**Heterocoagulation of shale particles and bubbles in the presence of ionic surfactants**

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**Abstract**

Adsorption of surfactants is one of the important feature governing interactions between particulate matters. When interactions occur between two particulates, which differ from each other, heterocoagulation takes place. This paper explains heterocoagulation of bubbles and carbonaceous metal-bearing shale particles. Heterocoagulation was experimentally studied using zeta potential, adsorption and contact angle tests. The results indicated that heterocoagulation in the presence of ionic (anionic sodium dodecyl sulfate SDS, and cationic dodecylamine hydrochloride DDA) surfactants was feasible. Based on the results, the heterocoagulation mechanism was evaluated, and thus the mechanism of shale flotation in the presence of ionic surfactants was elucidated.

**Keywords:** adsorption, heterocoagulation, shale, surfactants, flotation, particle, bubble

# **Introduction**

Interactions between two or more particulate matters (e.g. particles, bubbles, droplets) are of great scientific and practical interest in many areas of research and technology including separation processes. The particulate-particulate interactions determine the process kinetics and efficiency. These interactions can be controlled by surface forces leading to formation of either coagulates or heterocoagulates [1]. The term coagulation is used to describe formation of a colloidal system with the same particulates, while heterocoagulation refers to interactions of particulates, which may differ in a number of ways, e.g. type, composition, shape, size, surface charge, potential and hydrophobicity [2].Flotation is an example of a heterocoagulation process, where hydrophobic particles interact with bubbles in aqueous solutions.

Heterocoagulation of fine particulate matters in aqueous solutions is commonly described by the DLVO theory. The interaction between particulates (e.g. particles-bubbles) can be divided into three main types i.e. *i*) electrostatic (electrical double layer, *edl*), *ii*) dispersion (London-van der Waals), and *iii*)steric (resulted from the presence of either polymer or surfactant) [3]. According to the DLVO theory, the balance of these interactions between particulates in contact determines the coagulation process [4].

Coagulation of colloidal particulates consists of two processes, that is collision and attachment of two or more particulates, while in flotation detachment constitutes the third process [5]. The attachment process involves three elemental stages, i.e. *i*) thinning of a interfacial liquid film to a critical thickness, *ii*) film rupture from its critical thickness to formation of three-phase contact (TPC gas/liquid/solid), and *iii*) expansion of TPC line. The three-phase contact formation, and thus a successful particulate-particulate attachment, depends on a number of characteristics of a system including the surface charge and hydrophobicity of particulate matters, their size and roughness, temperature, water chemistry, hydrodynamics and many others.

Addition of coagulant (e.g. surfactant) destabilizes the system by changing the zeta potential and weakening repulsive hydration interactions or additional hydrophobic structural influences resulting from adsorption of a coagulant on a solid surface [6]. The extent to which the surfactant adsorbs on the solid surface is mainly determined by the value of the surface potential at certain pH. Adsorption of an ionic surfactant on the surface of particulate matter (e.g. bubble, particle, droplet) is possible due to various types of interactions of the surface and surfactant hydrophobic heads [7]. It leads to interactions between anionic surfactants with positively charged surfaces and cationic surfactants with negatively charged surfaces. The surfactant molecules adsorb with the tail facing the solution and, if a surfactant concentration is high enough, form a monolayer on the surface of particulate matter. Such modified particulates merge into aggregates by hydrophobic interactions. By considering electrostatic, hydrophobic and micellar interactions in the system adsorption of surfactants can be divided into four regions, i.e. *i*) adsorption due to electrostatic interactions between the charged sites on the mineral surface, *ii*) increased adsorption due to aggregation of hydrophobic groups of surfactants resulting in electrostatic neutralization of the surface, *iii*) adsorption due to chain-chain hydrophobic interaction, where the surface acquires the same charge as the adsorbing surfactant, and *iv*) above critical micelle coalescence *cmc*, monomer activity is constant, and thus adsorption also remains constant [8,9].

Methods to characterize heterocoagulation are diverse and include microscope, particle size distribution, zeta potential values and distribution, adsorption and others. Many researches have studied heterocoagulation in flotation [1,5,10,11,12,13,14,15,16], however the number of papers, which describe the interactions between bubbles and metal-bearing shale particles in the presence of ionic surfactants is limited. Therefore, the objective of the present study was to investigate and better understand the mechanism of fine shale particles and bubbles heterocoagulation in the presence of ionic surfactants through electrostatic and adsorption studies. The results were correlated with the charge of bubbles reported in literature and verified by microflotation tests.

# **Experimental**

## Metal-bearing shale

A geological sample of metal-bearing shale originated from the Kupferschiefer stratiform copper deposit. The shale rock samples were collected from the Polkowice-Sieroszowice mine. The chemical composition of sample was determined by X-ray fluorescence (XRF) and total organic carbon (TOC) analyses. The average percentage contents of Cu, total organic carbon, Ca, Fe, Zn, Al, Si and S were 6.0, 8.0, 11.8, 1.3, 0.3, 3.8, 10.6, 1.7, respectively. The investigated sample corresponds to the P-KS-2 shale sample described elsewhere [17]. The shale sample from Polkowice-Sieroszowice mine consisted of quartz (14%), sheet silicates (42%), carbonate minerals (33%) and copper minerals (9%) [17].

Figure 1 shows the SEM picture of shale fraction (100-200 µm). Shale is polymetallic and heterogeneous substance with many different functional groups and pore structures on the surface. The determined BET surface area was equal to 4.40 m2/g.



Figure 1. SEM of shale originated from Kupferschiefer

In order to obtain the narrow size fraction of shale particles, the collected rocks were first crushed, and then sieved. Two size fractions were used in this work *i*) 100-200 µm in flotation tests, and *ii*) -45 µm in zeta potential, adsorption and contact angle measurements.

## Surfactants

Sodium dodecyl sulfate (SDS, CH3(CH2)11OSO3Na) MW=223.38 g/mol, as an anionic surfactant, and dodecylamine hydrochloride (DDA, CH3(CH2)11NH2·HCl) MW=221.81 g/mol as a cationic surfactant were purchased from Alfa Aesar. Dimidium bromide-disulphine blue indicator and chloroform (CHCl3) used in adsorption tests were purchased from Alfa Aesar. Sodium hydroxide (NaOH) and chloric acid (HCl), both purchased from POCh, were used to adjust pH. All chemicals were specified to be of the highest purity, and thus were used without further purification. High purity water with a specific conductivity of 10-6 S/cm was used in all experiments as well as for cleaning and preparation of surfactant solutions.

## Zeta potential measurements

Zeta potential measurements were conducted at 25 °C using a zeta potential analyser (Malvern Zetasizer 2000). The suspension containing 0.010 g of shale particles (-45 µm) in 25 cm3 of aqueous solution of surfactants at the certain concentration at given pH was conditioned in a beaker for 10 min. Then, the suspension was placed in the electrophoresis cell. The value of zeta potential was determined as an average of five successive measurements.

## Adsorption tests

Adsorption isotherms were determined by using a two-phase (water-chloroform) titration method with a dimidium bromide-disulphine blue indicator. The suspension containing 0.8 g of shale particles, with the size fraction less than 45 µm, in 40 cm3 of aqueous solution of surfactants at given concentration was conditioned for 24 h at room temperature (25 °C). Then, the solid particles were separated by filtration. The residues were dried and used in the contact angle measurements. The solution after adsorption was taken from supernatant and titrated with surfactant solution of opposite charge (SDS for DDA isotherm and DDA for SDS isotherm). Titration was conducted to colour change of chloroform phase i.e. blue to pink for the DDA isotherm and pink to blue for the SDS isotherm. The experiments were carried out at natural pH of aqueous solutions of surfactants.

## Flotation tests

Flotation tests were carried out using a mono-bubble Hallimond tube. Its volume was 250 cm3, diameter 2.8 cm and height 33 cm. Such a tall tube was used to avoid particles entrainment during flotation. A 1 g of shale sample with the particle size of 100-200 µm together with either pure water or aqueous solutions of surfactants at given concentrations was conditioned for 5 min. Then, the mixture was transferred to the Hallimond tube and floated. In each experiment the air flow rate was constant and equal to 30 cm3/min, and the ultimate time of flotation was 40 min. The experiments were carried out at room temperature (25 °C) and natural pH of aqueous solutions of surfactants. Each flotation test was repeated twice.

## Contact angle measurements

Advancing rest contact angles were measured by the sessile drop technique using the PGX+ goniometer. A dry sample of shale (0.2 g) before and after adsorption experiments was pressed into pastilles for 30 s under the pressure of 30 bar in order to obtain a sample with a smooth and flat surface. Then, a liquid drop with pure water was introduced onto the pastille surface through a syringe equipped with a needle. The profile of sessile drop was analysed by a software and the average value of the contact angle was obtained. The contact angle experiments were carried out at room temperature (25 °C), and each experiment was repeated 5 times.

# **Results and discussion**

# **Zeta potential**

The zeta potential values of metal-bearing shale measured as a function of pH, in the presence of water and ionic (DDA and SDS) surfactants with different concentrations are given in Fig. 2. It can be clearly seen that the zeta potential of shale was affected by pH of water and changed with increasing the pH value, from +34 mV at pH=2 to -36 mV at pH=12. The shale particles were positively charged at lower pH and the reversal of charge to negative occurred at pH=3.0. At this pH the zeta potential is zero, what corresponds to the isoelectric point (*iep*). The obtain *iep* was within the values reported elsewhere [18]. The charge of shale, similarly to coal, was governed by dissociation of inorganic (e.g. carboxylic, phenolic and hydroxylic) functional groups on the surface. For such groups the degree and sign of charge is dependent on pH since H+ and OH‒ are the potential determining ions [19]. The surface of carbonaceous matters becomes more negative in the presence of hydroxyl ions and when pH decreases, the hydronium ions are adsorbed until the negative charge is neutralized [20].

For anionic surfactant (SDS) the zeta potential of shale particles did not change significantly at low concentrations (1 and 10 mg/dm3) in the pH range of 4-8. At pH higher than 8 and lower than 4, the magnitude of changes in the zeta potential was high, and it was more negative at pH > 8 and less negative at pH < 3 (Fig. 2a). The reversal of charge from negative to positive occurred at pH less than 3.0. The isoelectric point of shale slightly shifted from pH*iep*=3.0 in water to pH*iep*=2.7 and pH*iep*=2.3 at the SDS concentrations of 1 and 10 mg/dm3, respectively. As seen from Fig. 2a, the substantial download shift in the zeta potential values was observed for high concentrations of SDS (100 and 1000 mg/dm3). It was due to increased adsorption of surfactant molecules on the solid surface. In addition, no isoelectric point was noticed at high SDS concentrations.

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| (a) | (b) |
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Figure 2. Zeta potential of shale particles in the presence of (a) anionic SDS, (b) cationic DDAsurfactants

Figure 2b shows the influence of cationic surfactant concentration on the zeta potential values of shale. The shale particles can be either positive or negative, depending on the DDA concentration and pH of solution. As seen the values of zeta potential did not change at low DDA concentrations. The shale particles were positively charged at low pH values. The isoelectric point of shale moved toward higher pH values with the amine concentration and was ca. pH*iep*=10.2 and pH*iep*=10.9 for 100 and 1000 mg/dm3, respectively. At pH higher than *iep* the zeta potential of shale became negative. The charge reversal of the surface is due to changing hydrolysis of ammonium ions to neutral amine and/or amine precipitation [21,22,23,24,25].

In order to describe the influence of investigated surfactants on the surface charge of bubble, the values of zeta potential were taken from literature [26]. Figure 3 shows the influence of surfactant concentration on zeta potential values of shale particles (Fig. 3a, this work) and bubbles (Fig. 3b, [26]) at pH=6.5. As seen from Fig. 3b, the air bubbles exhibited negative charges in pure water. The values of the isoelectric point (pHiep) of bubble/water interfaces is close to 3 [27]. In the case of ionic surfactants, the sign of zeta potential of bubbles is determined by charge of the polar groups of surfactants. Cationic DDA produced positively, while anionic SDS negatively charged bubbles. The substantial shift in the zeta potential values was observed for high concentrations of both cationic and anionic surfactants. For DDA, the zeta potential values increased due to adsorption of hydrocarbon parts of amine molecules on the bubble surface. The reversal of charge of bubbles from negative to positive occurred at the DDA concentration of ca. 50 mg/dm3 (ca. 2.3·10-4 M). The zeta potential values of bubble and shale were similar to dodecylamine precipitate, and it is interesting to observe that the isoelectric points for shale particles in the presence of cationic surfactant are situated in the precipitation range of DDA and are close to *iep* of bulk DDA precipitate [23].

For anionic surfactants, the negative zeta potential values for bubbles and shale particles increased with concentration until it would reach plateau close to critical micelle concentration [22].



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Figure 3. Effect of SDS and DDA concentration on zeta potential of shale particles (this work) and air bubble ([26]) at pH=6.5

# **Adsorption isotherms**

Figure 4 shows the adsorption isotherms of cationic (DDA) and anionic (SDS) surfactants on the shale surface at natural pH and 25 °C as a function of equilibrium concentration in the solution. As seen, adsorption increased with the surfactant concentration. The level of adsorption of the cationic surfactant (DDA) was much higher than the anionic surfactant (SDS). It was due to electrostatic attractions between positively charged DDA and negatively charged shale, and electrostatic repulsions in the presence of SDS. It was confirmed by the zeta potential data where the magnitude in changes of zeta potential was much higher for DDA (Fig. 2). Adsorption of surfactants molecules on the moderate hydrophobic surface of shale, with the water contact angle equal to 50°, most probably occurred by the van der Waals interactions between hydrophobic parts of shale surface and reagent. Adsorption of surfactants is governed by the structure of surfactant molecules (e.g., type of polar head, structure and length of hydrocarbon chain) but also the characteristics of the shale surface i.e. charge, hydrophobicity and presence of functional groups, which may interact with surfactants molecules [7,19]. Shale is polymetallic and heterogeneous substance with many different functional groups and pore structures on the surface (Fig. 1). Mineralogy, which is very complex [17,28], as well as surface roughness, porosity and structure (Fig. 1.) control the adsorption kinetics and density of surfactants on the shale surface.

Figure 4 also shows that adsorption on the shale surface did not reach the plateau level even at very high concentration of both DDA and SDS. The experiments were conducted at the concentrations much lower than *cmc* values. The shape of adsorption isotherms is typical for sparingly soluble salt-type minerals in aqueous solution of ionic surfactants [29]. The adsorption isotherms show two regions based on the surfactant concentration i.e. *i*) at low concentration the surfactant adsorbs on the shale surface by chemisorption, and *ii*) the increase in the slope suggests the physical formation of precipitated surfactant-mineral ions salts.



Figure 4. Adsorption isotherms of SDS and DDA on the shale surface at natural pH

Adsorption of DDA on the negatively shale surface occurs by bonding between nitrogen from non-ionic form of RNH2 with divalent ions or hydrogen bonds between hydrogen in –NH2 groups and surface oxygen. Additionally, the cationic forms of RNH3+ can adsorb on anionic forms of surface groups (e.g. HCO3-, CO32-) by electrostatic attraction and hydrogen bonding. The anionic groups released by a mineral surface can react with cationic forms of amine (RNH3+), and then precipitate and adsorb on the surface by physical interactions [30].

In the case of SDS, the adsorption mechanism of surfactant molecules on the shale surface is also due to electrostatic interactions and hydrogen bonding. Electrostatic interactions occur at low concentration and pH, where the shale surface in positively charged (Fig. 2a). Adsorption is governed due to electrostatic attractions between negatively charged polar heads (i.e anionic forms, e.g. ROSO3-) and positively charged site of shale (e.g. Ca2+, CaHCO3+, CaOH+). At higher concentrations, the surfactant ions begin associating with each other and form surfactant aggregates or hemimicelles. At higher concentration of SDS, where shale is negatively charged (Fig. 2a), adsorption occurs due to hydrophobic bonding between the surfactant tail and the surface. Stronger adsorption and lower zeta potential values are due to a larger number of adsorbed surfactant molecules as well as precipitation of SDS. The adsorption of SDS on the negatively charged carbonaceous matter such as coal was also shown elsewhere [16,19,20,31].

# **Flotation studies**

The results of flotation tests of shale in water and in the presence of aqueous solutions of surfactants at natural pH are presented in Fig. 5, as flotation kinetics, and Fig. 6 as a relationship between (a) surfactant concentration, (b) zeta potential, read-off from Fig. 2, and ultimate recovery (after 40 min). As seen from Figs. 5 and 6, when shale was floated in pure water its recovery was very low and ca. 10% was floated after 40 min. It means that investigated shale particles did not float at natural pH of water and absence of surfactants. The relatively low recovery of shale was due to its entrainment. The mechanism of mechanical flotation (entrainment) of different substances was described elsewhere [32].

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| (a) | (b) |

Figure 5. Flotation recovery of shale in the presence of (a) anionic (SDS) and (b) cationic (DDA) surfactants at pH=6.5 as a function of time

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| (a) | (b) |

Figure 6. Dependencies of recovery on (a) concentration and (b) zeta potential of metal-bearing shale in the presence of anionic (SDS), cationic (DDA) surfactants at pH=6.5

The results clearly show that shale started to float in the presence of ionic (DDA, SDS) surfactants. The flotation performance was affected by both the surfactant concentration and zeta potential of shale. As seen from Fig. 6, the flotation recovery of shale continuously increased with concentration for all types of flotation surfactants. Increase in the recovery was also accomplished by the change in the zeta potential. The high recovery of shale was obtained when the magnitude of changes in the zeta potential was high, that is more negative for anionic (SDS) and more positive for cationic (DDA) surfactants (Fig. 6b).

# **Heterocoagulation mechanism**

The obtained results clearly show that there was no flotation of shale in pure water. In pure water both the shale (-14 mV) and bubble (-7 mV) surfaces were negatively charged and the double layer interactions were repulsive. A relatively low hydrophobicity of shale and strong repulsive interactions did not cause the rupture of the thin liquid film separating the bubble and shale surfaces, and thus heterocoagulation could not take place (Fig. 8).

At low concentration of cationic DDA (1 mg/dm3) the recovery of shale increased from ca. 10%, in water, to ca. 50%, while the zeta potential of shale did not change significantly, and adsorption only slightly increased (Fig. 7a). Although there was no charge reversal in the shale surface, the adsorption of amine cations at the negatively charged solid/liquid interface occurred and slightly enhanced the hydrophobicity of shale. The increase in flotation can be also explained by the preferential adsorption of amine molecules at the liquid/gas interface. During bubble attachment, the amine molecules are transferred to solid surface [24,33,34], and its presence makes the wetting film unstable. Wang and Miller [34] showed that adsorption of amine at the liquid/gas interface was ca. 100 times greater than at the silica interface. Before bubble attachment, the adsorption of amine at the solid surface was very low and molecules were randomly organized. DDA was transferred to the solid surface during thin liquid rupture and bubble attachment. After attachment, more ordered amine molecules were present at the solid surface, The explanation given above can also be referred to heterocoagulation of bubbles and shale, which is polymetallic and heterogeneous substance with many different functional groups (hydrophilic e.g. silicates, carbonates, and hydrophobic e.g. mineral and organic matter) and pore structures on the surface.

The increase in the concentration of cationic surfactant caused that the adsorption coverage at both bubble [22] and shale surfaces increased (Fig. 7a). Higher adsorption on the bubble surface decreased its impact velocity, as a result of higher degree of bubble immobilization [35]. It also caused the charge reversal of bubble and shale from negative to positive and increased the values of positive zeta potential. The changes in the electrostatic interactions between the bubble and shale surfaces caused that the wetting film became unstable and ruptured, and thus heterocoagulation took place (Fig. 8). The hydrophobicity of shale also increased with the DDA concentration, from 50° in water to 89° at the equilibrium concentration of 65 ppm (Fig. 7a). It means that DDA exhibited both frothing and collecting properties toward shale particles.



(a)



(b)

Figure 7. Correlation diagram of recovery, adsorption and zeta potential for metal-bearing shale as a function of concentration of (a) DDA and (b) SDS

At very low concentrations of anionic surfactant (SDS, < 1 mg/dm3) heterocoagulation did not take place since adsorption was very low and the values of zeta potential of shale did not change (Fig. 7b), and thus electrostatic repulsions prevented rupture the thin liquid film separating bubble and shale. At the SDS concentration of 10 mg/dm3 the recovery of shale increased to ca. 75%, although the adsorption coverage was very low and the zeta potential of shale changed only slightly. At higher concentration of SDS the stronger adsorption at the solid surface and lower zeta potential values were due to a larger number of adsorbed surfactant molecules as well as precipitation of SDS. The adsorption was governed by formation of hemimicelles [14] as well as the hydrophobic interactions between surfactant molecules and hydrophobic spots on the shale surface*.* Although both the shale particles and bubbles exhibited similar charge characteristics, rapid flotation occurred (Fig. 5b).

For hydrophilic or slightly hydrophobic surfaces, the DLVO forces mainly govern the stability of wetting film. Electrostatic interactions decrease with the surfactant concentration and in the case of hydrophobic surfaces, these interactions do not affect the kinetics of film rupture, and thus flotation. In the case of hydrophobic surfaces, the wetting film ruptures although all DLVO forces remain repulsive [36]. It is due to *i*) hydrophobic forces, and *ii*) nucleation mechanism caused by nanobubbles adhering at the hydrophobic surface [12,35,36,37]. Gases dissolved in water attach to the solid surface as nanobubbles and these bubbles facilitate the attachment of particles to larger bubbles during heterocoagulation [11]. The existence of nanobubbles in the contact region controls the stability and rupture of water films [2]. The attractive van der Waals force and concave surface of nanobubbles can destabilize the foam film between two gases [38], and the hydrophobic surface becomes dewetted. Recently, Zawala et al. [35] showed that for quartz in the presence of cationic surfactant (CTABr) the nucleation process started at the contact angle greater than 37°. The nucleation mechanism takes place on either hydrophobic surfaces or hydrophilic with hydrophobic spots on the surface, since the mechanism is influenced by the physical (e.g. roughness, porosity) and chemical (e.g. surfactant distribution) heterogeneity of the surface [2,36]. The rupture process is faster for more hydrophobic surfaces [36]. The shale surface is rough and heterogeneous with both hydrophilic (e.g. silicates, carbonates) and hydrophobic (mineral and organic matter) spots, as well as most probably with the heterogeneous adsorption layer of surfactants, therefore we assume that heterocoagulation of bubbles and shale particles in the presence of both cationic and ionic surfactants is governed by both electrostatic interactions and nucleation (Fig. 8).

Migration of gases dissolved in water influences the behaviour of wetting film and rupture phenomena [39]. Its influence can decrease with the surfactant concentration [38], and therefore overdosing of surfactant increases the time of three-phase contact formation, and thus decelerates the flotation kinetics [40, 41]. The decrease in the hydrophobicity (i.e. contact angle, *θ*) and floatability of solid particles (Fig. 7b) in the presence of SDS can be also explained as a results of reduced surface tension of liquid *γ*. It is also attributed to formation of bilayer adsorption of surfactant molecules, with some hydrophilic groups oriented toward the aqueous phase.



Figure. 8. Schematic illustration of shale-bubble heterocoagulation (not to scale)

# **Conclusions**

Adsorption of surfactants is one of the important feature governing the heterocoagulation process. The results showed that measurements of zeta potential provided a straight-forward way of ascertaining the adsorption mechanism at the shale surface for ionic (SDS, DDA) surfactants. Heterocoagulation of bubbles and shale particles in the presence of both cationic and ionic surfactants was governed by both electrostatic interactions and nucleation. The nucleation mechanism takes place on either hydrophobic surfaces or hydrophilic with hydrophobic spots on the surface, since the mechanism is influenced by the physical (e.g. roughness, porosity) and chemical (e.g. surfactant distribution) heterogeneity of the surface. The shale surface is rough and heterogeneous with both hydrophilic (e.g. silicates, carbonates) and hydrophobic (mineral and organic matter) spots, as well as most probably with the heterogeneous adsorption layer of surfactants.

**Acknowledgments**

The work was financed by a statutory subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wroclaw University of Science and Technology.

**References**

[1] Mitchell T.K., Nguyen A.V., Evans G.M., 2005. *Heterocoagulation of chalcopyrite and pyrite minerals in flotation separation*. Adv. Colloid Interface Sci. 114-115, 227-237.

[2] Schubert H., 2005. *Nanobubbles, hydrophobic effect, heterocoagulation and hydrodynamics in flotation*. Int. J. Miner. Process. 78, 11-21.

[3] Drzymala J., 2007. *Mineral processing. Foundations of the theory and practice in minerallurgy*. Ofic. Wyd. PWr., Wroclaw, ISSN 978-83-7493-362-9.

[4] Derjagin B.V., 1989. *Theory of stability of colloids and thin films.* Springer US

[5] Pyke B., Fornasiero D., Ralston J., 2003. *Bubble particle heterocoagulation under turbulent conditions*. J. Colloid Interface Sci. 265, 141-151.

[6] Hu, Y., Liu, L., Min, F., Zhang, M., Song, S., 2013. *Hydrophobic agglomeration of colloidal kaolinite in aqueous suspensions with dodecylamine*. Colloids Surf. A, 434, 281-286.

[7] Dobiáš B., 1993. *Coagulation and Flocculation: Theory and Applications*. New York: M. Dekker.

[8] Somasundaran P., Fuerstenau D.W., 1966. *Mechanism of alkyl sulfonate adsorption at alumina-water interface*. J. Phys. Chem. 70, 90-96.

[9] Somasundaran P., Zhang L., 2006. *Adsorption of surfactants on minerals for wettability control in improved oil recovery processes*. J. Pet. Sci. Technol. 52, 198-212.

[10] Fuerstenau D.W., Healy T.W., Somasundaran P., 1964. *The role of the hydrocarbon chain of alkyl collectors in flotation*. Trans. AIME 229, 321-323.

[11] Dai Z., Fornasiero D., Ralston J., 1998. *Influence of dissolved gas on bubble-particle heterocoagulation*. J. Chem. Soc. Faraday Trans. 94(14), 1983-1987.

[12] Mishchuk N.A., Koopal L.K., Dukhin S.S., 2002. *Heterocoagulation of hydrophobic particle and bubble during microflotation*. Colloid Journal 64(4), 457-464.

[13] Mishchuk N., Ralston J., Fornasiero D., 2006. *Influence of very small bubbles on particle/bubble heterocoagulation*. J. Colloid Interface Sci. 301, 168-175.

[14] Fuerstenau D.W., Pradip, 2005. *Zeta potential in the flotation of oxide and silicate minerals.* Adv. Colloid Interface Sci. 114-115, 9-26.

[15] Liang L., Wang L., Nguyen A.V., Xie G., 2017. *Heterocoagulation of alumina and quartz studied by zeta potential distribution and particle size distribution measurements.* Powder Technol. 309, 1-12.

[16] Çelik M.S., Ozdemir O., 2018. *Heterocoagulation of hydrophobized particulates by ionic surfactants*. Physicochem. Probl. Miner. Process. 54(2), 124-130.

[17] Rahfeld A., Kleeberg R., Möckel R., Gutzmer J., 2018. *Quantitative mineralogical analysis of European Kupferschiefer ore.* Miner. Eng. 115, 21-32.

[18] Polowczyk I., Kruszelnicki M., Kowalczuk P.B., 2018. *Oil agglomeration of metal-bearing shale in the presence of mixed cationic-anionic surfactants*. Physicochem. Probl. Miner. Process. doi: 10.5277/ppmp1885.

[19] Singh B.P., 1999. *The role of surfactant adsorption in the improved dewatering of fine coal*. Fuel 78, 501-506.

[20] Marsalek R., Taraba B., 2008. *Adsorption of the SDS on the coal*. Prog. Colloid Polym. Sci. 135, 163-168.

[21] Dibbs H.P., Sirois L.L., Bredin R., 1974. *Some electrical properties of bubbles and their role in the flotation of quartz.* Can. Metall. Q. 13(2), 395-404.

[22] Yoon, R-H., Yordan J.L., 1986. *Zeta-potential measurements of microbubbles generated using various surfactants*. J. Colloid Interface Sci. 113(2), 430-438.

[23] Laskowski J., Yordan J.L., Yoon R.H., 1989. *Electrokinetic potential of microbubbles generated in aqueous solutions of weak electrolyte type surfactants*. Langmuir 5, 373-376.

[24] Burdukova E., Laskowski J.S., 2009. *Effect of insoluble amine on bubble surfaces on particle-bubble attachment in potash flotation*. Can. J. Chem. Eng. 87, 441-447.

[25] Kowalczuk P.B., Zawala J., Drzymala J., Malysa K., 2016, *Influence of hexylamine on kinetics of flotation and bubble attachment to the quartz surface*. Sep. Sci. Techn., 51(15-16), 2681–2690.

[26] Jia W., Ren S., Hu B., 2013. *Effect of water chemistry on zeta potential of air bubbles*. Int. J. Electrochem. Sci. 8, 5828-5837.

[27] Bueno-Tokunaga A., Pérez-Garibay R., Martínez–Carillo D., 2015. *Zeta potential of air bubbles conditioned with typical froth flotation reagents*. Int. J. Miner. Process. 140, 50–57.

[28] Piestrzyński A., Pieczonka J., 2012. *Low temperature ore minerals associations in the Kupferschiefer type deposit, Lubin-Sieroszowice Mining District SW Poland.* Mineral. Rev. 62, 59-66.

[29] Martínez-Luévanos A., Uribe-Salas A., Lopez-Valdivieso A., 1999. *Mechanism of adsorption of sodium dodecylsulfonate on celestite and calcite*. Miner. Eng. 12(8), 919-936.

[30] Gao Z., Sun W., Hu Y., 2015. *New insights into the dodecylamine adsorption on scheelite and calcite: An adsorption model*. Miner. Eng. 79, 54-61.

[31] Crawford R.J., Mainwaring D.E., 2001. *The influence of surfactant adsorption on the surface characterisation of Australian coals*. Fuel 80, 313-320.

 [32] Wang L., Peng Y., Runge K., Bradshaw D., 2015. *A review of entrainment: mechanism, contributing factors and modelling in flotation*. Miner. Eng. 70, 70–91.

[33] Laskowski J.S., 2013. *From amine molecules adsorption to amine precipitation transfer by bubbles.* Miner. Eng. 45, 170-179.

[34] Wang X., Miller J.D., 2018. *Dodecyl amine adsorption at different interfaces during bubble attachment/detachment at a silica surface*. Physicochem. Probl. Miner. Process. 54(2), 81-88.

[35] Zawala J., Karaguzel C., Wiertel A., Sahbaz O., Malysa K., 2017. *Kinetics of the bubble attachment and quartz flotation in mixed solutions of cationic and non-ionic surface-active substances*. Colloids and Surfaces A 533, 118-126.

[36] Stockelhuber K.W., 2003. *Stability and rupture of aqueous wetting films*. Eur. Phys. J. E 12, 431-435.

[37] Derjagin B.V., Gutop Y.V., 1962. *Theory of breakdown rupture of free films*. Kolloidn. Zh. 24, 431-437.

[38] Karakashev S.I., Nguyen A.V., 2009. *Do liquid films rupture due to the so-called hydrophobic force or migration of dissolved gases?* Langmuir 25, 3363-3368.

[39] Nguyen P.T., Nguyen A.V., 2009. *Drainage, rupture, and lifetime of deionized water films: effect of dissolved gases?* Langmuir 26(5), 3356-3363.

[40] Kowalczuk P.B., Zawala J., 2016. *A relationship between time of three-phase contact formation and flotation kinetics of naturally hydrophobic solids*. Colloids and Surfaces A: Physicochem. Eng. Aspects 506, 371–377.

[41] Szczerkowska S., Wiertel-Pochopien A., Zawala J., Larsen E., Kowalczuk P.B., 2018. *Kinetics of froth flotation of naturally hydrophobic solids with different shapes*. Miner. Eng. 121, 90–99.