An investigation of the flotation minimum in the oleate flotation of hematite under alkaline conditions

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ABSTRACT

Over the years there have been a number of instances describing a minimum in the flotation recovery of hematite in the alkaline pH region when oleate is used as the collector. These cases usually coincide with the use of a commercial oleate sample containing other fatty acids and/or salts as the collector. It is the purpose of this paper to provide experimental data involving the effects of pH on the flotation of a natural hematite sample using two collectors containing oleate and compare these data to changes in surface tension and bubble characteristics of aqueous oleate systems also as a function of pH. The main aim of this paper is to highlight and address this difference in hematite flotation behaviour with oleate solution characteristics and develop a better understanding of these interactions. It is proposed that this flotation minimum is associated with a reduction in both contact angle and bubble-particle flotation rate constant under these conditions, even though the surfactant solution chemistries would suggest that flotation should still be strong in this region.

1. Introduction

The author has published the results of a number of studies on the oleate flotation of hematite as a function of pH (Quast, 1999, 2012a, 2016a; Quast and Quast, 2010; Joseph-Soly et al., 2015). Conditioning times and zeta potentials have also been used to investigate the hematite-oleate system (Quast, 2015, 2016b). These findings have shown that conditioning at acidic pH values involves the interactions of water-insoluble droplets or colloids with the mineral surface, whereas under alkaline pH conditions, soluble oleate species are adsorbed. One of the commercial reagents used in this study was very effective in floating hematite after short conditioning times, but very susceptible to the presence of fines (Quast, 2015). For this reason the optimum conditioning time determined previously was used in this study to mitigate the effect of conditioning time on hematite flotation. Suggested mechanisms include physical adsorption or precipitation of oleate colloids/micelles (Quast, 2016c) and chemisorption of oleate forming a ferric oleate complex as demonstrated by Joseph-Soly et al. (2015).

In this study, the oleate flotation as a function of pH for a sample of naturally occurring hematite ore from the Iron Prince deposit in the Middleback Ranges of South Australia using two surfactants containing oleate will be reported. These data, together with information derived from other literature sources, will be used as the basis for the discussions on the hematite-oleate-aqueous system. This study will therefore address the conundrum of why hematite flotation using these two collectors is depressed under pH conditions where the surfactant

activity of aqueous oleate is at a maximum as indicated by a minimum in surface tension/maximum in surface pressure.

2. Literature review

2.1. Adsorption studies

A maximum in the oleate adsorption density or flotation of hematite at its isoelectric point, usually close to neutral pH, has been observed by a number of researchers (e.g. Peck et al. 1966, Gutierrez and Iskra, 1977, Ofor, 1995). For fine mineral hematite in contact with sodium oleate, the contact angle and aggregation efficiency were maxima at the isoelectric point of hematite as reported by Song and Lu, (1994). Quast (1999) showed how the maximum in hematite flotation with oleate usually occurred under neutral conditions, where the isoelectric points of hematites are normally reported (see data of Kosmulski (2009) and Quast (2016a)).

2.2. Surface tension (and surface pressure) studies

It is not the purpose of this paper to discuss the phenomenon of the surface tension of aqueous surfactant solutions, as this has been reported in standard texts (e.g. Davies and Rideal, 1961; Gutierrez and Iskra, 1977; Ofor, 1995). The measurement of surface tension of aqueous surfactant systems using ring tensiometry has been criticised by various workers (e.g. Padday, 1969 and Boucher et al. 1967) although

Mankovich (1968) claimed extraordinary accuracy by taking "well-known precautions" into account. Lukenheimer and Wantke (1981) have suggested ways of eliminating errors involved in testing under conventional conditions, thus allowing an accurate measurement of the surface tension of surfactant solutions, and these were incorporated in the experimental procedure.

Over the years many researchers have recorded minima in the surface tension of oleate solutions in alkaline solutions. These include Bottazzi, 1913; Mikumo, 1927; Mullin, 1928; Powney, 1935; Cupples, 1935; Mankovich, 1953; Kulkarni, 1976; Williams, 1980; Wakamatsu et al. 1980; Pugh and Stenius, 1985; Pugh, 1986; Ananthapadmanabhan and Somasundaran, 1988; Muratoglu et al. 2000; Hernainz and Caro, 2001; Yu et al. 2015 and Atrafi and Pawlik, 2016. Kulkarni's data were analysed by Beunen et al. (1978) who found that the observed minimum in surface tension could be explained without resorting to the use of species at very low concentrations (acid soap complex) postulated without experimental justification. They assumed that at low pH, oleic acid will be mostly undissolved and that this precipitate acted as a reservoir of surfactant molecules which entered the solution in the dissociated form as the pH was increased. This increase in solution concentration resulted in increased adsorption at the interface with a consequent lowering of the surface tension. At the so-called "solubility edge", the surfactant became completely soluble and the solution concentration of the surfactant became constant, hence there was no further tendency for the surface tension to decrease as the pH was increased. Indeed, the conversion of neutral to charged surfactant species caused the monolayer to charge up. Thus, for pH values higher than the solubility edge, the increasing electrostatic repulsion of oleate ions from the interface caused the surface tension to increase. A minimum in surface tension exists, therefore, at the solubility edge.

Ananthapadmanabhan et al. (1978) reported a minimum in the surface tension of potassium oleate at pH 8 for measurements conducted from pH 4–12. This was ascribed to the maximum concentration of the acid soap at this pH.

Ananthapadmanabhan and Somasundaran (1981) reported that the surface tension minimum for potassium oleate solutions shifted to higher values of pH as the oleate concentration was raised. Also, de Castro and Borrego (1995) found that the surface tension minimum for aqueous solutions of sodium oleate shifted from pH 7 at low oleate additions to almost pH 10 at higher oleate conditions. This is in keeping with the position of the solubility edge of the oleate as shown in diagrams of its aqueous equilibria (see Quast, 2016a, 2016a, 2016c).

Theander and Pugh (2001) reported values of the surface tension of oleate solutions for concentrations between 10^{-6} molar and 10^{-5} molar. They reported two minima, between pH 8 and 9, and at about pH 11. The values of the surface tension also decreased rapidly beyond pH 12.

Recent data by Atrafi and Pawlik (2016) showed that the pH corresponding to the minimum in the surface tension of aqueous solutions of sodium oleate increased as the addition of oleate increased from 10^{-5} molar to 10^{-2} molar. The pH corresponding to the precipitation of oleic acid also increased from 7.5 to 10.3 as the oleate addition was increased from 10^{-5} molar to 10^{-2} molar. According to Pugh and Stenius (1985), the minimum in surface tension corresponds to the maximum concentration of an acid-soap species. According to the speciation diagrams reported by Pugh and Stenius (1985), the onset of precipitation also occurs at or near the pH of minimum surface tension. The data reported by Atrafi and Pawlik (2016) showed that the pH values corresponding to the precipitation of the oleic acid occurred at lower values than the observed minimum in surface tension at each oleate addition. The values of surface tension at pH 4 for all the oleate additions used were close to 40 mN/m and may correspond to an insoluble film of oleic acid at the air-water interface, since pH 4 is 1 pH unit below the traditional value of the pKa for oleic acid. The fact that it is this relatively low value at pH 4 could also mean the presence of some surface-active species in the solution. Surface tension values at low values of pH are lower than at high pH, supporting the view that the oleic acid form is

quite surface active compared to the soluble oleate anion. It also suggests that the adsorption of anions at the air-water interface could be inhibited by lateral electrostatic repulsive forces, whereas electrostatic repulsion forces between adsorbed oleic acid molecules could be lower although Laskowski (1988) measured an isoelectric point for oleic acid colloids around 2.5.

One of the few articles to actually report surface pressure of oleate as a function of pH was written by Kulkarni and Somasundaran (1975). They examined the effects of ionic strength and temperature on final surface pressure and showed that the maximum shifted to higher values of pH with increasing ionic strength and increasing temperature. Surface pressure maxima were in the pH range 7–9, decreasing rapidly at pH 10.

2.3. Bubble size and frothing

Iwasaki et al. (1960) and Cooke et al. (1960) measured the frothing characteristics of oleic acid as a function of temperature and pH. The concentration of oleic acid used was 10^{-4} molar, and the froth height was determined by a manual agitation method. Maximum frothing occurred at pH 11, with little frothing noted at pH values below 6. The decrease in frothing at lower pH values was attributed to the precipitation of the free acid, whereas the decrease at higher pH values was thought to be due to the "salting out" of soaps from solution. The froth height at pH 10.7 with additions of sodium chloride showed increased turbidity and reduced froth height with increasing additions of salt.

Titration of a sample of BDH "technical grade" sodium oleate after filtration to remove any insoluble material was conducted by Agars (1976). The titration curve suggested a pKa value of approximately 5.5. This same reagent was used to float manganese ions using a 2 m froth column at pH between its initial value of 10.9 down to 3.5. Observations included a decrease in frothiness as the pH was lowered, with a limit where there was no froth at pH 8. The addition of oleate corresponded to 3.64 mM. High purity nitrogen was used to generate the froth.

Nunez and Yalkowsky (1997) measured the foaming activity of potassium oleate as a function of pH and compared the rapid change in foam height to the reported values of pKa. They found that the rapid increase in foam height occurred at pH ~ 5, and compared this with literature pKa values of 4.8 and 5.0 as reported by Somasundaran and Ananthapadmanabhan (1978). Nunez and Yalkowsky (1997) used this method of determining the onset of foaming activity to estimate the value of the pKa for a number of surfactants.

Atrafi et al. (2012) measured the frothing behaviour of oleic acid as a function of pH. At pH 7.1, no foaming occurred for the addition of 20 mg/L sodium oleate. As the pH was raised, the foaming of the oleic acid solutions was significantly enhanced, although a small decrease was observed between pH 9 and 10. The authors reported very high foam growth rates and volumes at pH values below the pH of oleic acid precipitation (pH 8.4), which was interpreted that small to moderate amounts of precipitates played a synergistic role in the foam flotation process.

More recent data on the foaming characteristics of oleate have been reported by Shu et al. (2014). They reported a maximum in foam volume at pH 10.02 for a solution containing 8 g/L oleic acid. The foam volume was still high at pH 12.19. These authors postulated that the pKa of oleic acid was 9.89, much higher than that measured for saturated fatty acids by the author (Quast, 2016d).

Atrafi and Pawlik (2016) measured the bubble size distributions as a function of oleate concentration and its associated pH. At pH 10, bubble size was small (~1.5 mm) and independent of pH or oleate concentration. At lower oleate additions and lower pH values, the average bubble sizes were larger (~3 mm) corresponding to the dominance of colloidal species resulting from the lower solubility of the oleate. Since the concentration of insoluble precipitate increases at lower pH at the expense of other species, the authors concluded that oleic acid