface Roughness.

Surface roughness is the one of the most common property of the solid surfaces and it affects the timescale of the three-phase contact formation (Anfruns and Kitchener, 1977; Krasowska and Malysa, 2007a; Kosior et al., 2013). Generally, the greater surface roughness leads to shortening of the time of bubble attachment to the solid surface. In this



study, the surface roughness was mechanically modified using abrasive paper of different grid numbers and evaluated using the optical microscope (see Chapter 6.2).

Fig. 9.3. Advancing and receding contact angle (green line) and drop perimeter (red line) as a function of the growing and diminishing drop volume for T2500 (A), T1200 (B), T600 (C), and T100 (D) Teflon surfaces.

Influence of solid surface roughness on the contact angle hysteresis is presented in Figs 9.3 and 9.4. Figure 9.3 presents hysteresis loops of the dynamic advancing and receding contact angles for Teflon surfaces of different roughness. In these experiments (see Chapter 5.5), a ca. 2 µl sessile drop was placed on the surfaces, firstly the drop volume was slowly increased up to ca. 14 µl, and next the drop was diminished slowly to its initial volume. There are also presented variations of the drop perimeters during the drop volume changes. Each measurement was repeated at least 10 times for different areas of the surfaces studied. As is seen, the smoothest profile was observed for T2500 and the greatest Results and discussion

variations of the contact angle were measured for T100, that is, for the roughest surface studied.





Figure 9.4 presents the mean values of the advancing and receding contact angles for the studied solid surfaces. For the Teflon plates, contact angle hysteresis increased from ca. 41° for smooth Teflon (T2500) to ca. 56° for roughest Teflon surface (T100). Similar changes were observed for silanized glass, where hysteresis was ca. 43° and 48° for SG00 and SG600, respectively.

Figure 9.5 presents sequences of photos showing phenomena occurring during the collisions of the rising bubble with Teflon surfaces of different roughness in distilled water. Overall picture is similar to that reported earlier - time of the bubble attachment to Teflon surface in distilled water was strongly affected by the roughness of the Teflon surface. During first collision, the bubble attachment occurred only in the case of the T100, i.e. the roughest surface (see Fig. 9.5D), while in the case of smoother surfaces the bubble bounced backwards. As illustrated in Figs 9.5A-C the number of bouncing-approach cycles, prior the TPC formation, varies with roughness of the Teflon surface and four

bounces can be distinguished upon the bubble collision with the smoothest T2500 surface (Fig. 9.5A).



**Fig. 9.5.** Sequences of photos of the bubble colliding in distilled water with Teflon surfaces of different roughness located at distance L= 250 mm from the capillary orifice.

Figure 9.6 presents quantitative data on the bubble velocity variations during collisions with the T2500 (smoothest) T600 (medium roughness) and T100 (roughest) surfaces. Analysis of data presented in Fig. 9.6 shows that the velocity at each subsequent

collision was diminishing due to the dissipation of the kinetic energy associated with the bubble motion. After the kinetic energy dissipation, the bubble stayed practically motionless until the moment of the TPC formation. Such a moment is easy to detect due to rapid motion of the bubble bottom pole (note the velocity peak at t=105 ms). In the case of the rougher Teflon surfaces, the TPC was formed quicker - the bubble was attached to the T100, T600 and T1200 surfaces during the first, second, and third collision, respectively. Note that the impact velocity of the bubble first collisions was the same in all cases presented in Fig. 9.6.



**Fig. 9.6.** Bubble velocity variation at collision with T100, T600, and T2500 located at distance L= 250 mm from the capillary orifice.

Figure 9.7 presents the  $t_{TPC}$  and  $t_D$  values for the Teflon plates of different surface roughness in distilled water. As can be observed the  $t_{TPC}$  values for surfaces of T2500, T1200 and T600 are significantly higher than the values of  $t_D$ . The reasons of these significant differences are quite obvious – in those cases, the  $t_{TPC}$  values were strongly prolonged as a result of the bubble bouncing (see Figs 9.5 and 9.6). Data in Fig. 9.7 clearly illustrate also that in distilled water both the  $t_{TPC}$ , and  $t_D$  values are highly dependent on the Teflon surface roughness. The effect is significant because for the "smooth" surface roughness (1-5µm) the  $t_{TPC}$  was 105 ±4 ms and the  $t_D$  was 22 ±4 ms. When the surface roughness was increased up to 80-100  $\mu$ m (T100) the  $t_{TPC}$  and  $t_D$  were shortened by over an order of magnitude, i.e., from 105  $\pm$ 4 down to 3  $\pm$ 0.5 ms and from 22  $\pm$ 4 down to 2 $\pm$ 0.5 ms, respectively. Moreover, the homogeneity of solid surfaces on a macroscopic scale is always a problem as the surface roughness can differ locally. Therefore, in order to get reliable and statistically significant data, the experiments was repeated 20-40 times for each of the Teflon surfaces and each solution, and the  $t_{TPC}$  and  $t_D$  values, reported in this PhD Thesis, are the mean values. The results scatter depended on the Teflon surface roughness (see scatter bars in Figs 9.7 and 9.8).



Fig. 9.7. Time of the TPC formation and time of the water film drainage for Teflon surfaces of different roughness located at distance L= 250 mm from the capillary orifice.

Figure 9.8 presents the  $t_{TPC}$  and  $t_D$  values for the solid surfaces of similar roughness and contact angle hysteresis (ca. 41-43°) but of different advancing contact angles, i.e. SG00, T2500, and P00. Four bouncing-approach cycles were observed at these surfaces and after the 5<sup>th</sup> collision the bubble stayed captured motionless until the moment of the TPC formation. The  $t_{bouncing}$  was the same for all these surfaces,  $t_{bouncing}$ = 83 ±2 ms, but there were small differences in the  $t_D$  values. The  $t_D$  values varied from 18 ±5 ms for SG00 Results and discussion

to  $22 \pm 4$  ms for T2500 and  $34 \pm 5$  ms for P00. This effect is most probably related to some differences in hydrophobicity of these solid surfaces. As can be seen in Fig. 9.4, the P00 surface had the lowest value of the contact angle, and the highest one had SG00.



**Fig. 9.8.** Time of the TPC formation and time of the water film drainage for silanized glass, T2500, and P00 plates (surfaces of the similar roughness:  $1-5 \mu m$ ) located at distance L= 250 mm from the capillary orifice.

The main problem to be answered is the question of the reason and mechanism responsible for the significant shortening of the  $t_{TPC}$  and  $t_D$  with the roughness of these hydrophobic solid surfaces. The outcome of the bubble collision (bouncing or attachment) is a consequence of the two competing processes (Chesters and Hofman, 1982; Zawala et al., 2011): i) thinning of the intervening liquid film; and ii) the increase of the surface free energy of the system resulting from enlargement of the surface area due to the bubble's shape deformation. The bubble bouncing is the most pronounced in the case of the Teflon surfaces of the small roughness (below 60 µm). For the roughest Teflon surfaces, the  $t_{TPC}$  and  $t_D$  values were practically identical because the drainage and rupture of the intervening liquid film occurred during the first collision - there was no bouncing of the bubble. The crucial role of roughness of the hydrophobic solid surface, affecting time scale of TPC formation and bubble attachment, can be attributed to: (i) local differences in radius of the



**Fig. 9.9.** Schematic illustration of mechanisms of the TPC formation during collision of the rising macro-bubble with hydrophobic solid surface: (A) effect of irregularities and pillars on the film radius and (B) effect of the air micro- and/or nano-bubbles present at the hydrophobic surface.

liquid film formed at irregularities and pillars of rough solid surface (Fig. 9.9A), and (ii) presence of air entrapped in surface scratches and irregularities of the hydrophobic surface (Fig. 9.9B). The first mechanism takes into account fact that kinetics of the liquid film drainage is strongly affected by the film lateral dimensions – smaller film radius means that time needed for the film to reach a definite thickness is shorter. At rough hydrophobic surface, the TPC can be formed due to rupture of various local wetting films are much smaller than radius of the entire liquid film formed by the colliding bubble so these films need shorter time to drain to a critical thickness of their rupture. The second mechanism postulated takes into account influence of air presence at hydrophobic surface on kinetics of the TPC formation by the colliding bubble. As high affinity to air is a typical feature of hydrophobic surfaces, so air can be entrapped in scratches of hydrophobic surface during its immersion into aqueous phase. Thus, diminishing the  $t_{TPC}$  values with surface roughness can be a consequence of coalescence of the colliding bubble with nanoand/or micro-bubbles present at larger amounts at rougher hydrophobic surface. In the case of smooth hydrophobic surfaces the amounts of entrapped air is lower and therefore the  $t_{TPC}$  values are higher. The question which of the described mechanism prevails is still not fully answered because the both factors are interrelated and can affect outcome of the bubble collisions with the hydrophobic surfaces of different roughness. However, the experimental data on kinetics of the TPC formation in solution of surface active substances, presented below (see Chapter 9.2), supply strong evidences about crucial role of air presence at hydrophobic surfaces.

## 9.1.3. Effect of the Bubble Impact Velocity.



**Fig. 9.10.** Variations of the local velocity of the bubble colliding in clean water with T2500 plate, located at distances L=3 mm (white circles) and 250 mm (grey circles) from the capillary orifice.

The bubble impact velocity affects strongly the bubble bouncing as was showed earlier (Sunol and Gonzales-Cinca, 2010; Zawala and Malysa, 2011) and is also clearly illustrated in Fig. 9.10. Figure 9.10 presents the local velocity of the bubble, colliding with T2500 surface located 3 mm (white circles) and 250 mm (grey circles) from the capillary, as a function of time from the moment of the 1<sup>st</sup> collision. As is seen when the T2500 plate was located "far" (L= 250 mm) bubble impact velocity was equal its terminal velocity
$(U_b=34.7 \text{ cm/s})$ , while at L= 3 mm the bubble was still at the acceleration stage and impact velocity was much lower ( $U_b=19.4 \text{ cm/s}$ , only). Lower impact velocity means smaller amplitude and shorter time of the bubble bouncing - number of the bubble "approachbounce" cycles decreased from four to three cycles at this lower impact velocity. Consequently, the time of the TPC formation ( $t_{TPC}$ ) decreased from 105 ±4 ms to 65 ±4 ms, due to lowering the  $t_{Bouncing}$  (see Eq. 9.1). Time of the water film drainage was not influenced by the bubble impact velocity and was similar in both cases,  $t_D=21 \pm 3$  ms and  $t_D=22 \pm 4$  ms, for L= 3 mm and 250 mm, respectively.



**Fig. 9.11.** Time of the TPC formation (A) and time of the water film drainage (B) for solid surfaces located at distances L=3 mm (white bars) and 250 mm (grey bars) from the capillary orifice.

Figure 9.11 presents the  $t_{TPC}$  (Fig. 9.11A) and  $t_D$  values (Fig. 9.12A) for the solid surfaces studied located in distilled water at distances L= 3 mm (white bars) and 250 mm (grey bars) from the capillary orifice. Generally, for L= 3 mm there was observed one "approach-bounce" cycle less than for L= 250 mm, with the exception of T100 where the three-phase contact was formed always during the first collision. This diminishing of the number of bouncing cycles caused shortening of the  $t_{TPC}$  by ca. 35 ±5 ms. Please note, that variation of the distance between capillary and the solid surfaces did not affect the time of the film drainage – the  $t_D$  values were similar for both locations of the solid surfaces.

### 9.1.4. Effect of the Electrolyte Addition.

Influence of electrolyte concentration on stability of the foam films formed under dynamic conditions has been presented in Chapter 8.3. Similar studies on influence of NaCl presence on the time scale of the bubble attachment to hydrophobic surfaces were carried out and their results are presented in Fig. 9.12. There are presented the  $t_{TPC}$  (Fig. 9.12A) and  $t_D$  (Fig. 9.12B) values as a function of NaCl concentration for T2500, T600, and P00 surfaces. Is is clearly seen that the addition of NaCl neither influenced the time of the TPC formation nor the time of the film drainage. As the inorganic electrolytes do not adsorb on the water/air interfaces so they cannot change the fluidity of the bubble surface and therefore the drainage times of the liquid film formed were not affected by the NaCl presence.



**Fig. 9.12.** Time of the TPC formation (A) and time of the water film drainage (B) as a function of NaCl concentration for different solid surfaces located at distance L=3 mm from the capillary orifice.

### 9.1.5. Velocity of the Wetting Film Drainage.

Figure 9.13 presents variations of the bubble velocity (Fig. 9.13A) and of the film radius (Fig. 9.13B) during the bubble collisions with glass surface located in distilled water at distance L= 250 mm. As seen during the four "collision-bounce" cycles the size of the film formed was decreasing in the sequential collisions. After the 5<sup>th</sup> collision there was



**Fig. 9.13.** Variation of (A) the bubble velocity and (B) film radius during collisions with glass surface located in distilled water at distance L= 250 mm from the capillary orifice.

practically no bubble shape variations and changes in diameter of the liquid film formed. The film formed was stable and the buoyancy force determined dimensions of the film formed between the hydrophilic glass and motionless bubble. These experimentally determined sizes of the films formed were compared with the values calculated using formula derived in (Derjaguin and Kussakov, 1939; Princen, 1969; Ivanov et al., 1985):

$$R_{f}^{2} = \frac{FR_{b}}{2\pi\gamma}$$
(9.2)

where  $R_f$  is the film radius, F is the force causing film thinning,  $R_b$  is the bubble radius. If the buoyancy force is treated as a driving force, then Eq. (9.2) can be rewritten in a form:

$$R_{\rm f}^2 = \frac{2\Delta\rho g R_{\rm b}^4}{3\gamma} \tag{9.3}$$

The liquid film radius calculated from Eq. (9.3) for the bubble of radius  $R_b = 0.74$  mm in water ( $\gamma = 72.4 \text{ mN/m}$ ) is  $R_{f(theoretical)} = 0.16 \text{ mm}$ . This value is in an excellent agreement with the value determined experimentally -  $R_{f(measured)} = 0.15 \pm 0.01 \text{ mm}$ . This excellent agreement of the experimentally determined and calculated values show that Eq. (9.3) can be used for evaluation sizes of the films formed between motionless bubble and solid (non-transparent) surface.

Knowing size of the film formed between bubble and solid surface and time of film drainage, it is possible to calculate, based on literature models, average values of the film critical thickness ( $h_{cr}$ ) at the moment of their rupture. According to model of inhomogeneous film drainage proposed by Dimitrov and Ivanov (Dimitrov and Ivanov, 1978; Ivanov et al., 1985) and taking into account fluidity of the bubble interface (Scheludko, 1967), the film thinning velocity can be described by the following relation:

$$-\frac{\mathrm{dh}}{\mathrm{dt}} = \frac{\mathrm{nh}^3 \Delta \mathrm{P}}{2 \eta \mathrm{R}_\mathrm{f}^2} \tag{9.4}$$

where factor *n* depends on the interface mobility and is equal to 4 ,when the film is created between the interface with non-slip condition, e.g. solid surface, and a completely mobile liquid/gas interface, and n=1 for two tangentially immobile interfaces. The "total" pressure causing drainage of the film formed between bubble and solid surface is given by Eq. (8.22), what together with Eqs (9.3) and (9.4) gives:

$$-\frac{dh}{dt} = \frac{3nh^3\gamma^2}{2\eta g\Delta\rho R_b^5}$$
(9.5)



**Fig. 9.14.** Thickness of the wetting film as a function of drainage time for two tangentially immobile interfaces (dashed line) and for the film formed between solid surface and fully mobile bubble surface (solid line).

Figure 9.14 presents thickness of the liquid film as a function of the drainage time calculated using Eq. (9.5), for two tangentially immobile interfaces (dashed line) and for the film formed between solid surface and fully mobile, i.e. in distilled water, bubble interface (solid line). The estimated values of the film thickness for measured time of the film drainage for smooth surfaces and fully mobile bubble interface (n=4) are gathered in Table 9.1.

**Table 9.1.** Experimental values of the time of film drainage and theoretical values of the critical thickness of the film rupturing for smooth solid surfaces studied.

Solid surface	t <sub>D</sub> [ms]	h <sub>rupture</sub> [μm]
SG00	18 ±5	$1.36 \pm 0.19$
T2500	$22 \pm 3$	$1.21 \pm 0.08$
P00	35 ±5	$0.96 \pm 0.07$

The same method of the  $h_{cr}$  estimation can be applied for more rough Teflon surfaces. In those cases, the  $t_D$  is ca. 3 ms for all rough Teflon plates, i.e. T100, T600 and T1200, what gives the average thickness of rupturing:  $h_{cr}=3.25 \ \mu\text{m}$ . The only difference between these surfaces is the number of the collisions before the three-phase contact is

formed. As these Teflon plates were prepared from the same PTFE block so their surface properties - besides roughness- should be similar. Let's evaluate a hypothesis that if we have solid surfaces having identical chemical composition and differing only in their surface roughness then: (i) the  $h_{cr}$  values should be similar, and (ii) radius of the rupturing films is not determined by radius of the colliding bubble but is related to dimensions of the solid surface irregularities - rupture take place locally on pillars of the rough surface. As in the case of rough Teflon surfaces the film drainage time was 3 ms so, assuming that the  $h_{cr}$ value was 1.21 µm (identical as evaluated for T2500), we obtain that radius(es) of the rupturing film(s) were 62 µm. This value is within a range of irregularities sizes of the rough Teflon surfaces. However, it needs to be remembered and taken into account that in the case of T100, the TPC is formed during the 1st collision, that is, when the bubble deformation degree is the highest and therefore radius of the film formed by the bubble is the largest one. Thus, even if the films of  $R_{\rm f}$  = 62 µm were formed locally, on the asperities, there was still a lot of liquid at the other parts the film, which should flow out from the film during the collision time. Moreover, in the case of the T600 and 1200 surfaces the TPC was not formed during 1st collision, but during the 2nd and 3rd collisions, respectively. These differences indicate that most probably there is an additional factor - most probably air present at these hydrophobic surfaces of different roughness - which affects kinetics of the TPC formation. Air captured during immersion of Teflon plates into aqueous phase (Krasowska et al., 2007b) can change locally the liquid flow condition at solid surfaces, as showed by Vinogradova (Vinogradova, 1999), from no-slip to slipping flow conditions, what would result in faster velocity of the film drainage than predicted by the model presented above. Larger the solid roughness is, more air can be "captured" in the irregularities (Krasowska et al., 2007b). The differences in amounts of the air captured can be - together with differences in the asperities sizes - the reasons of difference in the kinetics of the TPC formation. At less rough T600 and T1200 surfaces smaller amounts of

air were entrapped and therefore the TPC was formed not at the 1st but during the 2nd and 3rd collisions, respectively. When air is entrapped at hydrophobic surfaces then the TPC formation can occur as a result of rupture of the local micro-films formed between the colliding macro-bubble and micro-bubbles present and already attached to hydrophobic surface. This picture (model) is sketched in Fig. 9.15 to illustrate that the model used above for the  $h_{cr}$  estimation refers to the wetting films thickness  $(h_{wf})$ , while in the case of the locally formed foam films  $(h_{ff})$  between colliding macro-bubble and micro-bubbles, attached to the solid surface, the foam film thickness can be quite different, i.e.  $h_{\rm ff} < h_{\rm wf}$ (see Fig. 9.15). Question of the air presence at the hydrophobic surfaces is further discussed below, in more details.



Fig. 9.15. Schematic illustration of the liquid film formed between colliding bubble and hydrophobic solid surface.

### 9.2. The TPC Formation in Solutions of Surface Active Substances.

#### 9.2.1. Effect of the Non-ionic Surface Active Substances.

In general, presence of surface active substances (SAS), that specifically adsorb at the liquid/air interface slows down the bubble velocity due to formation of dynamic architecture of the adsorption layer over surface of the rising bubble, which retards fluidity of the bubble surface. The bubble velocity variations depend on the type of the surface active substance but, in general, the most drastic velocity decrease occurs always at the lowest SAS concentrations. As shoved above (Fig. 7.4) it is also the case for for n-octanol and  $\alpha$ -terpineol solutions. In distilled water, the bubble terminal velocity was 34.7  $\pm 0.3$ Results and discussion

cm/s and decreased rapidly down to 15-16 cm/s at very low n-octanol  $(3 \cdot 10^{-5} \text{ M})$  and  $\alpha$ -terpineol  $(5 \cdot 10^{-5} \text{ M})$  "threshold" concentrations. Any further increase in n-octanol and/or  $\alpha$ -terpineol concentration had practically no influence on the terminal velocity (see Fig. 7.4). Figure 9.16 presents the sequences of photos of the bubble 1<sup>st</sup> collision with smooth T2500 surface in n-octanol solutions of different concentrations. It is clearly seen that in higher n-octanol concentrations, the bubble shape is less distorted and the amplitude of the bubble bouncing is smaller.



**Fig. 9.16.** Sequences of photos of the 1<sup>st</sup> collision between bubble and T2500 in n-octanol solutions of different concentrations.

Figure 9.17 presents quantitative data about influence of low n-octanol concentration on velocity variations during the bubble collision with T2500 (Fig. 9.17A) and T600 (Fig. 9.17B) surfaces. The Teflon plates were located at the distance 250 mm from the capillary orifice and the bubble impact velocities at the moment of the first collision were equal to their terminal velocities. As it is seen, the number of bouncing cycles and the amplitude of the bubble bouncing were diminished when the bubble impact velocity was lowered. As a consequence of lower impact velocity, smaller bouncing amplitudes and shorter bouncing time, the  $t_{TPC}$  values were also shortened. In the case of T2500 (Fig. 9.17A), the TPC was formed in distilled water after 105 ±4 ms while in  $6 \cdot 10^{-6}$  M and  $3 \cdot 10^{-5}$  M n-octanol solutions the  $t_{TPC}$  values were  $87 \pm 6$  and  $50 \pm 5$  ms,



**Fig. 9.17.** The bubble velocity variations during collisions, in water and n-octanol solutions of low concentrations, with T2500 (A) and T600 (B) surfaces located at distance L=250 mm.



**Fig. 9.18.** The bubble velocity variations during collisions, in n-octanol solutions of medium and high concentrations, with T2500 (A) and T600 (B) surfaces located at distance L=250 mm.

respectively. Similar effect of the shortening of the TPC formation time was found also for T600 surface as can be noted in Fig. 9.17B. Here, the effect was even more pronounced -  $t_{TPC}$  was almost 7 times shorter at these low n-octanol concentrations because the TPC was formed during the 1<sup>st</sup> collision, while in water the bubble bounced after the 1<sup>st</sup> collision. However, as showed in Fig. 9.18, at higher n-octanol concentrations the  $t_{TPC}$  values started to increase significantly, despite that the bubble impact velocity stayed at the constant level of ca. 15 cm/s. In the case of T2500 surface, the  $t_{TPC}$  increased from 42 ±7 ms for 1.10<sup>-4</sup> M

to 54 ±6 ms and 129 ±8 ms in  $6 \cdot 10^{-4}$  M and  $1 \cdot 10^{-3}$  M n-octanol solutions, respectively (see Fig. 9.18A). Similar phenomenon was observed for T600 surface (see Fig. 9.18B), where in  $1 \cdot 10^{-4}$  M and  $1 \cdot 10^{-3}$  M n-octanol solutions the  $t_{TPC}$  values were 7 ±1 and 74 ±6 ms, respectively.



**Fig. 9.19.** Bubble impact velocity (circles), time of the TPC formation (triangles) and time of the film drainage (squares) at T2500 surface, located at distance L=250 mm, as a function of n-octanol concentration.

Figure 9.19 presents a comparison of the influence of n-octanol concentration on the bubble impact velocity and time of the TPC formation at T2500 surface. There are also presented the  $t_D$  values, that is, the drainage time values illustrating influence of n-octanol concentration on stability of the liquid film formed between the hydrophobic solid and the bubble surfaces. As seen the courses of the  $t_{TPC}$  and  $t_D$  changes with n-octanol concentrations were quite different. At low concentrations, the  $t_{TPC}$  values were decreasing to reach a constant level, similarly as the impact velocity, while the  $t_D$  values stayed practically constant, i.e. within range of the experimental scatter, at a level of ca. 25 ms, Thus, the collision impact velocity had no influence on the drainage time. The reason of the difference between the  $t_{TPC}$  and  $t_D$  variations is rather obvious - the bubble bouncing has no influence on the time of drainage of the intervening liquid film formed between the "motionless" bubble and the Teflon surfaces. Further increase of n-octanol concentration, up to  $1 \cdot 10^{-3}$  M, caused prolongation of the  $t_D$  and the  $t_{TPC}$ , despite that the bubble impact velocity was identical as in  $3 \cdot 10^{-5}$  M n-octanol solutions.



**Fig. 9.20.** The  $t_{TPC}$  (A) and the  $t_D/t_{D(WATER)}$  (B) values as a function of n-octanol concentrations for the studied solid surfaces located at distance L= 250 mm. The lines are drawn to guide the eye.



**Fig. 9.21.** The  $t_{TPC}$  (A) and the  $t_D/t_{D(WATER)}$  (B) values as a function of  $\alpha$ -terpineol concentrations for Teflon of different surface roughness located at distance L= 250 mm. The lines are drawn to guide the eye.

Data presented in Fig. 9.20 confirms that indeed, at high n-octanol concentrations the  $t_{TPC}$  and the  $t_D$  values were longer not only for smooth T2500 surface, but also for all studied solid surfaces. Moreover, in the case of Teflon surfaces, prolongation of the  $t_{TPC}$ and the  $t_D$  values at high  $\alpha$ -terpineol concentration was also observed (see Fig. 9.21). In



**Fig. 9.22.** Time of liquid film drainage in  $1 \cdot 10^{-3}$  M n-octanol solution for solid surfaces located at distances L= 3 mm (white bars) and 250 mm (grey bars) from the capillary orifice.

n-octanol and  $\alpha$ -terpineol solutions, the bubble impact velocity was always smaller than in distilled water. The smaller impact velocity means, in general, the diminishing of the bubble bouncing, therefore the  $t_{TPC}$  prolongation at high n-octanol and  $\alpha$ -terpineol concentration was due to a longer drainage time of the liquid film between the bubble and hydrophobic solid surfaces. This effect is further documented in Figs 9.20B and 9.21B, where values of the film drainage time in n-octanol and  $\alpha$ -terpineol solutions are normalized in respect to the drainage time in distilled water ( $t_D / t_{D(WATER)}$ ). As clearly seen in Figs 9.20B and 9.21B, at high SAS concentration the film drainage times were significantly prolonged. Moreover, magnitude of this prolongation depended on roughness of the Teflon surface. Largest effect was observed for the Teflon1200, Teflon600, and SG600 surfaces, that is, for the surfaces of roughness within a range 10-60 µm. Similar effect of the  $t_{TPC}$  and the  $t_D$  prolongation at high concentrated SAS solutions was observed also, when the hydrophobic solid surfaces were located at distance L= 3 mm from the capillary orifice. A comparison of the time of film drainage in 1·10<sup>-3</sup> M n-octanol solution for the solid surfaces located at distances L= 3 mm ("close") and 250 mm ("far") is

presented in Fig. 9.22. As seen, within the range of the experimental scatter there is no difference between the  $t_D$  values measured at the solid surfaces located "close" and "far".



**Fig. 9.23.** Contact angles at the Teflon surfaces immersed for 18 hours in distilled water (grey bars) and in  $6 \cdot 10^{-4}$  M n-octanol solution (white bars).

The question to be answered is the possible mechanism (reasons) causing the prolongation of the film drainage time at high n-octanol and  $\alpha$ -terpineol concentrations. First possibility to consider is a modification of hydrophilic/hydrophobic properties of the Teflon surfaces due to adsorption of n-octanol and  $\alpha$ -terpineol at their high solution concentration. Despite that probability of the SAS molecules adsorption at highly hydrophobic Teflon surface during relatively short times of experiments, we have checked this possibility. The Teflon plates used in our experiments were immersed in 6·10<sup>-4</sup> M n-octanol solutions for 18 hours, i.e. the time period much longer than times of our experiments. Next, the plates were left at the laboratory table to dry and the advancing contact angles were measured. The obtained results are presented in Fig. 9.23. As seen, there is no any significant difference in the advancing contact angles measured at the Teflon surfaces after their long contact with n-octanol. Data of Fig. 9.23 show that there was no modification of the Teflon surfaces due to the SAS adsorption and therefore it

cannot be the reason of the prolongation of the  $t_D$  values. Thus, other mechanism(s) must be responsible for the significant variations of the  $t_{TPC}$  and  $t_D$  at high n-octanol and  $\alpha$ -terpineol concentration.



**Fig. 9.24.** Schematic illustration of the liquid (foam) film formed in a SAS solution between the colliding bubble and air micro- and/or nano-bubbles present at the hydrophobic solid surface.

The results presented above confirm correctness of the hypothesis described above (Chapter 9.1) that air is entrapped at the hydrophobic surfaces and its presence affects significantly affect the kinetics of the TPC formation. In distilled water, devoid of any surface active substances, the  $t_{TPC}$  values were monotonically decreasing with roughness of the Teflon surfaces (see Fig. 9.7) and this effect can be attributed to the increase in the amount of air entrapped into the solid surface irregularities of rougher solid surface. The prolongation of the  $t_{TPC}$  and  $t_D$  values at high n-octanol and  $\alpha$ -terpineol concentrations is the additional and strong evidence confirming that air is present at hydrophobic surfaces immersed into aqueous solutions. The mechanism of prolongation of the time of the bubble attachment to hydrophobic surfaces due to presence of micro- and/or nano-bubbles at rough hydrophobic surface is depicted schematically in Fig. 9.24. In solutions of any surface active substance an adsorption layer is formed at each solution/gas interface, that is, at the colliding bubble surface and at surfaces of the micro- and/or nano-bubbles already attached to the hydrophobic surface. Thus, instead of a wetting film formed between solid surface and the colliding bubble surface, there are formed locally the symmetric (foam) films between the colliding macro-bubble and the micro- and/or nano-bubbles. It also

means that rupture of the film and the TPC formation is occurring as a result of bridging (coalescence) of the colliding bubble and nano- or sub-microscopic bubbles already attached to the solid surface. As it is well known that stability of symmetric foam films increases with surfactant concentration (Exerowa and Kruglyakow, 1998) so prolongation of the  $t_D$  at high concentrations of n-octanol and  $\alpha$ -terpineol solution is a strong evidence, that there were locally the foam films formed, that is, there were air micro-bubbles attached to the hydrophobic solid surfaces. In distilled water and low concentrations of n-octanol and  $\alpha$ -terpineol solution is a strong evidence, that there were locally the foam films formed, that is, there were air micro-bubbles attached to the hydrophobic solid surfaces. In distilled water and low concentrations of n-octanol and  $\alpha$ -terpineol solutions the stability of those foam films formed locally was low because either there was no adsorption layer (distilled water) or the adsorption coverages were too low to assure a sufficient stability of these local foam films. Moreover, kinetics of the film drainage decreases with surfactant concentrations (adsorption coverage) due to immobilization of the solution/air interfaces (Radoev et al., 1974; Ivanov and Dimitrov, 1974; Exerowa and Kruglyakow, 1998). As described above (see Chapter 7.3), the minimum adsorption coverage needed for complete retardation the bubble surface fluidity was attained at 3·10<sup>-5</sup> M n-octanol and 5·10<sup>-5</sup> M  $\alpha$ -terpineol solutions.

As seen in Figs 9.19 and 9.20 the prolongation of the time of the film drainage was observed just above these "threshold" n-octanol and  $\alpha$ -terpineol concentrations. It indicates that prolongation of the  $t_{TPC}$  was caused by slower drainage and higher stability of the thin liquid films formed locally between the colliding bubble and air "pockets" (sub-microscopic bubbles) present at hydrophobic solid surfaces immersed into aqueous phase. This conclusion is also supported by data published by Melo and Laskowski (Melo and Laskowski, 2006) and Szyszka et al. (Szyszka et al., 2006) , where it is reported that the critical coalescence concentration (CCC) for  $\alpha$ -terpineol were 12 ppm (about 8·10<sup>-5</sup> M) and 1.6·10<sup>-4</sup> M, respectively. Prevention of the bubble coalescence means that stability of the liquid film formed between the colliding bubbles is increased and therefore there is no

bubble coalescence. As seen these CCC values are very close to the  $\alpha$ -terpineol concentration (3·10<sup>-4</sup> M), above which prolongation of the  $t_{TPC}$  was observed.

### 9.2.2. Influence of SAS Adsorption on the Film Drainage Velocity.

The  $t_D$  values determined in experiments are going to be used to evaluate, using literature models, the film thickness at the moment of the TPC formation. The following cases were considered:

(i) two tangentially immobile surfaces, the thinning velocity was calculated using Eq. (9.4) for n=1 (Reynolds, 1886; Dimitrov and Ivanov, 1978):

$$V = \frac{h^3 \Delta P}{2\eta R_f^2}$$
(9.6)

(ii) non-slip conditions of the solid surface and fully slip conditions of the bubble surface:  $\Gamma_{bubble}=0$ , the thinning velocity was calculated using Eq. (9.4) for n=4 (Scheludko, 1967):

$$V = \frac{2h^3 \Delta P}{\eta R_f^2}$$
(9.7)

iii) non-slip conditions of the solid surface and equilibrium adsorption coverage at the bubble surface:  $\Gamma_{bubble} = \Gamma_{eq}$ , using Eqs (4.55)-(4.56) (Ivanov et al., 1985):

$$V = \frac{h^{3} \Delta P}{2\eta R_{f}^{2}} \left( \frac{3 + b + \frac{h_{S}}{2h}}{3 + 4b + 2h_{S}} \right)$$
(9.8)

where *b* and  $h_s$  are coefficients calculated using Eqs (4.50)-(4.51) for equilibrium coverage over the bubble surface. The "total" pressure causing drainage of the film formed between bubble and solid surface was calculated from Eq. (8.22), neglecting the disjoining pressure term.

To calculate the thinning velocity, it is also necessary to know the radius of the draining film. Equation (9.3), applied above for the water films (see Chapter 9.1.5), was used. Data presented in Fig. 9.25 show that the film radiuses calculated from Eq. (9.3) are in a good agreement with the experimentally determined values. Figure 9.26 presents the



**Fig. 9.25.** Radius of the foam film formed between bubble and solid surface (glass plate and top-view camera) as a function of n-octanol concentration. Points present the experimental data, lines – values calculated according to Eq. 9.3.

dependences of the film thicknesses, at the moment of the TPC formation at T2500 surface, on n-octanol concentration. The film thicknesses were calculated using the theoretical models presented above and the experimental  $t_D$  values. As one could expect the film thicknesses are decreasing at high n-octanol concentrations, because the  $t_D$  values



**Fig. 9.26.** Thickness of the liquid film at the moment of the TPC formation at T2500 surface (L=250 mm) as a function of n-octanol concentration. The lines are drawn to guide the eye.

were the highest there. According to the model assuming full mobility of the bubble surface (Eq. 9.6), the film thickness decreases from 1.2  $\mu$ m in distilled to 0.7  $\mu$ m in 1·10<sup>-3</sup> M n-octanol solution, while according to the non-slip condition model (Eq. 9.7) these values are 2.3  $\mu$ m and 1.4  $\mu$ m, respectively. Certainly, for distilled water and low n-octanol concentrations assumption of the surface mobility seems to be more appropriate, while at high n-octanol concentration the bubble surface mobility is completely retarded, as showed in Chapter 3.1. Therefore, the film thickness values calculated from Eq (9.7) seem to be more appropriate for high n-octanol concentration. As seen in Fig. 9.26 at the highest n-octanol concentration of 1·10<sup>-3</sup> M the film thickness predicted from Eq. (9.7) is 1.4 ±0.1  $\mu$ m, that is, quite similar as in distilled water and low n-octanol concentrations. Thus, n-octanol adsorption lowered the film drainage velocity and therefore, despite the *t*<sub>D</sub> values were increased significantly longer at high n-octanol concentration, the film rupture thicknesses at T2500 seem to be similar as in distilled water and significantly larger than distances of the DLVO interactions.



**Fig. 9.27.** Thickness of the liquid film at the moment of the TPC formation at SG00 (A) and P00 (B) surfaces (L= 250 mm) as a function of n-octanol concentration. The lines are drawn to guide the eye.

Similar calculations were carried out for the films formed SG00 and P00 and these

data are presented in Figure 9.27 A and B, respectively. As seen there, the liquid films at

hydrophobic SG00 and P00 surfaces ruptured at similar thicknesses, ca. 1.2-1.4  $\mu$ m. These evaluations of the film rupture thicknesses, at the moment of the TPC formation, show that at hydrophobic surfaces the film rupture thickness are significantly greater that distances of the DLVO forces interaction (ca. 100 nm). Presence of air (nano- and micro-bubbles) on the hydrophobic solid surfaces can be a reason of the films rupture at such large thicknesses.

### 9.2.3. Effect of the Ionic Surface Active Substances.

In Chapter 8.2 it was showed that in distilled water and solutions of non-ionic surface active substances (n-octanol and  $\alpha$ -terpineol) the liquid/air interfaces is negatively charged. Figure 9.28 presents the zeta potential of smooth Teflon surface as a function of pH in  $5 \cdot 10^{-4}$  M and  $10^{-2}$  M NaCl solutions. As it is seen, the Teflon surface is negatively charged in entire range of the pH studied. In CTABr solutions, a preferential adsorption of the cationic surfactant at the bubble surface can results in electrical charge reversal at the gas/solution interface from negative to positive. The concentration of CTABr solutions used in experiments was low enough to ensure no charge reversal of the solid surfaces, i.e.



**Fig. 9.28.** The dependence of the zeta potential of smooth Teflon surface on pH, in  $5 \cdot 10^{-4}$  M (grey circles) and  $1 \cdot 10^{-2}$  M (black circles) NaCl solutions, obtained from streaming potential measurement.

 $c_{CTABr} \leq 2.10^{-5}$  M (Gu and Li, 2000; Exerowa et al., 2001). In the case of the Teflon the TPC formation seems to be mainly driven by the solid hydrophobic properties and the film rupture occurs via nucleation mechanism proposed by Derjaguin and Gutop (Derjaguin and Gutop, 1962; Krasowska and Malysa, 2007b). However, if the draining films were reaching thickness of an order 100 nm, then the DLVO electrostatic interactions should affect the film stability. As the Teflon (Fig. 9.28), PVC (Kirby and Hasselbrink Jr., 2004; Lameiras et al., 2008), and glass (Schulze, 1984; Gu and Li, 2000) surfaces are negatively charged at natural pH, so addition of CTABr should lead to shortening of the  $t_{TPC}$  due to attractive electrostatic interaction between oppositely charged the bubble and solid surface.



**Fig. 9.29.** The  $t_{TPC}$  (A) and the  $t_D$  (B) values as a function of CTABr concentrations for different solid surfaces located at distance L= 250 mm. The lines are drawn to guide the eye.

Figure 9.29 presents the  $t_{TPC}$  (Fig. 9.29A) and the  $t_D$  (Fig. 9.29B) values as a function of CTABr concentrations for the studied solid surfaces located at distance L= 250 mm. As it is seen, at high CTABr concentrations the  $t_{TPC}$  and the  $t_D$  values are increasing significantly. Thus, we have here similar effect as observed in the case of non-ionic SAS, despite that electrical charge of the bubble surface was changed from negative to positive (Zawala et al., 2008). For example, the  $t_{TPC}$  on smooth Teflon surface, located at L= 250 mm, increased from 141 ±14 ms to 240 ±36 ms for CTABr concentrations  $1\cdot10^{-6}$  M and  $1\cdot10^{-5}$  M, respectively. Similar effect was observed for Teflon surface located

at L= 3 mm, where the  $t_{TPC}$  was prolonged from 90 ±17 ms in  $1 \cdot 10^{-6}$  M to 260 ±25 ms in  $1 \cdot 10^{-5}$  M CTABr solutions (see Fig. 9.30). Thus, despite that at high CTABr concentrations the interfaces of the film, formed between the bubble and hydrophobic solids studied, were oppositely charge and attractive electrostatic interactions should have caused the film destabilization, the time of the TPC formation was prolonged. It shows that at high CTABr concentrations the film lifetime (stability) was increased.



**Fig. 9.30.** The  $t_{TPC}$  (A) and the  $t_D$  (B) values as a function of CTABr concentrations for different solid surfaces located at distance L= 3 mm. The lines are drawn to guide the eye.

These results indicate again that, as discussed above, air was entrapped at the hydrophobic surfaces immersed into aqueous solutions and there were formed locally the symmetric (foam) films between the colliding macro-bubble and the micro- and/or nanobubbles (see Fig. 9.24). CTABr molecules were adsorbed at the macro-bubble and microbubbles surfaces and if the films reached locally distances of the electrostatic interactions, then there were repulsive interactions between liquid/gas interfaces bearing identical surface charges. Note also please (Figs 9.29 and 9.30), that the significant prolongation of the film lifetime was observed for  $c_{CTABr} > 3 \cdot 10^{-6}$  M and as was reported by Exerowa et al. (Exerowa et al., 2001) the foam film of high stability were formed at similar CTABr concentrations.



**Fig. 9.31.** The  $t_{TPC}$  (A) and the  $t_D$  (B) values as a function of Rh 1.2 concentrations for the studied solid surfaces located at distance L= 3 mm. The lines are drawn to guide the eye.

Data presented in Fig. 9.31 supply further evidences that air is present at hydrophobic solid surfaces and the TPC is formed as a result of rupturing of the foam films formed locally between the colliding bubble and nano- or micro-bubbles present at these surfaces. Figure 9.31 presents the  $t_{TPC}$  (Fig. 9.31A) and the  $t_D$  (Fig. 9.31B) values as a function of concentration of the anionic type biosurfactant (Rhamnolipid Rh1.2) for different solid surfaces located at L=3 mm. As can be observed the influence of the Rh1.2 concentration is quite similar as presented above for non-ionic and cationic surface active substances - increasing Rh1.2 concentration caused prolongation of the times of the TPC formation and the film drainage. For example, in the case of the T2500 surface the  $t_D$  was prolonged from  $45\pm10$  ms in  $1\cdot10^{-6}$  M to  $270\pm23$  ms in to  $1\cdot10^{-4}$  M Rh1.2 solution. It is worthy to underline here, according to the literature data (Cohen et al., 2003; Cohen and Exerowa, 2007), the foam films of high stability were obtained at this Rhamnolipid concentration range. Thus, the  $t_D$  prolongation in high Rh1.2 concentrations shows that there were formed locally the foam films between the colliding macro-bubble and air entrapped at these hydrophobic surfaces.

## Conclusions

Rapid phenomena occurring during collisions of the rising bubble with liquid/air and liquid/solid interfaces were studied to determine the kinetics and mechanism of the bubble bouncing, coalescence at liquid/air interface and the three-phase contact (TPC) formation at liquid solid/interface. It was found that properties of the liquid films formed by the colliding bubble at liquid/air and liquid/solid interfaces are the factor of crucial importance for kinetics of the bubble coalescence and the TPC formation at liquid/gas and liquid/solid interfaces, respectively.

Bubble impact velocity affects the time of the bubble bouncing ( $t_{bouncing}$ ) Turing collisions with various interfaces. With increasing impact velocity the bubble bouncing time was prolonged and consequently, the times of the bubble coalescence ( $t_c$ ) and the TPC formation ( $t_{TPC}$ ) were prolonged. In distilled water, the impact velocity was modified by variation of the distance, L, between the interfaces and point of the bubble formation. Lowering of the bubble impact velocity ( $U_{imp}$ ) from 34.8 cm/s (L= 250 mm) to 19.4 cm/s (L= 3 mm) caused: (i) shortening of the  $t_c$  at free surface from 73±1 ms to 42±1 ms, and (ii) decreasing of the  $t_{TPC}$  at hydrophobic surfaces; e.g. in the case of T2500 surface the  $t_{TPC}$  decreased from 105±4 ms to 65±4 ms,

The mechanism of prolongation of the  $t_c$  at water/air and the  $t_{TPC}$  at water/solid interfaces at higher bubble impact velocity is related to size of the liquid film formed during the bubble collisions. The bubble bounces when the thinning water film between the bubble and interface does not reach its rupture thickness during the collision time. Higher impact velocity means larger deformation of the bubble shape and larger radius of the liquid film formed, i.e. longer time is needed for the film drainage.

Presence of a surface active substances (SAS) can lower the bubble terminal velocity even by over 50%, due to formation of the dynamic architecture of the adsorption

layer (DAL) over the rising bubble surface, and causes significant shortening of the bubble bouncing time ( $t_{Bouncing}$ ). Moreover, presence of the adsorption layers changes the film drainage conditions; from slipping to non-slipping at high SAS concentrations. Therefore, the film drainage velocity is significantly slowed down in high SAS concentrations.

It was showed that shortening of the bubble coalescence time,  $t_c$ , at low surface active substances (n-octanol) concentrations was related to decrease of the bubble impact velocity. With increasing SAS concentration the bubble velocity was further decreasing until fluidity of the bubble surface was completely retarded by the DAL formed, but stability of the liquid (foam) film formed was increasing. It was found that n-octanol concentration of  $5 \cdot 10^{-6}$  M, was a minimum concentration ("threshold" concentration) assuring formation of the foam films, which were able to survive the disturbances caused by the colliding bubble. At this threshold concentration the bubble coalescence time increased rapidly to ca. 1200 ms. The  $t_{film}$  values were used for calculations thicknesses, which could be reached by the draining films formed by the colliding bubbles. These evaluations showed that for n-octanol concentrations  $c < 5 \cdot 10^{-6}$  M the film rupture thicknesses were of an order 5-7 µm. For  $c = 5 \cdot 10^{-6}$  M the rupture thicknesses of the films formed by the colliding bubble dropped by over order of magnitude, below 400 nm, and at higher n-octanol concentrations the draining films could reach similar thicknesses as measured for microscopic foam films under static conditions, i.e. below 100 nm.

Addition of electrolyte  $(5 \cdot 10^{-4} \text{ M NaCl})$  practically did not affect the bubble bouncing and coalescence times on free surface, in distilled water, as well as in presence of non-ionic surface active substance (n-octanol). Similarly, the addition of NaCl neither influenced the time of the three-phase contact formation nor the time of the film drainage on hydrophobic surfaces. As the inorganic electrolytes do not adsorb on the water/air interfaces so they cannot change the fluidity of the bubble surface and therefore the drainage times of the liquid film formed were not affected by the NaCl presence. Roughness of solid surfaces and concentration of surface active substance solutions are the factors strongly affecting the time of the three-phase contact formation by the bubble colliding with hydrophobic surfaces. When the Teflon roughness was increased from ca. 1 to 80  $\mu$ m then the  $t_{TPC}$  values were shortened even by over order of magnitude, from 105 to a few milliseconds only. The effect of surface roughness on the kinetics of the bubble attachment was attributed to: (i) the radiuses of the local liquid films formed at irregularities of solid surface of different roughness, and (ii) the presence of air entrapped in the scratches, grooves and irregularities of the hydrophobic surface.

The influence of non-ionic (n-octanol and  $\alpha$ -terpineol) and ionic (CTABr and Rhamnolipid) SAS on the time of bubble attachment to hydrophobic surfaces depends on solutions concentration. At low concentrations, the time of the TPC formation was decreasing, mainly due to lowering the bubble impact velocity and shortening the bubble bouncing time ( $t_{Bouncing}$ ). At high concentrations of non-ionic and ionic surface active substances studied, the time of the TPC formation was prolonged as a result of significant increase of the drainage ( $t_D$ ) time of the films formed at different hydrophobic surfaces.

Fact, that the  $t_D$  values increased similarly significantly at high concentrations of ionic and non-ionic SAS shows that: (i) air was present at hydrophobic surfaces immersed into aqueous phase, and (ii) the TPC was formed as a result of coalescence of the colliding bubble with the air "pockets" (nano- and/or sub-microscopic bubbles), already attached to the hydrophobic surfaces.

When air is entrapped in irregularities of hydrophobic surface then foam films are formed locally between the micro- and/or nano- bubbles and the colliding bubble and stability of these local foam films determines kinetics of the TPC formation. Stability of the foam films increases with concentration of ionic and non-ionic surface active substances and therefore, at high SAS concentrations, the time of the TPC formation was prolonged, that is, the bubble attachment was hindered. The evaluations of the film rupture thicknesses, using the RDI model, at the moment of the TPC formation, show that at hydrophobic surfaces the film rupture thicknesses ( $h_{cr}$ ) are above 1 µm, i.e. the  $h_{cr}$  are significantly greater that distances of the DLVO forces interaction (ca. 100 nm).

The finding that at high concentrations of various surface active substances the time of the TPC formation and the bubble attachment to hydrophobic surface are clearly prolonged can have also some important practical implications for flotation process. It shows that too high concentrations (overdosage) of surface active substances (frothers and/or collectors) can be counterproductive, because the flotation kinetics can be slowed down as a result of prolongation (hindrance) the TPC formation time.

# **List of Publications**

## A) Journals

- **1.** D. Kosior, J. Zawala, K. Malysa, "When and how α-Terpineol and n-Octanol can inhibit the bubble attachment to hydrophobic surfaces", Physicochem. Probl. Miner. Process. 47 (2011) 169-182.
- D. Kosior, J. Zawala, K. Malysa, "Influence of n-octanol on the bubble impact velocity, bouncing and the three-phase contact formation at hydrophobic solid surfaces", Colloids Surf. A: Physicochem. Eng. Aspects (2012), DOI: 10.1016/j.colsurfa.2012.10.025.
- **3.** D. Kosior, J. Zawala, M. Krasowska, K. Malysa "Influence of n-octanol and aterpineol on thin film stability and bubble attachment to hydrophobic surface", Phys. Chem. Chem. Phys., 15 (2013) 2586-2595.
- **4.** D. Kosior, J. Zawala, R. Todorov, D. Exerowa, K. Malysa, "Bubble bouncing and stability of liquid films formed under dynamic and static conditions from n-octanol solutions", to be submitted

## **B)** Conference Proceedings

 D. Kosior, J. Zawala, M. Krasowska, K. Malysa, "On the mechanism of the action of frothers in the colliding bubble attachment to hydrophobic surfaces of different roughness", 26<sup>th</sup> International Mineral Processing Congress IMPC 2012, New Delhi, India, September 24-28, Conference Proceedings, paper No. 255, pp. 3208-3215.

## **C)** Conference Contributions

- D. Kosior, <u>J. Zawala</u>, M. Krasowska, K. Malysa, "Air at hydrophobic surfaces and three-phase contact formation", 8<sup>th</sup> European Conference on Foams, Emulsion and Applications EUFOAM 2010, Borovets, Bulgaria, July 14-16, Book of Abstracts, 2010, P21-P16 (poster).
- <u>D. Kosior</u>, J. Zawala, K. Malysa, "Role of "entrapped" air at the hydrophobic solid surface in kinetics of the three-phase contact formation", 13<sup>th</sup> European Student Colloid Conference ESC 2011, Falkenberg, Sweden, June 14-17, Book of Abstracts, 2011, p. 66 (poster).
- **3.** D. Kosior, J. Zawala, M. Krasowska, <u>K. Malysa</u>, "Influence of surface roughness and concentration of surface active substances on kinetics of the bubble attachment to hydrophobic solid", 25<sup>th</sup> Conference of the European Colloid and Interface Society ECIS 2011, Berlin, Germany, September 4-9, Abstracts, 2011, No. 313, p. 162 (poster).

- 4. <u>D. Kosior</u>, J. Zawala, K. Malysa, "Influence of the surface active substances on the bubble impact velocity, bouncing and the three-phase contact formation at hydrophobic solid surfaces", 5<sup>th</sup> International Workshop Bubble & Drop Interfacial B&D 2012, Krakow, Poland, May 20-24, Book of Abstracts, 2012, OC-2, p. 50 (oral).
- <u>D. Kosior</u>, R. Todorov, D. Exerowa, K. Malysa "Properties of n-octanol stabilized thin liquid films under static and dynamic (colliding bubble) conditions", 5<sup>th</sup> International Workshop Bubble & Drop Interfacial B&D 2012, Krakow, Poland, May 20-24, Book of Abstracts, 2012, P-20, p. 96 (poster).
- 6. D. Kosior, <u>J. Zawala</u>, K. Malysa, "*Effect of the frother overdosage on kinetics of the three-phase contact formation at hydrophobic surfaces*", 19<sup>th</sup> International Symposium on Surfactans in Solution SIS 2012, Edmonton, Canada, June 24-28, Book of Abstracts, 2012, No. 119, p. 106 (oral).
- <u>D. Kosior</u>, J. Zawala, K. Malysa, "Influence of the impact velocity on stability of foam films formed by the rising bubbles", 9<sup>th</sup> European Conference on Foams, Emulsion and Applications EUFOAM 2012, Lisboa, Portugal, July 8-11, Book of Abstracts, 2012, OD 6.5, p. 84 (oral).
- <u>D. Kosior</u>, J. Zawala, K. Krasowska, K. Malysa, "On the mechanism of the action of frothers in the colliding bubble attachment to hydrophobic surfaces of different roughness", 26<sup>th</sup> International Mineral Processing Congress IMPC 2012, New Delhi, India, September 24-28, Book of Abstracts, 2012, Vol. 1, p. 212 (oral, poster).
- D. Kosior, J. Zawala, <u>K. Malysa</u>, "Influence of n-octanol on the bubble bouncing and coalescence time at solution surface", Smart and Green Interfaces 2013 Workshop of COST MP1106, Prague, Czech Republic, March 21-22, Program and abstracts, 2013, p. 56 (oral).
- 10. <u>D. Kosior</u>, J. Zawala, K. Malysa, "Mechanism of three-phase contact formation by a bubble colliding with hydrophobic surfaces of different roughness", 14<sup>th</sup> European Student Colloid Conference ESC 2013, Golm, Germany, June 10-13, Abstract Book, 2013, p.40 (oral).
- 11. <u>D. Kosior</u>, J. Zawala, K. Malysa, "Bubble bouncing and kinetics of the three-phase contact formation at hydrophobic surface in n-octanol solution", 4<sup>th</sup> International Conference on colloid Chemistry and Physicochemical Mechanics IC-CCPCM 2013, Moscow, Russia, June 30 July 05, Book of Abstracts, 2013, A08, p. 82 (oral).
- 12. <u>D. Kosior</u>, A. Niecikowska, J. Zawala, K. Malysa, "Influence of CTABr on kinetics of the bubble attachment to hydrophilic/hydrophobic surfaces", 4<sup>th</sup> International Conference on colloid Chemistry and Physicochemical Mechanics IC-CCPCM 2013, Moscow, Russia, June 30 – July 05, Book of Abstracts, 2013, AP14, p. 330 (poster).
- 13. <u>D. Kosior</u>, J. Zawala, R. Todorov, D. Exerowa, K. Malysa, "Bubble bouncing and stability of liquid films formed under dynamic and static conditions from n-octanol

*solutions*", 27<sup>th</sup> Conference of the European Colloid and Interface Society ECIS 2013, Sofia, Bulgaria, September 1-6, *accepted* (oral).

- 14. D. Kosior, A. Niecikowska, J. Zawala, K. Malysa, "Influence of cationic surfactant on kinetics of the three phase contact formation at mica and Teflon surfaces", 27<sup>th</sup> Conference of the European Colloid and Interface Society ECIS 2013, Sofia, Bulgaria, September 1-6, accepted (poster).
- **15.** J. Zawala, D. Kosior, <u>K. Malysa</u>, "Air presence at hydrophilic solid surface and kinetics of bubble collision experiment and simulations", 27<sup>th</sup> Conference of the European Colloid and Interface Society ECIS 2013, Sofia, Bulgaria, September 1-6, accepted (oral).

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