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EFFECT OF POLYMER-SURFACTANT INTERACTION ONTO THE SPHERICAL AGGLOMERATION

The effect of polymer-surfactant interaction has been studied at the solid surface. The flotation tailings from KGHM Polska Miedz S.A. were used for both the adsorption and spherical agglomeration investigations. The adsorption isotherms of sodium oleate suggest a competition between polymer and surfactant. The preadsorption of polymer causes the increase of sodium oleate adsorption onto the mineral surface. The agglomeration results partially agree with the sodium oleate adsorption in the polymer presence. Polymer excess causes a decrease of agglomerate size.

Key words: polymer-surfactant interaction, spherical agglomeration, adsorption, surfactant, polymer

INTRODUCTION

The polymer-surfactant interaction occupies an increasingly important place among the available cosmetic, pharmaceutical and oil technology (Goddard and Grubert 1999, Hackey et al., Sakar and Somasundaran 2002). Water soluble polymers often interact strongly with surfactants in aqueous solution. The strong interaction of polymer-surfactant shows two break points at a surface tension curve. These points attributed to the formation of the micelles on the polymer chain, called the critical aggregation concentration (cac), and the second point corresponds to the normal micellisation of the surfactant (cmc) (Kwak 1998, Adler et al., 2000). The properties of a variety of polymer-surfactant mixtures in water have been extensively studied (Shimabayashi, et al., 1997, Langevin, 2001, Torn et al., 2003).

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In contrast, there is little information about the polymer-surfactant interaction at the solid-solution interface. In the case of poly(ethylene oxide), PEO, and sodium dodecyl sulphate, SDS, the experimental data show a competitive adsorption between surfactant and polymer at the solid-water interface. For this reason the adsorption of both polymer and surfactants used to modify the surfaces to impart desired chemical properties. For instance: integration of cationic surfactant (CTAB) with polymer onto the silica surface (Shubin, 1994, Magny et al., 1994). If the surfactant was preadsorbed onto silica surface and then the polymer was added, surfactant was desorbed from the silica surface. When the surfactant polymer ratio approached 1:1 creation of the complex occurred and substantial increase in adsorption was observed (Dedinaite et al., 2000).

In this paper, we present a part of investigations of polymer-surfactant interaction onto the mineral surface and the effect of this interaction on the spherical oil agglomeration. We compare the behavior of mineral suspensions when the order, in which the surfactant and polymer were added, is changed.

EXPERIMENTAL

MATERIAL AND METHODS

The commercial polymers used in this investigation were PAM (polyacrylamide) and PEO (poly(ethylene oxide) samples, with the molecular weight of 5 000 000. PEO was obtained from BDH Chemicals Ltd., (England) and PAM was purchased from Aldrich Chemical, Inc., (USA). Both reagents were used without any further purification. Sodium oleate (SOL) was purchased from Riedel-de Haen (Germany) and it was used as received. Cationic surfactants CTAB and DDA HCl were purchase from POCH-Gliwice (Poland). n-heptane and kerosene were also obtained from POCH-Gliwice.

Adsorption isotherms were measured using the depletion methods. Approximate 1 g of mineral sample was transfer to the each of the flasks having 100 ml of aqueous SOL or polymer solution of the different initial concentration. The flasks were shaken for 24 hours. The supernatant was separated and centrifuged. The final concentration of both PEO and PAM in the supernatant was determined by complexation with tannic acid. The adsorption density was calculated from the residual concentration.

The agglomeration tests were carried out in a special designed mixing unit. In each experiment, 2 g mineral sample were used. These samples were suspended in 50 ml of sodium oleate solution. Then an appropriate 50 ml of water emulsion (n-heptane and keroseine) was added. The cationic surfactant (CTAB) was added to the emulsion as an emulsifier reagent. The mineral water suspension and emulsions were extensive mixed for 50 s. at 10000 rpm. The agglomerated material was recovered on a 100 μm sieve and dried in an oven and weighed.

RESULTS AND DISCUSSION

The adsorption of polymers and surfactants onto the solid surface should be considered a delicate balance on polymer-surfactant, polymer-solid and surfactant-solid interactions. The adsorption polymer and surfactant can be additive, cooperative and competitive (Persson et al., 2000). Adsorption isotherms, given in Figures 1 and 2, presented the effect of polymer addition onto the sodium oleate adsorption. These experiments were carried out at the constant pH (pH=8.0).
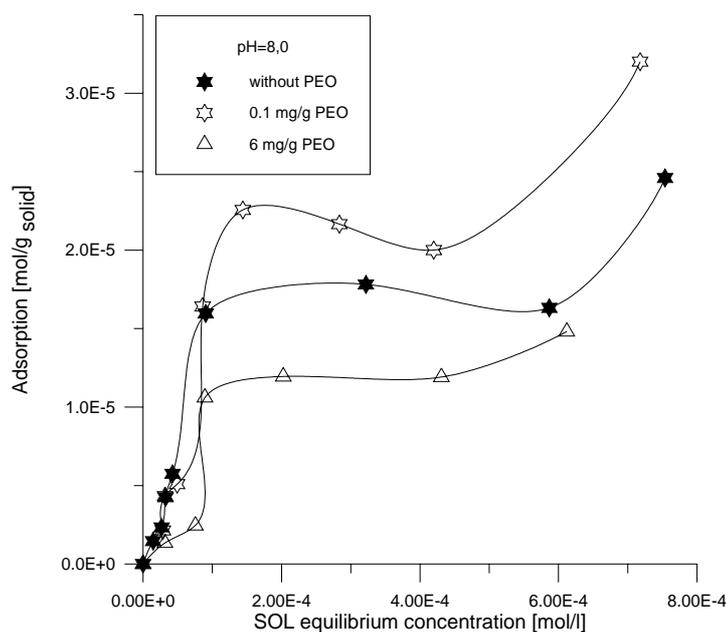
Fig. 1. Adsorption isotherms of SOL on the flotation tailings in the presence of preadsorbed PEO

One can see that preadsorption of PEO on the surface of flotation tailings caused that the adsorbed amount of SOL increased at the low concentration of preadsorbed PEO. The adsorbed amount of SOL was decreased at the high PEO concentration (6 mg/g PEO).

Fig. 2 shows the adsorption isotherms of SOL on the flotation tailings in the presence of PAM.

The SOL isotherms also showed a decrease in the presence of preadsorbed PAM. In this case, the degree of SOL adsorption depends on the quantity of preadsorbed polymer.

Effect of surfactant pretreatment on the polymer adsorption was investigated. The results of these investigations are presented in Fig. 3 and Fig. 4.
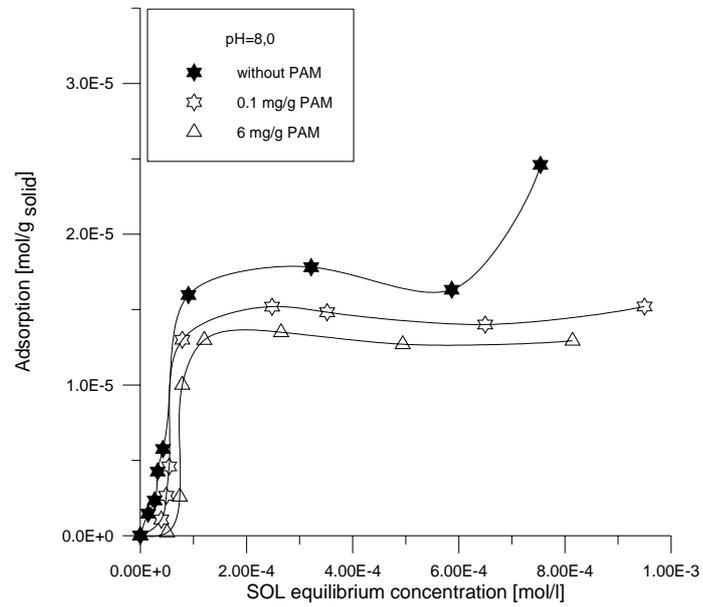
Fig. 2. Adsorption isotherms of SOL on the flotation tailings in the presence of preadsorbed PAM
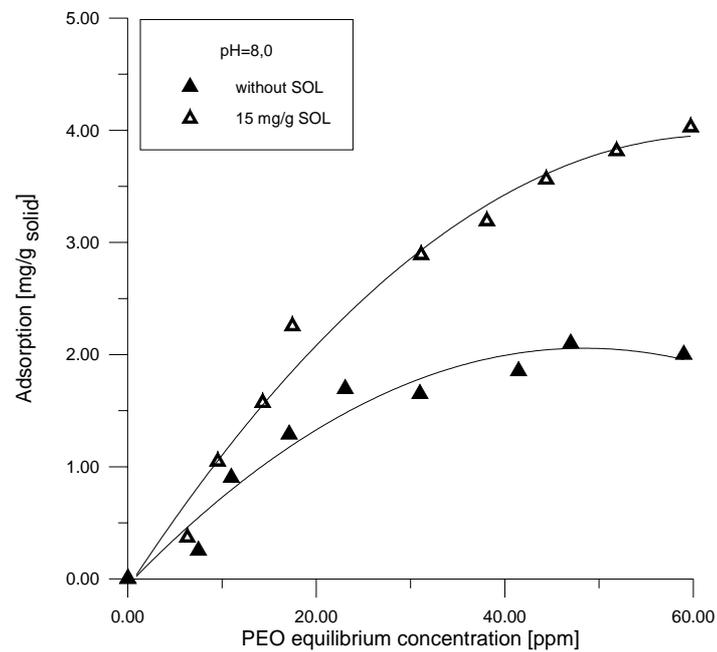
Fig. 3. Adsorption isotherms of PEO on the flotation tailings in the presence of preadsorbed SOL
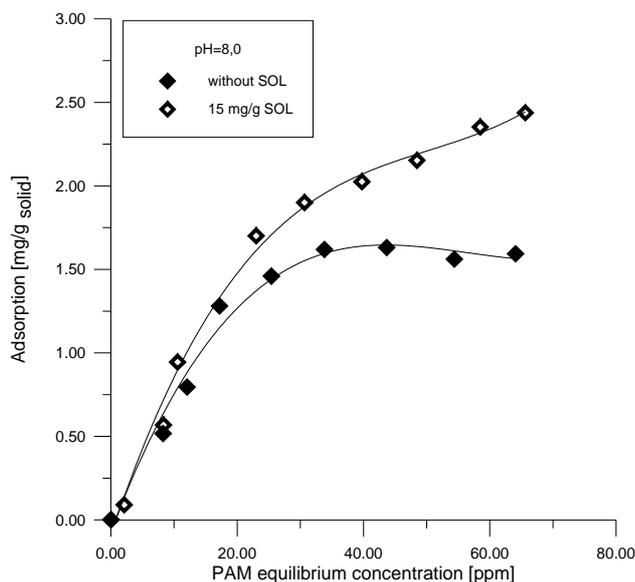
Fig. 4. Adsorption isotherms of PAM on the flotation tailings in the presence of preadsorbed SOL

Preatreatment of the mineral suspension with sodium oleate (15 mg/g) causes an substantial enlargement of the polymer adsorptions. The same behaviour was observed for the kaolin suspension with the presence of nonionic polymer (PAM-A) and three surfactant reagents (Besra et al, 2002 a,b,c).

In order to elucidate the structure and hydrophobicity of adsorbed layer on the mineral surface, the following agglomeration experiments were carried out.

Table 1. Agglomeration of flotation tailings with n-heptane and kerosene

SOL concentration (mole/l)	CTAB concentration (mole/l)	Volume of oil (ml)	Results
$2 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	n-heptane 0.4	Flocculation
$2 \cdot 10^{-3}$	$1.75 \cdot 10^{-4}$	n-heptane 0.5	Flocculation
$2 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	n-heptane 0.5	Spherical agglom.
$2 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	n-heptane 0.6	Spherical agglom.
$2 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	n-heptane 0.8	Paste
$2 \cdot 10^{-3}$	$1.75 \cdot 10^{-4}$	Kerosene 0,5	Flocculation
$2 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	Kerosene 0.2	Spherical agglom.
$2 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	Kerosene 0.3	Spherical agglom.
$2 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	Kerosene 0.6	Paste

The agglomeration process may be considered as a collision between hydrophobic particle and hydrophobic oil droplet. These collisions lead to adhesion as a result of the formation of pendular oil bridges (Kawashima and Capes, 1974). A further factor

of importance for spherical agglomeration was a quantity of cationic surfactant added to the oil-water emulsion. The process pre-emulsification of the oil phase is important for spherical oil agglomeration. From both investigated cationic surfactants (CTAB and DDA HCl) dodecylamonium hydrochloride seem be much better.

Agglomerate size is controlled by the balance between agglomerate interaction determined by capillary forces and the destructive forces determined by the shear regime. The shears forces were constant at our experiments (stirrer speed and mixing time were constant). It means that size agglomeration was controlled by chemical factors.

The changes in the medium diameter of agglomerates for the polymer-surfactant systems are presented in Figure 5 and Figure 6.
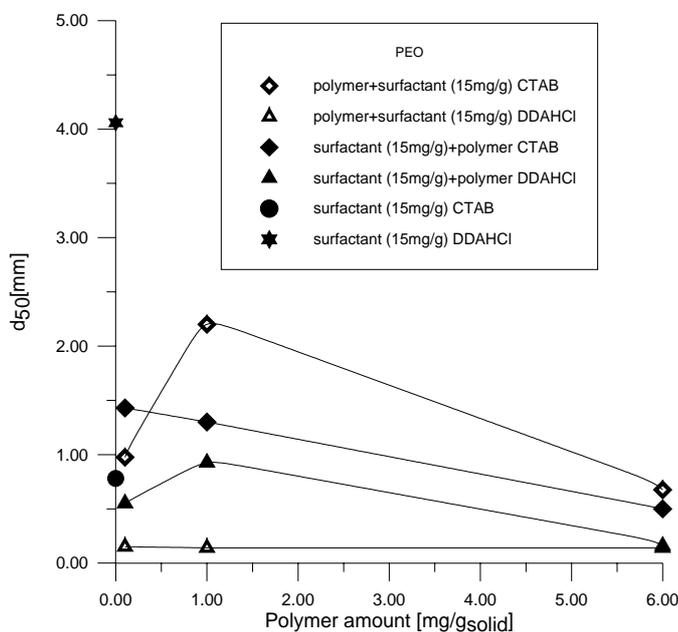
Fig. 5. Influence of surfactant-polymer interaction (SOL-PEO) on the agglomerate size

Figure 5 shows the effect of increasing polymer quantity on agglomerate diameter. Generally, the size agglomerates decrease at high polymer addition and it does not dependent on the order of a polymer addition versus surfactant. The same behaviour can be observed for SOL-PAM system (Fig. 6).

From the data presented in Figs 5 and 6 can be seen that the agglomerates resulting from a polymer pretreatmen of the mineral surface are large than those produced from a surfactant pretreatment. It may be tentatively concluded that for the small quantity of polymer (1.00 mg/g of powder) the preadsorption of polymers would be preferable to produce large agglomerates.
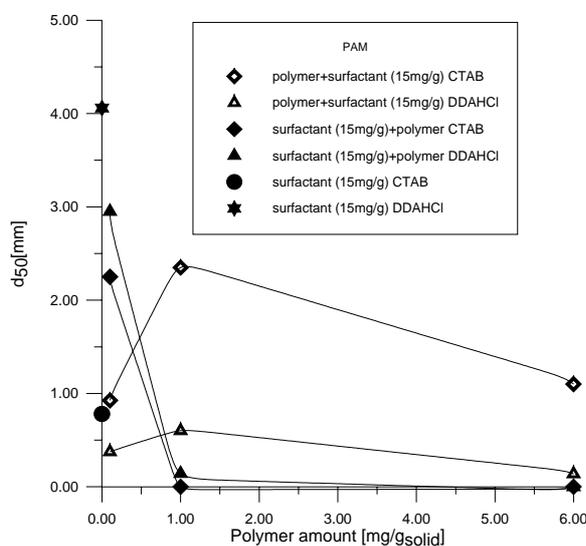
Fig. 6. Influence of surfactant-polymer interaction (SOL-PAM) on the agglomerate size

From the practical point of view (solid paste creation) the presented data represent the initial stage of developing a suitable process optimisation procedure. For this task completes a number of quantitative conclusions must be draw.

CONCLUSION

The experimental data presented here clearly demonstrate the importance of understanding the role of polymer-surfactant interaction for the spherical agglomeration of mineral suspensions. It is shown here that, it is possible to control the size of aggregates by controlling both the order and quantity of polymer and surfactant addition. The adsorption isotherm reveals the difference in the polymer-surfactant interactions onto the mineral surface. The surfactant initially binds on the mineral surface can be impeded the polymer adsorption. On the other hand, a small quantity preadsorbed PEO caused an increase of the sodium oleate adsorption. It was found that the polymer-surfactant interactions have been facilitated the spherical agglomeration process in the range of low polymer dosage.

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W pracy badano wpływ wzajemnego oddziaływania między cząsteczkami polimeru i surfaktantu, które mają miejsce na powierzchni ciała stałego, na proces adsorpcji i sferycznej aglomeracji. Badania przeprowadzono na odpadach po flotacji siarczkowych rud miedzi, otrzymanych z ZWR Lubin. Do modyfikacji powierzchni mineralnej użyto poliakryloamidu oraz politlenku etylenu oraz oleinianu sodu. Stwierdzono, na podstawie pomiarów adsorpcyjnych, ze wstępna adsorpcja polimeru na powierzchni minerału poprawia wyniki adsorpcji olenianu sodu. Wyniki wstępnych testów aglomeracyjnych wskazały, że nafta nadaje się lepiej jako ciecz apolarna niż n-heptan. Do emulgacji fazy olejowej lepiej stosować DDA HCl niż CTAB, Wyniki sferycznej aglomeracji w części są zgodne z wynikami adsorpcji. Nadmiar użytego polimeru zmniejsza w wyraźny sposób średnią wielkość powstających sferycznych aglomeratów.