Oil agglomeration of metal-bearing shale in the presence of mixed cationic-anionic surfactants

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Abstract: This paper reports oil agglomeration of fine metal-bearing shale particles in the presence of cationic (dodecylamine hydrochloride) and anionic (sodium dodecyl sulfate) surfactants and their mixture. The experimental results demonstrated that there was a strong relationship between zeta potential, hydrophobic coagulation, oil agglomeration and particle hydrophobicity in the presence of cationic surfactant, whereas shale neither coagulated nor agglomerated in the presence of anionic surfactant. Addition of either anionic or cationic surfactant in emulsification of a bridging oil increased the size of agglomerates and reduced the concentration of surfactant used in the suspension. The results pointed to synergism between cationic and anionic surfactants in oil agglomeration. Based on the results obtained from this study, the mechanism of oil agglomeration of shale in the presence of ionic surfactants and their mixture was elucidated.

Keywords: kerosene, adsorption, hydrophobic coagulation, surfactants, synergism, zeta potential

1. Introduction

Oil agglomeration is aggregation of fine hydrophobic particulates in the presence of a bridging liquid i.e. oil, which is dispersed in the aqueous suspension of solid particles. Oil droplets wet and bridge hydrophobic particles forming aggregates. Size enlargement of formed aggregates refers to oil agglomeration, which is a complex process, and results from interparticle collision, adhesion of particles coated by the bridging liquid and formation of stable aggregates (Laskowski, 2001; Drzymala, 2007). The size and shape of solid-oil aggregates depend on the amount and type of oil, while the agglomerate strength is mainly governed by particle hydrophobicity, also called aquaoleophilicity expressed by the contact angle in a particle-oil-water system, and the oil-water interfacial tension (Drzymala et al., 1986). Oil agglomeration of particulates suspended in water is only possible if their surface is partially wetted by a bridging liquid (oil). For either hydrophilic or weakly hydrophobic substances it is possible if their surface is previously modified by, for instance, surfactant adsorption (hydrophobic coagulation) (Huang and Berg, 2003; Duzyol and Ozkan, 2010; Özer et al., 2017; Çelik and Ozdemir, 2018). Surfactants used to modify the solid surfaces also adsorb at the oil/water interface by lowering the interfacial tension, which can lead to weakening of binding liquid bridges and agglomerate breaking during agitation, or even might prevent agglomeration (Laskowski, 1992; Cebeci and Sönmez, 2004). A surfactant mixture cannot only create mixed films at the interfaces but also insoluble complexes can be formed (Kume et al., 2008).

Oil agglomeration has been widely applied for either aggregation of fine particles or selective separation of minerals and substances. It has been commonly used for carbonaceous materials such as coal (Mehrotra et al., 1983; Drzymala et al., 1986; Özer et al., 2017), however the number of studies on hydrophobic coagulation as well as oil agglomeration of carbonaceous metal-bearing shale using a surfactant-in-oil emulsion is limited. Hence, the objective of the present study was to investigate the

mechanism of oil agglomeration of metal-bearing shale, from the Kupferschiefer stratiform copper deposit, in the presence of cationic and anionic surfactants, and their mixture through electrostatic, adsorption and wettability tests.

2. Experimental

2.1 Materials

Experiments were carried out using metal-bearing shale particles originated from the Kupferschiefer stratiform copper deposit (Fore-Sudetic Monocline copper ore). The shale samples were collected from the Polkowice-Sieroszowice mine located in SW Poland. The collected rock samples were crushed and sieved in order to obtain the narrow size fraction (-45 μm) used in the experiments. The size distribution analysis showed that d_{50}, d_{10}, and d_{90} were 16.5 μm, 3.2 μm, and 45.5 μm, respectively. The mineralogical analysis of the sample indicated that shale consisted of quartz (14%), sheet silicates (42%), carbonate minerals (33%), and copper minerals (9%) (Rahfeld et al., 2018). The average contents of copper, total organic carbon, Ca, Fe, Zn, Si, and S were 6.0, 8.0, 11.8, 1.3, 0.3, 10.6, and 1.7%, respectively. Additionally, the SEM analysis of the sample indicated that shale was a polymetallic, polymineral and heterogeneous substance with many different functional groups and pore structures on the surface (Fig. 1), with the BET surface area equal to 4.40 m^2/g.
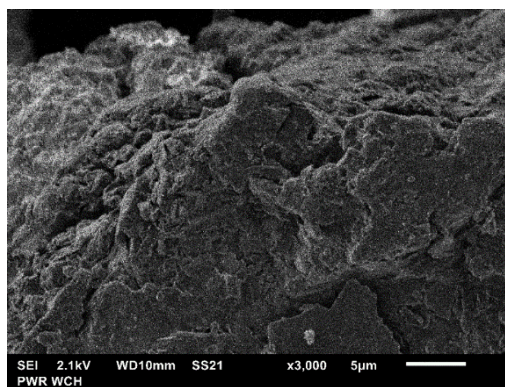

Fig. 1. SEM of shale originated from Kupferschiefer

A cationic surfactant dodecylamine hydrochloride (DDA, $CH_3(CH_2)_{11}NH_2 \cdot HCl$, MW=221.81 g/mol) and an anionic surfactant sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}OSO_3Na$, MW=223.38 g/mol), purchased from Alfa Aesar, were used for the experiments. A dimidium bromide-disulphine blue indicator and chloroform ($CHCl_3$) purchased from POCH were used for the surfactant adsorption tests. Kerosene was used in agglomeration tests as a bridging oil. 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 preparation of surfactant solutions and cleaning.

2.2 Zeta potential measurement

Zeta potential of kerosene droplets and shale particles in either water or aqueous solution of ionic surfactants was measured at 25 °C using a zeta potential analyser (Malvern Zetasizer 2000). The suspension containing 0.010 g of shale particles in 25 cm^3 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. For the measurement of zeta potential of kerosene, the small amount of oil was mixed with 10 cm^3 of either water or aqueous solutions of ionic surfactants. The value of zeta potential was determined as an average of five successive measurements.

2.3 Adsorption test

Adsorption isotherms were determined using 0.8 g of shale particles and 40 cm^3 of aqueous solution of ionic surfactant at given concentration. The suspension was conditioned for 24 h at 25 °C, and then

filtered. The residues were dried and used in contact angle measurements, while the solution was titrated using a two-phase (water-chloroform) method with a dimidium bromide-disulphine blue indicator and surfactant solution of opposite charge (SDS for DDA isotherm and DDA for SDS isotherm). The experiments were conducted at natural pH of aqueous suspension of shale (ca. 8.5).

2.4 Stability test

Stability measurements were carried out in a glass vial, with a height of 7 cm, using 0.4 g of shale particles and 20 cm^3 of either water or aqueous solution of ionic surfactants at certain concentrations. A mixture was shaken vigorously, and then placed into a thermostated measurement chamber of Turbiscan LabExpert turbidimeter in order to determine the suspension stability expressed by the so-called Turbiscan Stability Index (*TSI*). *TSI* is a statistical parameter calculated from the stability kinetics. The values of *TSI* change in the range from 0 and 100. The higher values of *TSI*, the greater changes occur in the system, and therefore the more unstable the system is (Wiśniewska et al., 2013). Therefore, *TSI* is also called an instability index, and represents process instability. More information about *TSI* can be found elsewhere (Wiśniewska et al., 2013; Polowczyk et al., 2015). The changes in the suspension stability were monitored for 15 min every 30 sec. Stability measurements were conducted at 25 °C.

2.5 Contact angle measurements

A 0.2 g of dry sample of shale before and after surfactant 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. Advancing contact angles were measured by a sessile drop technique using a PGX+ goniometer. A liquid drop of pure water was placed onto the pastille surface through a capillary tube and a micro-pump. Values of contact angles were determined from profiles of sessile drops. Each experiment was repeated 5 times, and average values were reported. The experiments were conducted at room temperature (25 °C).

2.6 Agglomeration tests

Agglomeration experiments were carried out using a glass stirred tank (inner diameter 6 cm and height 15 cm) with a mechanical overhead stirrer equipped with a 3-blade turbine. In each experiment, 2 g of shale particles was mixed for 5 min with 100 cm^3 of either pure water or aqueous solution of surfactants at certain concentration. Then, the mixture was left for 24 h in order to adsorb the surfactant on the shale surface. In oil agglomeration kerosene was used as a nonpolar bridging oil. Kerosene was added into the shale suspension in the form of emulsion. An emulsion of kerosene (0.8 cm^3) in either water or aqueous solution of ionic surfactants (25 cm^3 of 1000 mg/dm^3 SDS or DDA) was prepared using an ultrasonic homogenizer (Sonopuls HD 2070). The previously prepared and stored suspension of shale was mixed again, the freshly prepared emulsion was poured into the suspension, and the resulting mixture was agitated over a certain agitation period. Each agglomeration test was performed under predetermined optimum conditions i.e. time 10 min, mixing speed 1000 rpm, natural pH of solution (ca. 8.5), room temperature 25 °C. The slurries after the tests were gently separated, dried and sieved in order to determine the size of agglomerates. An efficiency of agglomeration process was expressed as the mean size of agglomerates d_{50}.

3. Results and discussion

### 3.1 Effect of cationic and anionic surfactant

Fig. 2 shows the effect of cationic (a) and anionic (b) surfactant concentration on hydrophobic coagulation and oil agglomeration of shale particles. The figures represent the variations of instability, expressed as Turbiscan Stability Index (*TSI*), oil agglomeration, expressed as the size of agglomerates d_{50}, zeta potential values, wettability, expressed as the advancing contact angle, and adsorption, with the surfactant concentration at natural pH of suspension i.e. 8.5.

As seen from Fig. 2a, the stability of suspension decreases, and thus values of *TSI* increase, upon the addition of cationic (DDA) surfactant. In the case of anionic (SDS) surfactant, instability of suspension

either remains constant or slightly decreases (Fig. 2b). The changes in the system stability are due to changes in wetting properties of shale particles with the surfactant concentration. The advancing contact angle of shale, measured by the sessile drop technique, in the presence of DDA increases from 50° in pure water to 90° at 500 mg/dm³ (Fig. 2a), and slightly decreases to 43° at relatively high concentration of SDS (Fig. 2b). In the case of DDA, it indicates on hydrophobic coagulation (shear flocculation) of shale particles. An adsorption level of cationic DDA is much higher than anionic SDS. It is confirmed by zeta potential values, where the magnitude of changes is much higher for DDA. Shale is negatively charged in water (pH$_{iep}$=3) and low concentrations of DDA and positively charged at high concentrations. The reversal of charge from negative to positive occurs at the DDA concentration of 22 mg/dm³ at pH 8.5. For the anionic SDS the shale particles exhibit negative zeta potential values in the whole range of concentration, and the magnitude of changes in the negative values increases with the surfactant concentration.
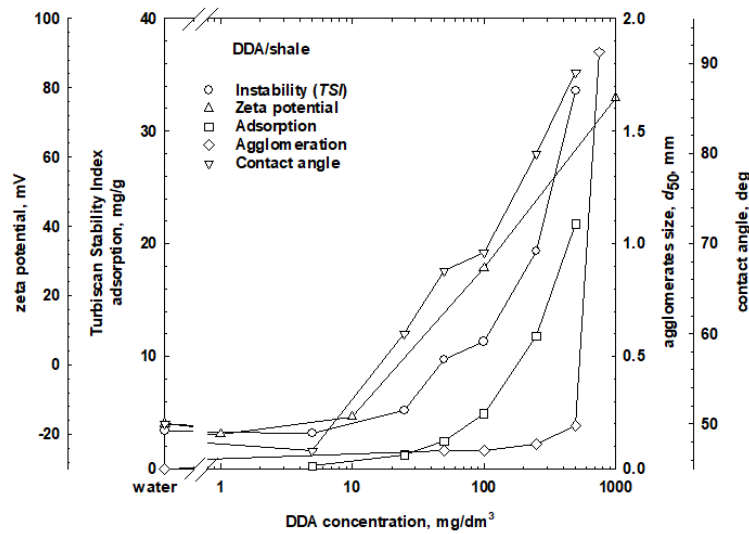
(a)
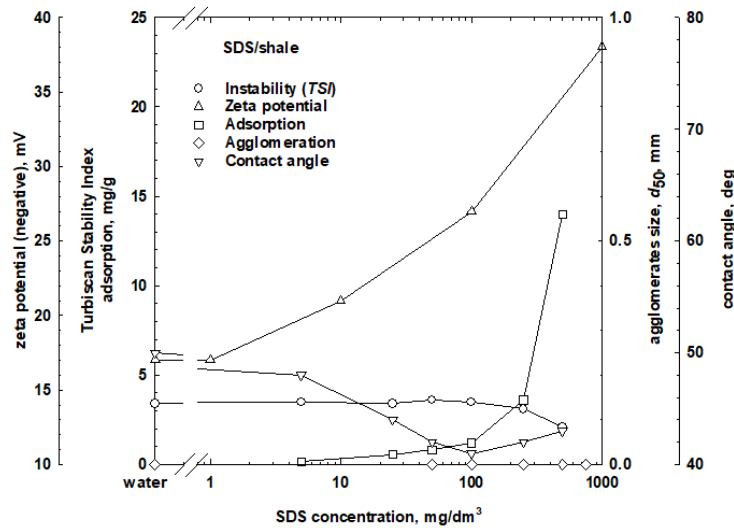
(b)

Fig. 2. Zeta potential, instability, adsorption, agglomeration and contact angle for metal-bearing shale as function of (a) DDA and (b) SDS concentration

Adsorption of ionic surfactants on the negatively charged surface of shale is a result of several interactions at the solid-solution interface, and is mainly governed by the structure of surfactants molecules i.e. type of polar head, structure and length of hydrocarbon chain, but also the surface properties of shale. Shale is a polymetallic substance and exhibits chemical heterogeneity due to the

presence of many different functional groups and pore structures on the surface. Its complex mineralogy (Piestrzyński and Pieczonka, 2012; Rahfeld et al., 2018), structure, roughness, surface charge, and heterogeneity have the strong impact on the adsorption density of ionic surfactants, and thus hydrophobic coagulation. The results clearly indicate that adsorption of DDA and SDS on the shale surface takes place due to electrostatic interactions and hydrogen bonding. In the amine-shale system, adsorption occurs by hydrogen bonds between nitrogen from non-ionic form RNH_2 with divalent ions. Additionally, cationic forms of amine (RNH_3^+) react with anionic groups (e.g. HCO_3^-, CO_3^{2-}) released by a mineral surface, and then precipitate and adsorb on the surface by physical interactions (Gao et al., 2015). In the case of anionic surfactant, adsorption is governed by electrostatic interactions between anionic (e.g. $ROSO_3^-$) groups of SDS and cationic (e.g. Ca^{2+}, $CaHCO_3^-$, $CaOH^+$) groups of shale.

Fig. 2a also shows that there is a correlation between zeta potential, adsorption, instability (*TSI*), wettability and degree of agglomeration for the shale/cationic surfactant system. It indicates on the strong correlation between hydrophobic coagulation (shear flocculation), oil agglomeration, and particle hydrophobicity in the presence of DDA. Agglomeration is affected by the surfactant concentration, zeta potential of both shale particles and kerosene droplets as well as the hydrophobicity of solid particles. In pure water and low concentrations of cationic surfactant the negatively charged shale particles do not agglomerate with negatively charged kerosene droplets (zeta potential in water - 47 mV, Fig. 3). The degree of agglomeration increases with the DDA concentration. In the presence of DDA shale is positively charged, while the kerosene droplets in the oil/water emulsion are negatively charged. It indicates on the electrostatic interactions, which leads to rupture the thin liquid film between hydrophobic shale (CA=90°) and oil, and thus formation of stable agglomerates. The average agglomerates size in the presence of DDA is 1.9 mm at the concentration of 750 mg/dm³. A relatively high performance of agglomeration is possible when the magnitude of changes in the zeta potential, adsorption and contact angle is high. The more hydrophobic the shale particles are, the more powerful hydrophobic coagulation is, and the higher degree of oil agglomeration is.
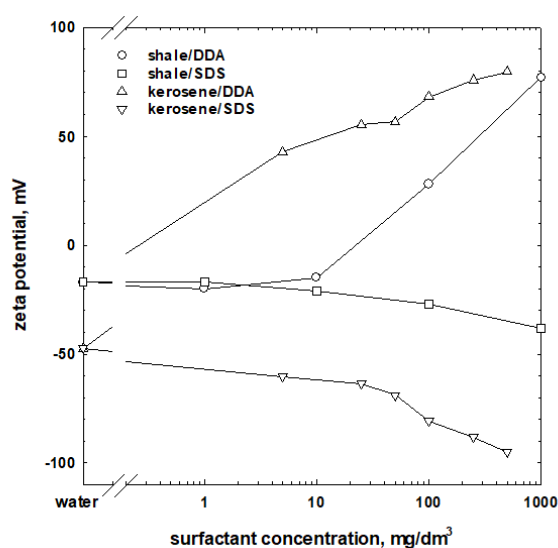

Fig. 3. Dependencies of zeta potential values of kerosene droplets and shale particles
on ionic surfactant concentration

In the case of SDS, no correlation between hydrophobic coagulation, oil agglomeration and hydrophobicity, in the whole range of surfactant concentration, is observed (Fig. 2b). At high concentrations of SDS, the system instability slightly decreases but the values of negative zeta potential of shale increase and the contact angle decreases. A lack of aggregation in the presence of SDS is due to *i*) relatively low adsorption of SDS, *ii*) low degree of particle hydrophobicity (CA=43°), and *iii*) electrostatic repulsion between negatively charged shale particles and kerosene (Fig. 3) (the thin liquid film separating the oil and shale surfaces is stable). In oil agglomeration, the solid particles should have a certain degree of wettability to achieve the successful agglomeration (Drzymala, 2007; Duzyol and Ozkan, 2010).

3.2 Effect of mixed cationic/anionic surfactants

The effect of emulsification of bridging oil in either water or aqueous solution of ionic surfactants on agglomeration of shale particles is shown in Fig. 4. It shows the influence of surfactant concentration, expressed in mg/dm^3, on the mean agglomerates size as well as pictures of resulted agglomerates. As previously described, oil agglomeration of shale is possible with DDA and kerosene as the bridging liquid, while there is no aggregation of shale in the presence of SDS in the suspension and oil/water emulsion. The effect of emulsification of bridging oil before addition to the suspension can be explained by the zeta potential data presented in Fig. 3. As seen from Fig. 3, the zeta potential of kerosene in pure water is negative (-47 mV) and changes with addition of anionic and cationic surfactants. The anionic surfactant increases the negative values of zeta potential of kerosene droplets, while cationic DDA changes the zeta potential to positive. The charge reversal from negative to positive occurs at the DDA concentration of c.a. 0.5 mg/dm^3. Surfactants are located at the oil/water interface in a such way that their hydrocarbon tails are directed towards the oil droplet, while the hydrophilic portions are facing the aqueous solution. The greater the ionic surfactant concentration, the greater the zeta potential of oil droplets. The values of zeta potential at the concentration of 500 mg/dm^3 are -95 and +80 mV for SDS and DDA, respectively.
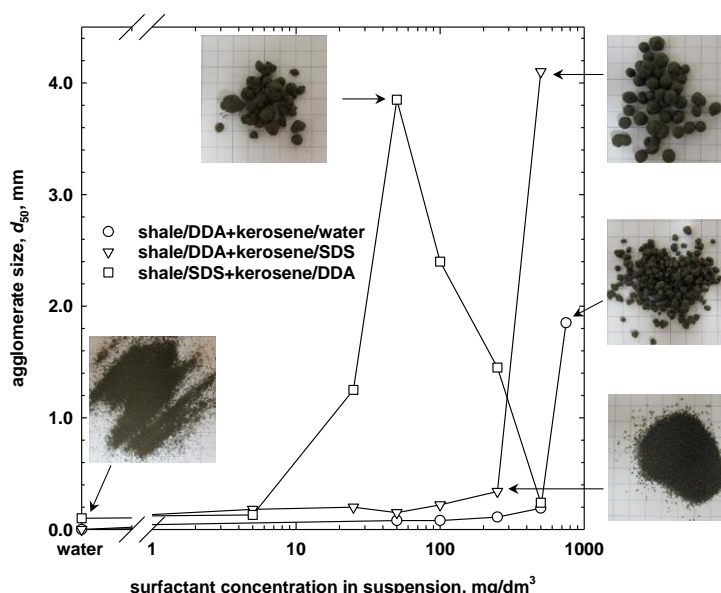

Fig. 4. Size of agglomerates as a function of ionic surfactant concentration in shale/liquid suspension (constant concentration of DDA or SDS in oil emulsion equal to 1000 mg/dm^3)

If the emulsion is added to the suspension of solid particles, introduced oil droplets collide with the particles, and then adhere to them, when *i)* the solid surface is hydrophobic enough, and *ii)* the surface charge of droplets is opposite to the particles charge (Polowczyk et al., 2014; 2015). However, the use of surfactants in oil agglomeration entails the risk of excessive lowering of the interfacial tension below the critical value, which results in weakening the oil bridges and, as a consequence, a lack of formation of stable agglomerates (Cebeci and Sönmez, 2004; Ozkan et al., 2005). Particle collision becomes ineffective and oil droplets are strongly emulsified in water (Laskowski, 1992).

Fig. 4 shows the agglomerates size after the process when the binder liquid is introduced into either shale/DDA or shale/SDS suspension in the form of an emulsion with the surfactant of an opposite charge than the one added to the suspension i.e. a mixed cationic-anionic surfactant system. Mixtures of surfactants, such as anionic-cationic, anionic-non-ionic, cationic-non-ionic, amphoteric-non-ionic, possess much higher surface activities than their individual components (Yu and Zhao, 1989; Xiao et al., 2005; Kume et al., 2008). Such synergism increases with the degree of charge difference between surfactants, meaning that synergism between cationic and anionic is higher than between anionic/anionic or nonionic/nonionic compounds (Rosen and Hua, 1982).

Fig. 4 shows that addition of negatively charged kerosene droplets to the suspension of positively charged shale particles (shale/DDA+kerosene/SDS) resulted in larger and more spherical

agglomerates in comparison to agglomeration in the shale/DDA+kerosene/water system. At the concentration of DDA equal to 500 mg/dm^3, the agglomerates size in the mixed cationic-anionic surfactants system is 4.1 mm, while only 0.19 mm, for individual surfactant. The concentration of SDS in the emulsion remains at the same level in all samples. Better agglomeration performance in the mixed surfactant system is due to strong electrostatic interactions between shale particles and kerosene droplets enhancing their adhesion. It points to synergism between cationic and anionic surfactants during oil agglomeration. Moreover, the presence of surfactant during emulsification of bridging oil results in smaller diameter of oil droplets and formation of larger agglomerates (Bastrzyk et al., 2011).

The results show that there is no aggregation of shale in the presence of SDS and oil/water emulsion. Shale started to agglomerate when positively charged kerosene droplets were added to the suspension. As seen from Fig. 4, the average size of agglomerates in the mixed anionic-cationic system, when SDS is used in the suspension and DDA in emulsion (at the same dosage in all samples), increases with the SDS concentration, reaching the maximum size of 3.9 mm at 50 mg/dm^3, and then decreases. The increase in the average agglomerates size in the presence of positively charged oil droplets can be explained by adsorption of amine molecules at the shale surface due to electrostatic interactions. According to Laskowski (2013) and Wang and Miller (2018) in froth flotation amine molecules are transferred by bubbles to the solid surface. Since surfactant at both liquid/gas and oil/liquid interfaces are located in the same way, i.e. hydrocarbon tails are directed towards the oil droplet/air bubble, while the hydrophilic portions are facing the aqueous solution, by analogy it can be stated that also in oil agglomeration amine is transferred to the solid surface, and its presence increases the surface hydrophobicity and makes the wetting film between oil and solid surface unstable. Decrease in the agglomerates size with increasing the concentration of SDS in the suspension is probably due to lower adsorption of amine molecules on the shale surface due to competitive adsorption between cationic and anionic surfactants. It decreases the surface hydrophobicity and interfacial tension. Bastrzyk et al. (2011) showed that due to too low interfacial tension the strength of the liquid bridges between particles was too small, and thus the agglomerates were unstable. Moreover, the mixed aqueous solution of cationic-anionic surfactants is often unstable and different structures, such as vesicles, rod-like micelles, coacervates, and precipitates, can be formed (Kume et al., 2008). Precipitation renders the surface ineffectivity in the solution, and if occurs, decreases the performance of oil agglomeration, heterocoagulation, flocculation, flotation etc.

The results clearly indicate that addition of ionic surfactant, of an opposite charge than the one added to the suspension, in emulsification of bridging oil increases the size of agglomerates and reduces the concentration of surfactant used in the particle suspension. The use of emulsion, instead of pure oil binder, reduces the amount of oil required to form agglomerates, shortens the agglomeration time, and thus reduces the overall costs of a process (van Netten et al., 2016).

4. Conclusions

The results showed that carbonaceous metal-bearing shale originated from the Kupferschiefer stratiform copper deposit can be effectively agglomerated in the presence of kerosene and mixed cationic-anionic surfactants. Oil agglomeration of fine shale particles was governed by both hydrophobicity and electrostatic interactions. The results clearly pointed to synergism between cationic and anionic surfactants in oil agglomeration of shale.

Acknowledgments

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