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Flotation of hematite using C6–C18 saturated fatty acids ☆

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Abstract

The homologous series of saturated fatty acids investigated in this study generally show a steady gradation of properties with chain length. The solution pK_a values were assumed constant at 4.9, however reported pK_a values could be lower or higher. Hematite flotation response and surface pressure for aqueous solutions of these fatty acids were measured as a function of pH. For the shorter chain fatty acids, the undissociated acid was shown to be the predominant surface active species with flotation, supplemented by the physical adsorption of acid anions as the chain length increased. The reduced solubility of the longer fatty acid carbon chains made these reagents ineffective as flotation agents. The maximum flotation response of hematite using tetradecanoic acid corresponded with the precipitation edge of the reagent. The results show that the values of surface pressure of the surfactants are not always a good indication of their effectiveness as flotation collectors.

Keywords: Flotation reagents; Flotation collectors; Iron ores

1. Introduction

The dependence of the characteristics of the hematite–aqueous interface and aqueous soap solutions on pH have been known for a long time, but little attention has been given to the correlation between the solution properties of the mineral and soap and the resultant flotation upon aeration of the suspension. Kulkarni and Somasundaran (1975) published results for the hematite–oleate system and showed how the solution species, in particular the concentration of oleate acid–soap control the flotation of the hematite. Surface tension of the oleate solution could also be correlated to the flotation behaviour, and the concentration of the acid–soap species. In a later publication, Ananthapadmanabhan and Somasundaran (1981) gave a linear plot between the pH of maximum flotation of hematite and the pH of minimum surface tension as a function of oleate concentration. These data fell on a single line and was used to demonstrate how they are both coincident with the maximum of oleate acid–soap concentration. The changes in the surface tension of aqueous oleate solutions with pH has been revisited in recent publications (e.g. De Castro and Borrego, 1995; Theander and Pugh, 2001).

Beunen et al. (1978) showed mathematically that the surface tension minimum could be accounted for by considering the undissociated acid as representing a reservoir of surfactant molecules that dissolved as the pH was raised. This increase in surfactant concentration resulted in increased adsorption at the interface with a consequent lowering of surface tension. As the pH passed through a certain value, the so-called solubility edge, the solution concentration became constant. Further increases in pH caused increasing electrostatic repulsion of the negative surfactant from the interface causing an increase in surface tension, leading to a surface tension minimum at the solubility edge.

It is the purpose of this paper to investigate the flotation of hematite using saturated fatty acids with six to 18

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carbon atoms in the chain. It is hoped that the correlation between flotation recovery and the surface tension of the soap solution will allow the formulation of a model for the flotation of hematite using these reagents.

2. Literature survey

2.1. Hematite surface chemistry

The electrical nature of the hematite–water interface is the result of the hydrolysis of the surface species followed by pH-dependent dissociation of the surface hydroxyls. A characteristic property of the hematite surface is the condition under which the surface charge is zero. This is called the zero point of charge (zpc) and is usually determined by some form of acid–base titration technique. Surface characteristics can also be investigated using electrokinetic phenomena, which involve the inter-relation between mechanical and electrical effects at a moving interface. Electrokinetic results are generally expressed in terms of the zeta potential, which may be calculated from the electrophoretic mobility of particles through a field of known strength. The term, isoelectric point (iep) refers to conditions under which the zeta potential is zero. The surface potential need not be zero when the zeta potential is zero, particularly in the case of specifically adsorbed ions, hence the zpc and iep need not be the same. Kosmulski (2001) has tabulated many values of the iep of naturally occurring samples of hematite, with values ranging from 5.3 to 7.8. Kulkarni and Somasundaran (1976) determined the iep of a natural hematite sample to be 3.0, whereas the zpc of the *same* hematite, using titration techniques, was determined as 7.1. The explanation for these results was mineral heterogeneity i.e. the presence of fine silica in the hematite exerted its influence on the surface properties measured by electrophoresis.

2.2. Saturated fatty acids containing 6–18 carbon atoms

The reagents used were straight chain, saturated fatty acids containing between six and 18 carbon atoms in the chain. The fatty acids will be designated by C plus the number of carbon atoms e.g. hexanoic acid is C6. Some physical properties are listed in Table 1. The data for this table was taken from Kirk-Othmer (1993) and Markley (1960).

Table 1
Physical properties of saturated fatty acids

Acid	M.Wt.	M.Pt. (°C)	B.Pt. (°C)	Density (g/ml)	Surface tension (mN/m) 70 °C
C6	116.2	−3.4	205.8	0.929	23.4
C8	144.2	16.7	239.7	0.910	23.7
C10	172.3	31.6	270.0	0.895	25.0
C12	200.3	44.2	298.9	0.883	26.6
C14	228.4	53.9	326.2	0.858	27.4
C16	256.4	63.1	351.5	0.853	28.2
C18	284.5	69.6	376.1	0.847	28.9

For the purpose of this study it is more relevant to consider solution properties of these acids, some of which are listed in Table 2. The data for this table was taken from Landolt-Bornstein (1960), Stainsby and Alexander (1949), Kirk-Othmer (1993), Fuerstenau and Palmer (1976) and Cary and Rideal (1925).

The acidity constant K_a, is a fundamental solution property of fatty acids. As seen from Table 2, there are a number of values given in the references cited. A number of workers have taken literature values for the pK_a of the short chain fatty acids in water and extrapolated it to obtain an overall pK_a value for the aliphatic carboxylic acids. The pK_a values determined in this way include 4.7 (Du Rietz, 1958), 4.8 (Perrin et al., 1981), 4.9 (John and McBain, 1948; Lucassen, 1966), 4.9–5.0 (Jukes and Schmidt, 1935), 5.1 (Halford, 1931) and 5.3 (Sutherland and Wark, 1955). The data used in this study for determining the solubility of the fatty acids as a function of pH was that of Lucassen (1966).

The solubilities of the fatty acids in water listed in Table 2 decrease with increasing chain length as would be expected. Solution aggregation, as determined by the concentration at which a measured solution property changes abruptly over a narrow concentration range, is usually reported as a critical micelle concentration. This coincides with the onset of the formation of substantial amounts of colloidal aggregates in solution, and this must be taken into account in the determination of the solubility characteristics of the fatty acids.

The solubility of some of the fatty acids as a function of pH was determined using the data of Lucassen (1966) and plotted as Fig. 1 for C10–C18. Another solution characteristic of surfactant solutions is their surface tension, usually expressed in the units of mN/m. The surface tension of the aqueous fatty acid solutions reported in this paper were measured using a du Nouy Tensiometer, where the force necessary to pull a ring from the surface was correlated to the surface tension of the solution. The surface pressure, Π, is related to the surface tension, γ, by

$$\Pi = \gamma_0 - \gamma$$

where γ_0 is the surface tension of the solvent. The surface pressure represents the lowering of the surface tension due to the addition of the solute.

Powney (1935) investigated the effect of pH on the surface tension of oleate and laurate solutions, and reported a

Table 2
Solution properties of saturated fatty acids

Acid	pK_a	Sol. in water (M)	Cmc (M)	ESP on 0.01 N HCl (mN/m)
C6	4.86	8.3×10^{-2}	1.0×10^{-1}	
C8	4.90	4.7×10^{-3}	1.4×10^{-1}	
C10		3.0×10^{-4}	2.4×10^{-2}	
C12	4.80	1.2×10^{-5}	5.7×10^{-2}	25.0
C14	5.75	1.0×10^{-6}	1.3×10^{-2}	14.2
C16	4.70	6.0×10^{-7}	2.8×10^{-3}	11.3
C18	4.75	3.0×10^{-7}	4.5×10^{-4}	4.2