# Heterocoagulation of hydrophobized particulates by ionic surfactants

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**Abstract:** Hydrophobic particulates, i.e. bubbles, precipitates, and coal particles are shown to exhibit similar isoelectric point (iep) values in the presence of ionic surfactants. While coal in anionic surfactant solutions exhibits negative zeta potentials in the entire pH region, coal in cationic surfactant solutions undergoes a charge reversal in alkaline pH. Adsorption and zeta potential measurements together with previously published results indicate that ionic surfactants adsorb on coal through hydrophobic bonding driven by entropy. Physicochemical similarities in the adsorption mechanisms of ionic surfactants onto the bubbles, precipitates, and coal particles are proposed to be responsible for the observed iep values and also heterocoagulation phenomena.

*Keywords: heterocoagulation, coal, flotation, adsorption, ionic surfactants*

## 1. Introduction

Bubble/particle interactions in flotation systems are the key phenomenon in determining whether the solid particle will report to the froth phase. It has been shown in several publications that the charge of both air bubbles and mineral particles play a major role in the attachment process. One of the earlier findings states that when the particles carry minimum charge, they exhibit maximum flotation recoveries (Derjaguin and Dukhin, 1960). This assertion may be true only for a limited number of systems. Dibbs et al. (1974) indeed showed that bubbles produced in quartz/dodecyl amine hydrochloride (*DAH*) system gave the best flotation recoveries when quartz particles were charged opposite to that of the bubbles.

Usui and Sasaki (1978) showed that ionic surfactants assume the charge of the polar group of the surfactant. McShea and Callaghan (1983) showed that air bubbles exhibited negative charges in pure water and acquire different charges depending on the solution composition. Yoon and Yordan (1986) confirmed that the above finding is in general true except for the hydrolyzable surfactants, e.g. amine, where the bubble charge is significantly affected by the hydrolysis products. Bubbles generated with nonionic surfactants can be charged either positive or negative depending on the pH.

Laskowski and his coworkers (Castro et al., 1986; Laskowski et al., 1988) measured the charge of air bubbles and that of precipitates generated in solutions of primary alkyl amines and fatty acids under different conditions. They found that negatively charged colloidal species may appear above pH 11 for dodecyl amine hydrochloride (*DAH*) when its solubility was exceeded. Similarly, lauric acid precipitates exhibited an isoelectric point (iep) of 3.5, and only formed below approximately pH 7 (Vurdela et al., 1987). The presence of such a precipitate was suggested to significantly affect the zeta potential of mineral particles. Ulexite, a semi-soluble boron mineral, in the presence of various multivalent ions, i.e. $Ba^{2+}$, $Mg^{2+}$, $Ca^{2+}$, and $Al^{3+}$, was found to exhibit excellent floatability when particles, colloidal precipitates, and bubbles acquired a similar charge (Celik et al., 1998).

Flotation is a heterocoagulation process between hydrophobic particles and bubbles inclusive of the hydrodynamic conditions (Schulz and Stockelhuber, 1993; Schubert, 2005). The term heterocoagulation is usually used to describe the formation of colloidal particulates or coagulates, which consist of more than one type of particles such as composition and shape, size, surface potential

and charge. Heterocoagulation studies between different particulates have become an area of increasing scientific study largely due to the use of the atomic force microscope (*AFM*) (Mitchell et al., 2005). While interparticle forces are often sufficiently strong for particles smaller than 20 μm to form the stable bubble–particle aggregates, big particles can only be kept attached to the bubble by capillary forces at the three-phase contact. Heterocoagulation of particle-bubble interactions was also modeled under turbulent conditions (Pyke et al., 2003).

In the present paper, adsorption and electrokinetic behavior of a low-ash coal adsorbed by ionic surfactants, anionic and cationic, were investigated and correlated with the charge of the bubbles and precipitates reported by Laskowski and his coworkers (Castro et al., 1986; Vurdela et al., 1987; Laskowski et al., 1988).

## 2. Experimental

### 2.1 Materials

Buller seam coal from New Zealand containing 1.8% ash by weight on a dry basis was prepared in the same manner described elsewhere (Celik, 1989). Briefly, it involves size reduction in a roll crusher followed by dry screening over 150 μm sieve. The finer fraction (- 150 μm) was discarded to avoid possible contamination. Then, + 150 μm size fraction was micronized in a water-cooled coffee grinder, and this product was used for the zeta potential and adsorption measurements. The specific area of this sample by BET technique using krypton adsorbate was found to be 0.92 m$^2$/g.

The anionic and cationic surfactants, sodium dodecyl sulfate (*SDS*) and dodecyl amine hydrochloride (*DAH*) were supplied by Aldrich and Eastman Chemical companies, respectively. Both chemicals were specified to be of highest purity thus were used as received. All the solutions were prepared using double distilled and deionized water in the presence of $2 \cdot 10^{-3}$ mol/dm$^3$ NaCl.

### 2.2 Methods

The zeta potential of coal particles was measured by means of a Zeta Meter, according to the procedure described elsewhere (Celik, 1989). All the measurements were carried out at ambient temperature (23±1°C).

The equilibrium concentration of *SDS* was determined by a modified methylene blue method (Wang et al., 1979). The residual concentration of *DAH* was determined spectrophotometrically based on the formation of *DAH*-Metanil yellow complex (Takeda and Usui, 1987).

The adsorption experiments were performed in 20 cm$^3$ scintillation vials with Teflon-lined caps. Each vial contained 10 cm$^3$ of surfactant solution prepared in the presence of $2 \cdot 10^{-3}$ mol/dm$^3$ NaC1 and 200 mg coal sample (S/L: 0.02). The details of the experimental procedure can be found elsewhere (Celik and Yoon, 1991).

## 3. Results and discussion

The results of the zeta potential measurements for *SDS* are shown in Fig. 1. In the absence of surfactant, the coal exhibits an isoelectric point of approximately 5. The slope of the zeta potential of the iep is -$(\partial \zeta_E / \partial_{pH})$iep = 25.4 which is within the values reported in literature (Morganski and Rowell, 1988). However, in the presence of *SDS*, the zeta potentials become negative in the entire pH range. Increasing the surfactant concentration produces more negative potentials in the acidic pH but approaches to that in the absence of surfactant in the alkaline pH. Similar results were also reported with ethoxylated sulfonates and sodium dodecyl benzene sulfonate (Celik, 1989). The zeta potential measurements on micro bubbles generated with *SDS* also showed a trend similar to that found in Fig. 1 (Yoon and Yordan, 1986).

The dependence of pH on adsorption of *SDS* onto the coal sample is illustrated in Fig. 2. It is evident that the adsorption of *SDS* onto the coal gradually decreases above pH 8. Nonionic surfactants and ethylated sulfonates displayed a similar pH dependency as observed with ionic surfactants (Celik, 1989; Celik and Yoon, 1991). Although the drop observed with nonionics and ethoxylated sulfonates was ascribed to the hydrolysis of the nonionic portion of the surfactants, this evidence together with the above data on *SDS* reveals that the coal is gradually losing its hydrophobicity in the alkaline pH.
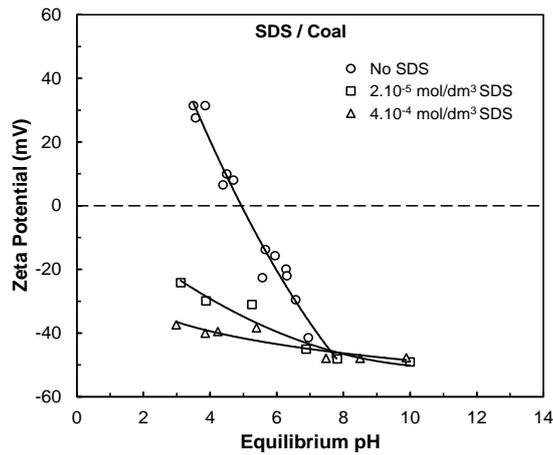
Fig. 1. Zeta potential of Buller coal as a function of pH in the absence and presence of *SDS*
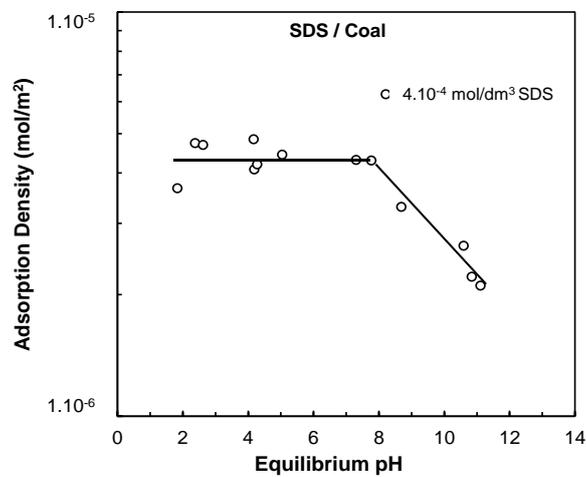


Fig. 2. Effect of pH on the adsorption of *SDS* on Buller coal

Figure 3 shows the zeta potential of coal in the presence of *DAH* as a function of pH. As the surfactant concentration is increased, the iep shifts toward higher pH values, and the charge reversal occurs much sharper. At high concentrations of *DAH*, the charge reversal is also influenced by the precipitation of *DAH* in the form of surface or bulk precipitate. The thermodynamic species diagram for *DAH* at $4 \cdot 10^{-4}$ mol/dm³ reveals that the onset of bulk precipitation of the free amine should occur at pH values above 9.4. The occurrence of precipitation at slightly lower values is attributed to the surface precipitate which is known to appear before the onset of the bulk precipitate (Ananthapadmanabhan and Somasundaran, 1985). Bubbles stabilized by *DAH* and precipitates were reported to exhibit zeta potential profiles similar to that observed in Fig. 3 (Laskowski et al., 1989). The appearance of surface precipitate in the quartz/*DAH* system is found to correlate with the onset of a rapid increase in contact angle vs. pH data (Smith and Scott, 1990).

Dibbs et al. (1974) explained the charge reversal of the bubble at high pH by the adsorption of hydrolyzed species of amine to the neutral species, i.e. $RNH_2$. Yoon et al. (1986) indeed confirmed that the bubbles generated by an unhydrolyzable surfactant, cetyipyridinium chloride solutions, do not undergo charge reversal. The pH of the bulk precipitate, however, seems to coincide with the drop in flotation recoveries. This is in line with the species diagram of amine (Novich and Ring, 1985; Ananthapadmanabhan and Somasundaran, 1985). Laskowski (1988) suggests that the high negative potentials of the air bubbles may be responsible for the drop observed in the flotation of quartz with amine.
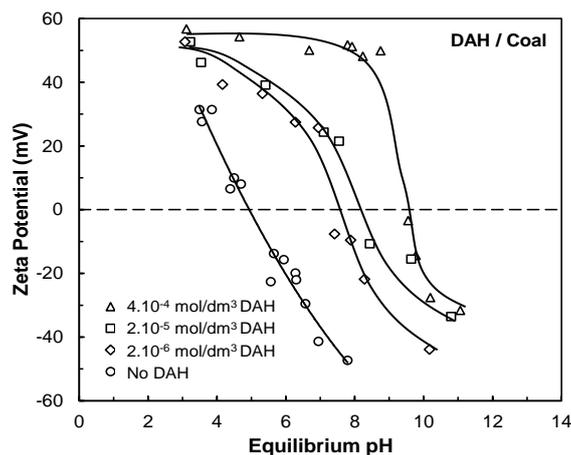
Fig. 3. Zeta potential of Buller coal in the absence and presence of *DAH*

The dependence of pH on adsorption of *DAH* onto coal illustrated in Fig. 4 exhibits an interesting behavior. The abstraction of *DAH*, as measured by the depletion technique, increases whereas the bulk precipitation tests conducted independently also show the same trend. Precipitation tests were carried out with coal supernatants adjusted to the same pH and salinity in the presence of *DAH*. Subtraction of precipitation from abstraction data results in an adsorption curve which decreases above pH 8 (adsorption = abstraction - precipitation). It should be noted that this behavior may dominate in most oxide/cationic surfactant and also in fatty acid systems.

Wang et al. (2009) using vibrational spectroscopy has revealed that there is no pronounced adsorption of amine onto a silica surface at low pH but increases with increasing pH due to weak electrostatic interactions. They also claimed that significant adsorption of amine at the air/water interface occurs where the amine loaded bubble transfers its amine molecules to the almost bare quartz surface upon collision through heterocoagulation. This mechanism has been confirmed through the preferential adsorption of low amine concentrations at the air/solution interface leading to a net positive charge which will result in film rupture due to heterocoagulation with the negatively charged water/solution interface (Alexandrova et al., 1999).
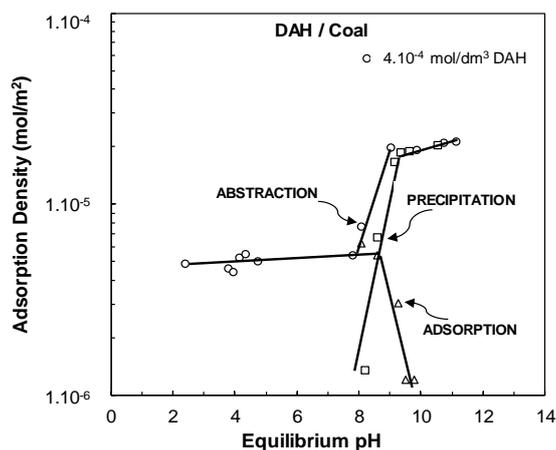


Fig. 4. Effect of pH on the adsorption of *DAH* on coal

In both surfactant types, the common factor is the presence of the hydrocarbon chain which adsorbs onto hydrophobic sites of the coal surface through the alkyl part of the molecule. As the hydrophilic functional groups start dominating in the alkaline pH, the adsorption of both ionic and nonionic surfactant decreases in the alkaline pH. This clearly indicates that hydrophobic bonding is the major driving force for the adsorption of ionic and nonionic surfactants on coal.

The iep data for bulk precipitate, bubble and coal in the presence of *DAH* is illustrated in Fig. 5 together with the precipitation ($2 \cdot 10^{-5}$ mol/dm³) and micellization ($1.3 \cdot 10^{-2}$ mol/dm³) boundaries. The

iep data for coal is superimposed on data extracted from paper by Laskowski et al. (1989). It is seen that the iep of coal and bubble in the presence of *DAH* approximately overlaps; this may indicate that the mechanisms proposed by Yoon et al. (1986) and Laskowski et al. (1989) for the charging of air bubbles with cationic surfactants may also be valid for the adsorption of *DAH* onto coal. The positive zeta potentials observed in the case of bubbles are due to adsorption of the hydrocarbon part of the amine molecules onto hydrophobic bubbles with the polar head sticking out (Chernyshova et al., 2000). Similarity found for the charge of bubbles and the precipitate was ascribed to the armoring of bubbles by the partially hydrophobic surfactant precipitate (Yoon and Yordan, 1983). In a study similar to the concept presented here, ulexite (Sodium Calcium Borate) in the presence of various multivalent ions, i.e. Ba, Mg, Ca, and Al was found to exhibit excellent floatability even when particles, colloidal precipitates, and bubbles acquired a similar charge, which indicated that attractive structural forces exceeded the forces of electrostatic repulsion. While calorimetric studies using anionic and cationic surfactants showed that ionic surfactants adsorbed on hydrophobic coal through their hydrophobic moiety (Celik and Yoon, 1993), a significant decrease in hydrophilicity of lignite was found with cationic surfactant (*CTAB*) adsorbed onto oxygen containing functional groups like carboxylates (Liu et al., 2017).
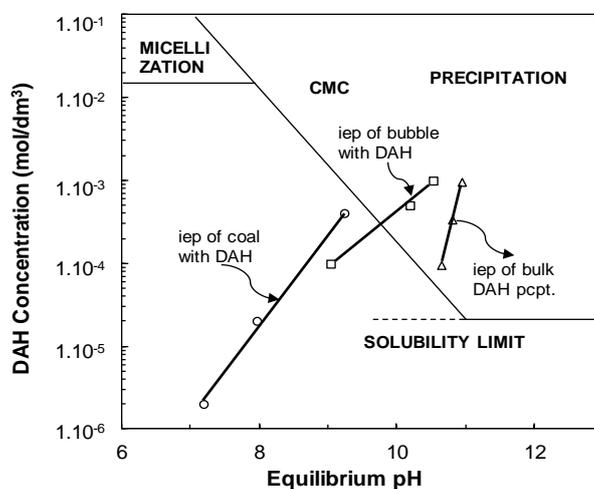


Fig. 5. Thermodynamic equilibrium diagram illustrating the iep of coal, precipitate and bubble in aqueous solution of *DAH*. The iep data of coal with *DAH* is superimposed on data extracted from Laskowski et al. (1989)

In a separate study, heterocoagulation of chalcopyrite and pyrite was observed to occur in the acidic medium of pH 5.5. While the iep for chalcopyrite is around pH 5.5, that of pyrite occurs at pH lower than 3. The colloidal interaction forces predicted the heterocoagulation process to occur at pH<6, when the energy barrier falls to ~5 kT or less, and the stability ratio for the (Brownian) heterocoagulation is higher than 1 (Mitchell, 2005). The calculated DLVO curves vs. separation distance at pH 5.5 exhibited minimum energy barrier indicating that the minimum charge of particles may be a prerequisite for heterocoagulation. It is interesting to note that the pH range of the heterocoagulation coal/DAH, bubble/DAH, and bulk DAH precipitate occurs in the pH range of 7.5-9, 9-11, and 11-11.5, respectively. The schematic presentation of heterocoagulation phenomenon occurring between coal particles, bubbles, and precipitates are also illustrated in Fig. 6.

Our results generally reveal that the bubbles, precipitates, and hydrophobic particles in ionic surfactant solutions exhibit similar charge characteristics, and consequently, the iep values. Based on our earlier findings on adsorption of nonionic surfactants onto coal (Celik, 1989; Celik et al., 1991) the driving force for adsorption is the hydrophobic interaction between alkyl moiety of the molecule and the hydrophobic particulates. The water films on hydrophobic surfaces are unstable, and can be spontaneously removed when two hydrophobic bodies approach each other within certain critical distances (Yoon and Yordan, 1991). As the water molecules are removed from the surface region, they will gain entropy, resulting in a negative free energy of the system.
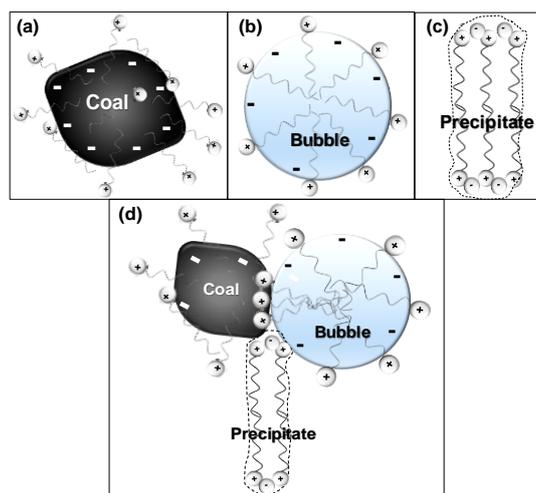
Fig. 6. Schematic view of heterocoagulation process (a) Coal-*DAH* (b) Bubble-*DAH* (c) *DAH* precipitate (d) Bubble-coal-*DAH* precipitate

## Conclusions

Adsorption of ionic surfactants onto coal decreases in the alkaline pH. In the case of the cationic surfactant colloidal precipitates form in the alkaline pH. Coal in the presence of the anionic surfactant exhibits negative zeta potentials in the entire pH region. Coal in the presence of the cationic surfactant undergoes a charge reversal in the alkaline pH.

The iep data for coal, bubble and precipitate in cationic surfactant solutions approximately follow the same pattern indicating that the adsorption mechanism for all these particulates is similar. Based on our earlier findings the driving force for adsorption is controlled by the hydrophobic bonding which in turn is driven by entropy changes of the system.

An implication of the similar charge characteristics of particles, bubbles and precipitates in flotation pulps can coexist, and their interaction lead to heterocoagulation.

Our present research is geared towards the role of coagulation in bubble-particle attachment in flotation, i.e. whether the formation of agglomerates coincides with the onset of the sharp rise in flotation recoveries against collector concentration.

## Acknowledgements

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