

The use of zeta potential to investigate the interaction of oleate on hematite



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ARTICLE INFO

Article history:

Received 29 June 2015

Revised 27 September 2015

Accepted 6 November 2015

Available online 14 November 2015

Keywords:

Zeta potential

Oleate

Hematite

Isoelectric point

Effect of silica

ABSTRACT

The aim of this paper was to investigate how the use of zeta potential measurements on the hematite–oleate system as a function of pH could provide additional information on this system. From the literature survey it was found that the presence of oleate causes a reduction in both the zeta potential and isoelectric point of hematite compared to their values in the absence of oleate. There have been a number of suggested mechanisms including the adsorption of soluble oleate solution species and precipitation of oleate salts and/or oleate colloids or micelles, depending on the pH and the concentration of oleate in solution. These phenomena were investigated using two hematite samples containing differing amounts of silica. The results for oleate addition to the hematite sample containing the lower amount of silica followed the anticipated trends indicating lower values of zeta potential and isoelectric point with increasing oleate addition. The situation for the hematite sample containing the higher amount of silica, even though it only contained 2.5% silica, was more complex. Although the increased addition of silica reduced the values of the zeta potential, there appeared to be a major influence of the silica driving the values of the zeta potential below those of the oleate at acid values of pH. It was proposed that this was due to a combination of the presence of silica and oleate, suggesting that the mechanism was the physical adsorption or heterocoagulation of colloidal hematite on fine silica followed by the adsorption of oleate species onto the hematite. An attempt was made to correct the equilibrium oleate concentration to account for the adsorption of oleate onto the surface of the hematite, but this was only significant at the very low addition rate of the oleate.

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1. Introduction

The author has investigated and published a number of articles on the surface chemistry and flotation of hematite over many years (Quast, 1999, 2000, 2005, 2006, 2010, 2012, 2015a,b; Quast and Quast, 2010). Most of these articles involved the measurement of the interfacial chemistry characteristics of the hematite surface and laboratory flotation tests conducted on these hematite samples as a function of pH. It is the purpose of this paper to investigate how the use of zeta potential measurements on hematite as a function of pH in the presence of oleate can provide additional information on the interaction of oleate species with the hematite surface as a function of pH. This can be seen as complementing the detailed analysis of the hematite–oleate system at pH 7 previously published by the author (Quast, 2010). At pH 7, the interaction of oleate with hematite was confirmed as chemisorption, with the orientation of the adsorbed oleate species progressing from horizontal to two-point to vertical as the addition of oleate was

increased. It is the purpose of this paper to report details of an experimental study involving the effects of oleate addition on two samples of naturally occurring hematite containing different levels of impurities.

2. Literature survey

2.1. Surface chemistry of the oleate/aqueous system

A reference located in searching electronic databases by Swaroop (1970) provided information concerning measurements of zeta potential of aqueous solutions of sodium oleate, oleic acid and a 1:1 mixture of the two species at pH 4.5. This was close to the accepted value of the pKa of fatty acids, as used in the construction of solution equilibria diagrams referred to later. Under these conditions, the concentration of undissociated oleic acid should dominate over oleate ions. Swaroop's numerical data was plotted by the current author in Fig. 1. The obvious difference between Swaroop's data and that of all other data obtained is that all the values of zeta potential are positive. I have plotted the solubility

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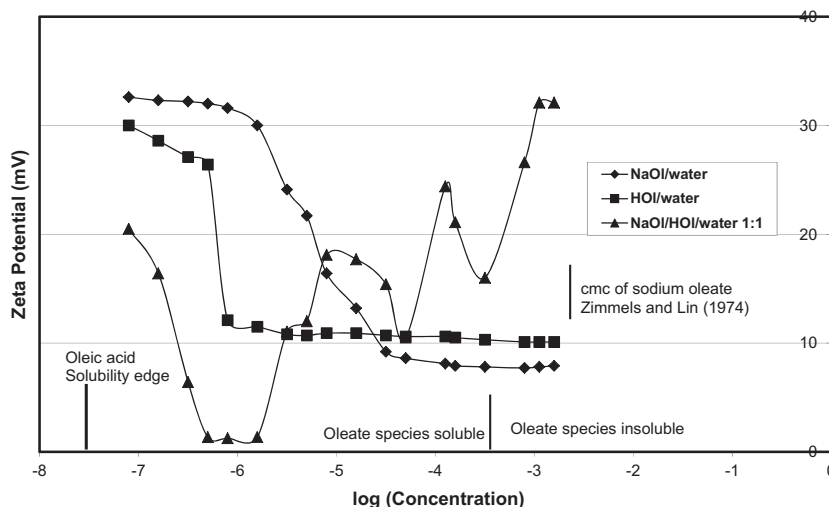


Fig. 1. Zeta potential as a function of log (concentration) (molar) of oleate species at pH 4.5 and 35 °C (data of Swaroop, 1970).

transition between soluble and insoluble species from Swaroop, plus the generally accepted values of the aqueous solubility of oleic acid and the critical micelle concentration from Zimmels and Lin (1974). Although the values of whatever species are being measured in Fig. 1 are often reduced with increasing addition of reagents, the values still remain positive. Positive oleate species have been identified by Laskowski and his co-workers (see later), but at pH values lower than 4.5. Swaroop (1970) reported that the sodium oleate is present as micelles, even though the additions are below the accepted value of the cmc. The oleic acid is assumed to be present as an emulsion. There are major changes in the zeta potentials of oleic acid and sodium oleate at approximately 10^{-6} and 10^{-5} molar respectively, a finding also reported by other authors (see later). The peaks in the zeta potential/pH curve were accompanied by visual changes in the brightness of the field of view.

Drzymala (1985) calculated the surface charge on oleic acid droplets as a function of pH which showed a high value of surface charges, from approximately $-200 \mu\text{C}/\text{cm}^2$ at pH 5 to $-700 \mu\text{C}/\text{cm}^2$ at pH 8. These values were seen as unrealistic since the theoretical maximum surface charge should only be $128 \mu\text{C}/\text{cm}^2$ based on the cross-sectional area of the carboxyl group of the oleic acid molecule. The experimental titration curves for the oleic acid could better be explained by the formation of spherical aggregates of 0.2–0.3 μm in diameter consisting of fine oleic acid droplets similar in size to micelles, the formation of mesospheres of similar size containing both oleic acid and oleate ions, the formation of acid soap (HOI–NaOI) at intermediate values of pH and the presence of micelles in addition to oleic acid droplets and simple oleate species. These characteristics emphasise the complexity of the oleic acid–aqueous system as a function of pH. The equilibrium diagram for the aqueous oleic acid system has been reported and discussed by many authors (e.g. Somasundaran and Ananthapadmanabhan, 1979; Ananthapadmanabhan et al., 1979; Kulkarni and Somasundaran, 1980; Yap et al., 1981; Ananthapadmanabhan and Somasundaran, 1981; Pugh and Stenius, 1985; Pugh, 1986; Morgan et al., 1986; Jung et al., 1987; Antti and Forsberg, 1989) and a graph based on the data reported by Jung et al. (1987) is presented in Fig. 2. This shows the increasing value of the pH of the limit of solubility of oleate as the concentration of added oleate is increased. It also highlights a major area in the acid pH region where oleic acid is present as insoluble phases, variously described as oleic acid droplets, emulsions, insoluble films etc.

Drzymala (1987) used the experimental zeta potential data of Lekki to estimate the changes in the surface potential of oleic acid in NaCl solutions. These data are plotted in Fig. 3. Drzymala (1987) assumed that the measured values of zeta potential represented the values in the diffuse layer of the oleic acid–aqueous interface. These data showed that the values of the zeta potential linearly progressed from -37 mV to -100 mV as the pH was increased from 3 to 7 in 10^{-3} M NaCl. Surface potentials were calculated to change from 0 (extrapolated) to approximately -230 mV as the pH was raised from 2 to 7. The intrinsic ionisation constant was estimated as 4.4.

Vurdela and Laskowski (1987) measured the isoelectric points of a number of fatty acids, including sodium oleate using microelectrophoresis. The values of the isoelectric points were all around 3, in agreement with the hypothesis of Jung et al. (1987).

Laskowski (1988) reported the electrophoretic mobility characteristics for oleic acid as a function of pH. The isoelectric point for oleic acid was measured as 2.5. This meant that chemisorption of oleate occurs in alkaline solutions while the precipitation of oleic acid on the mineral surface was responsible for its physical adsorption in an acidic environment. In addition, the isoelectric point of microbubbles in aqueous solutions of sodium oleate was also around pH 3 (Laskowski et al., 1989).

Laskowski (1993) described how the changes in the zeta potential and isoelectric points of minerals in the presence of fatty acids can be explained by the presence of colloidal species in solution. These colloidal precipitates have isoelectric points around 2–3, and apparently coagulate/precipitate onto solid particles and bubbles and determine the zeta potential–pH relationship for the mineral particles and bubbles generated in such solutions. Laskowski suggested that the interpretation of the electrokinetic measurements carried out in aqueous solutions of weak electrolyte surfactants may lead to erroneous conclusions if the presence of such colloidal species is ignored. He cited cases for hematite (Akhtar and Lai, 1975) and values of the effects of sodium salts on the zeta potentials of siderite. When the isoelectric data of Akhtar and Lai (1975) for the hematite–oleate system were superimposed onto a domain diagram for the oleic acid–water system, the dramatic change in isoelectric point of the hematite corresponded very well to the change from oleic acid being in the colloidal suspension to that of oleate ions being present in true solution.

Kaibara et al. (1997) used turbidity and light scattering techniques to suggest a very complex series of oleate complexes

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