

The adsorption behavior of surfactants on mineral surfaces in the presence of electrolytes – A critical review

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ABSTRACT

How saline water affects the adsorption of surfactants on mineral surfaces and the subsequent flotation behavior is still unknown despite the widespread application of saline water in mineral flotation. However, in the field of surfactants, the effect of electrolytes on the adsorption of surfactants on solids has been well studied. This paper presents a comprehensive review of surfactant adsorption on solids in the presence of electrolytes based on the previous research findings. The review shows that the presence of electrolytes significantly influences the solubility and aggregation of surfactants in the liquid phase either through electrostatic interactions or “salting-in” and “salting-out” effects. In the process of surfactant adsorption on solids, electrolytes influence the adsorption density of ionic surfactants and non-ionic surfactants by affecting the surfactant-surfactant interactions and surfactant-solid interactions. Once surfactants adsorb on solids, electrolytes modify the structure and morphology of adsorbed surfactant layers and even induce the structural transition. This paper provides a thorough understanding of surfactant adsorption on solids in the presence of electrolytes and guides the application of surfactants in mineral flotation using saline water.

1. Introduction

Froth flotation has been widely applied in the concentration of valuable minerals from low-grade ores and in the ash reduction of fine coals. Flotation is a complicated process involving the collision between particles and bubbles, the attachment of particles to bubbles and the formation of stable particle-bubble aggregates (Dai et al., 2000). The surface wettability of mineral particles is crucial to determining the flotation efficiency since only the hydrophobic particles can attach to the rising air bubbles and be recovered. Surfactants consisting of both hydrophilic polar groups and hydrophobic alkyl chains are able to adsorb at a liquid-air or solid-liquid interface and play a critical role in mineral flotation.

In flotation, surfactants are commonly used to reduce the bubble size and form a stable froth by adsorbing at liquid-air interfaces as frothers. The application of surfactants as frothers in flotation has been extensively investigated and reviewed (Rao et al., 1982; Laskowski, 1993; Cho and Laskowski, 2002; Farrokhpay, 2011; Khoshdast and Sam, 2011).

Meanwhile, in flotation, surfactants are also used to modify the surface wettability of mineral particles by adsorbing at solid-liquid interfaces as collectors. For example, amphiphilic surfactants with both hydrophilic polar groups and hydrophobic alkyl chains are used to

improve the flotation of oxidized coals (Harris et al., 1995; Sarikaya and Özbayoğlu, 1995; Renhe Jia and Fuerstenau, 2000; Qu et al., 2015) since conventional oil collectors are unable to achieve a satisfactory combustible recovery due to the presence of oxygen-containing groups on coal surfaces (Sun, 1954; Sarikaya and Özbayoğlu, 1995; Bolat et al., 1998; Chang et al., 2017). The polar groups of surfactants can interact with the oxygenated groups on coal surfaces through hydrogen bonding or electrostatic attraction with the hydrocarbon chains oriented outwards to enhance the surface hydrophobicity (Dey, 2012). In the flotation of sulphide minerals such as pyrite, chalcopyrite, galena and sphalerite, xanthates composing of alkyl chains and xanthogenate groups are most commonly used as the collectors (Fuerstenau et al., 1968; Leppinen et al., 1989; Herrera-Urbina et al., 1999; Miller et al., 2002; Zhang et al., 2013). Xanthogenate groups can bind to the metal atoms on mineral surfaces with the alkyl chains oriented into the liquid phase. Surfactants have also been applied in the flotation of other types of minerals. For example, Sis and Chander (2003) demonstrated that the flotation efficiency of phosphate was significantly improved by the addition of non-ionic nonylphenol polyethylene glycol ether. Deng et al. (2016) reported that 2-amino-6-decanamidoheptanoic acid effectively recovered diaspore from bauxite ores containing aluminosilicate minerals by adsorbing on diaspore surfaces through the formation of Al–O and Al–N bonds. However, the influence of surfactants on

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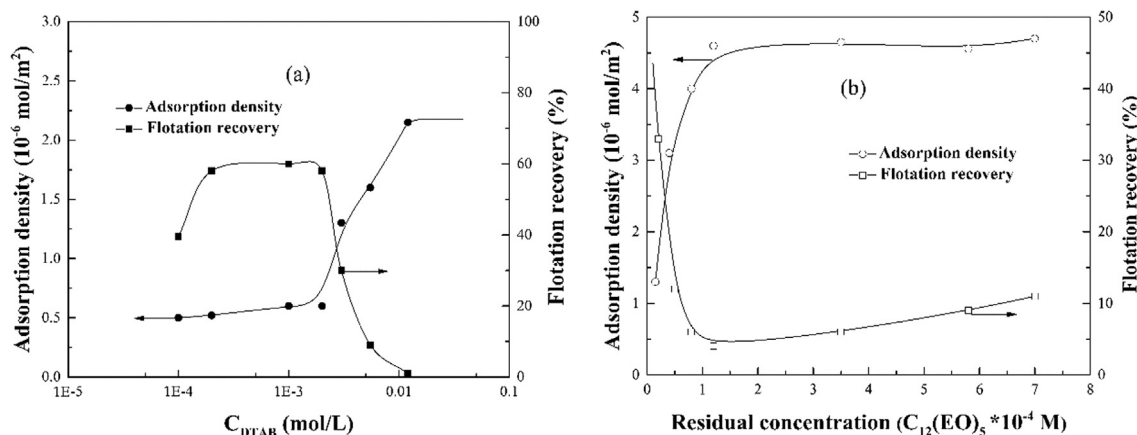


Fig. 1. (a) DTAB adsorption (●) and flotation recovery (■) of silica as a function of DTAB concentration at 0.001 M KCl and at pH 9 (reproduced from Koopal et al. (1999)); (b) adsorption of C₁₂(EO)₅ (○) and flotation recovery of talc (□) as a function of the residual concentration of surfactant. Reproduced from Pugh and Tjus (1990).

mineral flotation is not monochromatic. The flotation efficiency may be decreased by surfactants at high surfactant concentrations (Pashley and Israelachvili, 1981; Scamehorn et al., 1982; Bremmell et al., 1999; Cao et al., 2006; Chwastiak, 2009; Wang et al., 2016).

The effects of surfactant adsorption on flotation behavior are mainly determined by the orientation of surfactant molecules on mineral surface. When surfactant adsorption occurs with the hydrophilic polar groups attaching to mineral surfaces and the hydrophobic hydrocarbon chains oriented towards the liquid phase, which is termed as “head-on” adsorption, the surface hydrophobicity of minerals and flotation efficiency are enhanced. On the other hand, the surface hydrophobicity of minerals and flotation efficiency are reduced when surfactant adsorption occurs with the hydrocarbon chains attaching to the mineral surface and the polar groups oriented towards the liquid phase, which is termed as “head-out” adsorption. Koopal et al. (1999) reported that the recovery of silica passed through a maximum with the adsorption of cationic surfactant dodecyl trimethylammonium bromide (DTAB) as shown in Fig. 1a. At a low surfactant concentration, the flotation recovery of silica increased from ~40% to ~60% with an increase in surfactant concentration, which was attributed to the “head-on” adsorption of DTAB on silica. However, at a high surfactant concentration, the flotation recovery of silica dropped from ~60% to ~0% with the further adsorption of DTAB, which was ascribed to the “head-out” adsorption of DTAB on silica. The depression of flotation by surfactant adsorption was also reported in the flotation of hydrophobic minerals. Pugh and Tjus (1990) found that the flotation recovery of talc decreased from ~44% to ~6% with the adsorption of polyethylene oxide non-ionic surfactant C₁₂(EO)₅, as shown in Fig. 1b. This was caused by the adsorption of hydrophobic part of the surfactant on the mineral surface resulting in the decrease of mineral surface hydrophobicity.

Due to the scarcity of freshwater and the concerns of environment protection, flotation plants have been driven to minimize the use of freshwater. The use of recycled water, groundwater and seawater results in an increase in the salinity of process water. In Western Australia, bore water containing high ionic strength has been used by the large nickel deposits for the flotation of pentlandite (Peng and Seaman, 2011; Peng et al., 2011; Peng and Bradshaw, 2012). In Chile, seawater is frequently used for the flotation of Cu-Mo sulphide ores since the mine sites are located in marine areas with limited resources of freshwater (Castro, 2012; Castro et al., 2012; Laskowski et al., 2014). Table 1 shows the ionic composition of seawater used in Cu-Mo flotation plants in Chile. It can be seen that the water contains a high concentration of Mg²⁺ (approx. 1300 ppm) and Ca²⁺ (more than 400 ppm) (Castro et al., 2012). In South Africa, saline water is also used for the recovery of platinum group elements through flotation (Wang and Peng, 2014). In Australia, water reuse has led to the high salinity of

process water in coal preparation plants (Ofori et al., 2010).

Despite the widespread application of saline water in mineral flotation, the effects of saline water on the adsorption of surfactants on mineral surfaces and the subsequent flotation performance are unclear. In the field of surfactants, it has been demonstrated that electrolytes have a great effect on the adsorption of surfactants on solids (Atkin et al., 2003; Biswal and Paria, 2010; Tucker et al., 2012; Zhang et al., 2015). It is expected that electrolytes may affect mineral flotation by modifying surfactant adsorption on mineral surfaces. In the following sections, this paper reviews the effect of electrolytes on the sub-processes of surfactant adsorption on solids.

2. Effects of electrolytes on the solubility and aggregation of surfactants in liquid phase

Most surfactants have a good solubility in water due to the hydrogen bonding between the polar groups of surfactants and water molecules. However, the solubility of surfactants is easily influenced by temperature and water salinity (Rico-Rico et al., 2009). Another characteristic of surfactants is the formation of aggregates in solution which is an entropy-driven process (Fernández-Castro et al., 2011; Bickel et al., 2014; Liu et al., 2016). The onset concentration of surfactants to form micelles is called the critical micelle concentration (CMC) which can also be influenced by the presence of electrolytes (Wennerstrom et al., 1991; Ahmadi et al., 2014). In general, surfactants can be classified into ionic surfactants and non-ionic surfactants depending on the type of the hydrophilic polar groups. The effects of the electrolytes on the solubility and aggregation behavior vary with the type of surfactants.

2.1. Ionic surfactants

2.1.1. The solubility of ionic surfactants

Multivalent metal ions, such as Ca²⁺, Mg²⁺, Ba²⁺ and Al³⁺, can significantly reduce the solubility of ionic surfactants in solution since they can bind to the surfactant ions through electrostatic attraction (Peacock and Matijević, 1980; Baviere et al., 1983; Matheson et al., 1985; Talens-Alession, 1999; Rico-Rico et al., 2010; Yu et al., 2012). The reduction of water solubility of surfactants by electrolytes may limit the application of surfactants in mineral flotation. For example, when using fatty acids as fluorite collectors, calcium ions in the liquid phase can interact with fatty acid ions under certain conditions through electrostatic attraction and form calcite-fatty acid complexes. It was reported that fluorite flotation was not affected significantly when the complexes precipitated at mineral surfaces but was depressed when the complexes formed out in the bulk solution due to the decrease of the collector

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