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Influence of nonionic surfactant concentration on the removal of the finest grains on gas bubbles

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In this paper, the influence of surfactant (Span 20) concentration (within 10^{-7}–10^{-3} M, in aqueous solution) on the removal of the marble finest grains in water sheath of gas bubbles as well as on the grain aggregations in the solution has been studied. There could have been observed the irregular changes of water and grains removal depending on the surfactant concentration. The marble grain aggregation does also change irregularly with the increase of the surfactant concentration. During the experiments, pH of the suspension increased (from initial pH 5.8) or decreased (from pH 10). ΔpH changes irregularly with the change of surfactant concentration. The suspension tends to achieve a pH value, close to that of pH PZC. The higher is the grain aggregation the lower is the grain removal in case of a hardly significant water removal, up to 10^{-5} M of Span 20. For the higher concentrations there is a higher removal of grains and water as well as a more considerable aggregation of the grains.

1. INTRODUCTION

Because of the exhaustion of rich beds of valuable minerals we face the necessity to reach for the poor ones, where the valuable mineral occurs in the state of dispersion throughout the gangue.

In order to release the valuable mineral grains from the gangue one has to grind, as effectively as possible, the whole of the bed. An unavoidable result of such an operation is the formation of large amount of finely dispersed suspension.

The presence of the finest grains of the gangue causes certain problems in the flotation procedure, related to the changing stability of the aggregates grain-gas bubble, to the increased froth stability, and consumption of flotation reagents.

These factors result in reduction of the flotation efficiency and selectivity [1–5]. In consequence, one of the actual scopes of physicochemical studies is to solve the problem of co-flotation of the finest gangue-grains (slime) together with the valuable mineral.

The contamination of the froth flotation concentrate is due to the formation of slime covers of the large grains of valuable mineral [6–8], and to the removal of slime in the gas bubbles water sheath [8–11], and in apolar liquid (collector) droplets water sheath [12,13].

In order to explain this problem in a more profound way, further investigation has been taken up, namely the one concerning the influence of nonionic surfactant concentration (emulsifier or frother substance) in the water solution on the removal of the marble slime in water sheath of gas bubbles.

In this investigation, the marble was used because it is one of several forms of calcium carbonate occurring in the gangue.

2. EXPERIMENTAL

2.1. The grain and water removal

In order to determine the removal of water and slime on gas bubbles, an earlier described single-gas-bubble flotation-column (a modified Hallimond flotation tube) was used [10,14]. At first, the suspension of marble grains (of diameter below 20 μm) in water solution of Span 20 (pure monolaurate sorbitan, Fluka) was introduced into the column. Then, the apolar liquid was introduced (e.g. heptane) on the suspension surface. After that, the single nitrogen bubbles, one after another, were passed through the suspension (at constant flow rate, 3 cm^3/min., during 30 min.). After they have passed through the water suspension and the layer of apolar liquid, they collapsed. In such a case, the water coming from the sheath of the gas bubbles, and the slime grains contained in it, were collected in the burette (what made it possible to know the removed volume of water, or that of water and slime). The content of the burette was placed in the cuvette, and, after the evaporation of water, the mass of the removed slime was weighed.

After the experiment was over, final pH of the suspension (of the one, which remained in the flotation column) was determined.

2.2. The grain aggregation

In order to investigate the aggregation of slime grains in water solution of Span 20, a measure cylinder was applied (volume capacity 50 cm^3). It was supplied with a tap on the level of 20 cm^3 from the bottom. After the cylinder was filled with the suspension, it was let for about 10 minutes. After that time, two zones have been observed in the suspension: the supernatant together with a fluffy deposit zone above the tap, and the compact deposit zone below the tap. Then, 30 cm^3 of suspension was poured out from the cylinder into the cuvette. After the evaporation of water the mass of non-sedimented slime was weighed. The mass was reversibly proportional to the degree of grain aggregation.

3. RESULTS AND DISCUSSION

Figure 1 represents the influence of Span 20 concentration (from 10^{-7} to 10^{-3} M) on the removal of water together with slime (Curve 1), of the slime only (Curve 2), and of the water only (Curve 3). The initial pH of solution (suspension) was 5.8. In Figure 1 there can be observed the irregular changes of water and slime (or the only slime alone) removal depending on surfactant concentration. Curve 1 and 2 are poly-extreme ones. Minimum and maximum points occur at the same Span 20 concentration. However, the removal of the water only, takes place starting from the concentration 10^{-5} M of Span 20, and it increases with the increase of surfactant concentration.

Figure 2 represents the influence of Span 20 concentration (from 10^{-7} to 10^{-3} M) on the removal of water with slime (Curve 1), of slime only (Curve 2) and of water only (Curve 3). The initial pH of suspension was 10. The curves in Figure 2 show the removal of water and slime (or the slime, only) changes irregularly with the change of Span 20 concentration, and the removal of water, only, increases continuously for concentrations higher than 10^{-5} M.

Figure 3 represents the influence of Span 20 concentration on the grain marble slime aggregation. From this figure, it results that also the aggregation of the grains changes irregularly with the increase of Span 20 concentration.

During the experiments, pH of the suspension increased (or decreased) by different values depending on the surfactant concentration, and on the value of initial pH. The pH changes are represented in Figure 4. The arrows directed upwards from initial pH 5.8 show the increase of the final pH, while the arrows directed downwards from initial pH 10.0 show the decrease in final pH. ΔpH changes irregularly with the change of Span 20 concentration, and the slime suspension tends to achieve pH value within the range 9.1–9.5. At pH close to the last mentioned value the marble surface attains the equilibrium with water (characterized by a point of zero charge of the surface) [13,15–18]. This is the result of the marble surface reaction with water. The carbonate and calcium ions enter the solution, and, then, because of hydrolysis, a series of products is formed. Those products remain in equilibrium with the marble surface. According to [15–18], the most important of those reactions, which regulate pH of the solution are (1) and (2):

$$\text{marble surface: } -CO_3^- + H_2O \rightarrow \text{surface: } -HCO_3 + OH^- \quad (1)$$

$$\text{marble surface: } -Ca^+ + H_2O \rightarrow \text{surface: } -CaOH + H^+ \quad (2)$$

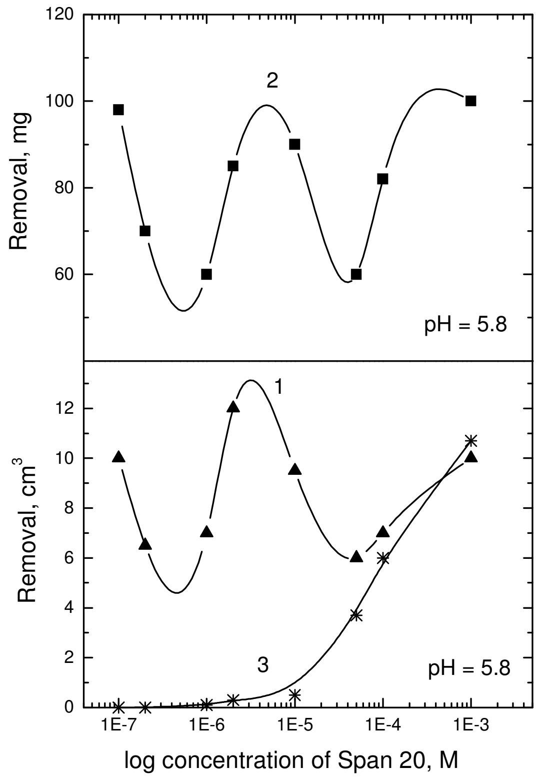

Fig. 1. Influence of Span 20 concentration on the removal of water with slime (Curve 1), the slime only (Curve 2), and water only (Curve 3). Initial pH of suspension, equal to 5.8.

In the result of Reaction (1) the increase of final pH takes place starting from initial pH 5.8 (Fig. 4, at the bottom). As the result of Reaction (2) there can be observed the decrease of final pH from initial pH 10 (Fig. 4, at the top). At pH within the range 9.1–9.5, close to pH PZC, the yields of reactions become equal. From Figure 4 it results that the changes in yields of both reactions (stabilization of pH) irregularly depend on Span 20 concentration.

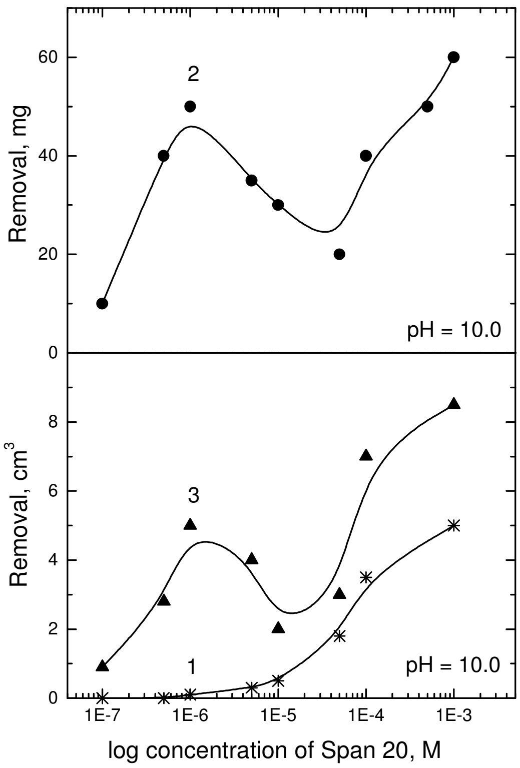

Fig. 2. Influence of Span 20 concentration on the removal of water with slime (Curve 1), the slime only (Curve 2), and water only (Curve 3). Initial pH of suspension equal to 10.0.

While comparing Figure 1 and 2 with Figure 4, it can be seen that the grain removal changes agree with the change of ΔpH within the whole range of Span 20 concentration. The more the value of final pH nears the value of pH PZC, the higher is the slime removal. If we compare Figures 1,3,4, for the concentration of Span 20 from 10^{-7} up to 10^{-5} M, then, it can be seen there is no agreement between the changes in grain aggregation and grain removal, and grain aggregation and ΔpH. For the higher concentration, however, such an agreement can be observed.

It can be concluded the main reason of the above relationship is adsorption of Span 20 molecules on the grains of marble slime, which causes the screening of the grain surfaces by the surfactant molecules. The degree of covering the grain surface by the surfactant, the thickness and the structure of adsorption layers depend on the Span 20 concentration in solution. In consequence, the changes of

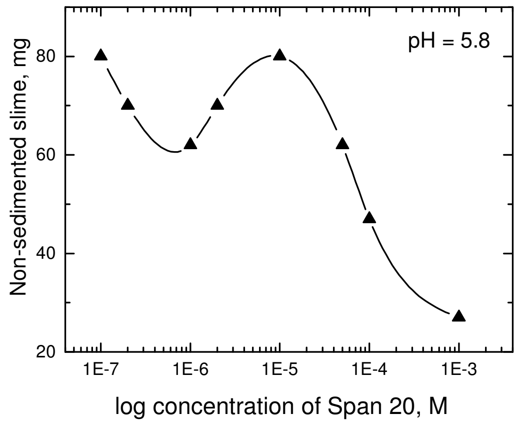

Fig. 3. Influence of Span 20 concentration on the amount of non-sedimented slime. Initial pH of suspension equal to 5.8.

the value of contact interface between the slime grains and water result in the change of the yield of Reaction (1), and (2), as well as in the change of final pH. The changes of the mentioned parameters seem to be influenced by Span 20 concentration. At the same time, the surfactant adsorption on the grain changes the extent of hydrophobization of single grains, and provokes the slime aggregation.

While analysing the causes of slime removal on gas bubbles, the phenomena occurring at water-gas interface (except for water-slime interface) should be taken into consideration. The adsorption-hydration sheath around the bubble is formed due to the surfactant adsorption on the gas bubbles, and the hydration of the surfactant polar groups, Then, the chance of keeping the grains in the water sheath of gas bubbles (slime removal), in case of a small thickness of the water sheath of gas bubbles (low water removal), at Span 20 concentration up to 10^{-5} M, does also depend on the aggregation extent (Figs 1-3). In such cases, the higher is the extent of grain aggregation, the lower is its removal.

In case of considerably higher water removal on gas bubbles, i.e. in a thick water sheath (for Span 20 concentration higher than 10^{-5} M) there takes place a considerable removal of the finest grains. Figure 1 and 2 (Curve 2 and 3) are a proof in favour of the supposition that such a process does really take place. In such water sheath, it is possible to maintain the grain aggregates along with the single grains. In consequence, for these Span 20 concentrations there is a higher slime aggregation, and its higher removal (Figs 1,3).

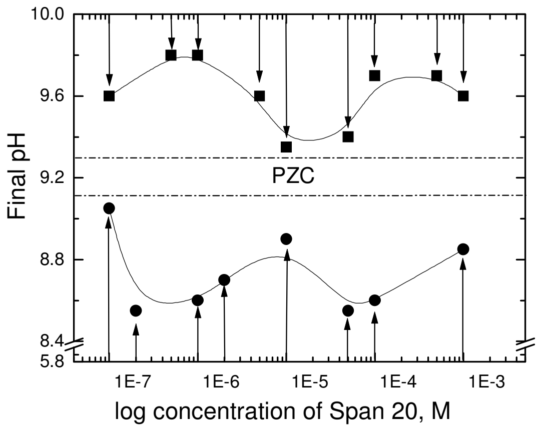

Fig. 4. Influence of Span 20 concentration on final pH of suspension. The arrows indicate the increase or decrease of the final pH value, from initial pH 5.8 or 10.0, respectively.

4. CONCLUSIONS

The surfactant concentration (by adsorption on slime grains) influences the interaction at slime-water and grain-grain interfaces (i.e. pH value of suspension, and the slime aggregation). In consequence, the surfactant concentration influences the slime removal in water sheath of gas bubble by adsorption on slime (the change of its hydrophilic properties and aggregation of slime grains). It is obvious the surfactant concentration influences the slime removal also by its adsorption on the gas bubbles, and forming the water sheaths on them. In conclusion, surfactant influence on the transfer of the slime to the froth concentrate can be related to a series of physicochemical phenomena taking place on the grain-water, grain-grain, and gas bubble-water interface. These phenomena occur simultaneously and that is why it cannot be found out, which one of them plays the most important part. While making the optimum flotation parameters there should be studied all the possible ways of the gangue slime removal into the valuable-mineral foam-concentrate.

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CURRICULUM VITAE

Kazimierz Jurkiewicz is a university teacher at Maria Curie Sklodowska University, Lublin (Poland). In 1963, he received his M.Sc. in the Department of Chemical Technology (headed by Prof. K. Akerman), and his D.Sc., in 1971, in the Department of Physical Chemistry (headed by Prof. A. Waksmundzki). He concluded his habilitation paper in 1990. He worked as a post-doctoral research chemist in the Department of Physical Chemistry (headed by Prof. L. D. Skrylev) of the State University in Odessa (former USSR), in 1977, and in the Department of Analytical Chemistry (headed by Prof. P. K. Dasgupta) of Texas Technical University, Lubbock, USA (in 1986). His research areas are: physicochemical studies on separation of metal ions (and minerals), and surfactants from solutions, basing on the properties of solid-solution and gas-solution interfaces as well as on metal complexation; comparison of foam separation effectiveness to the other techniques of ion and surfactant separation.