Bubbles facilitate ODA adsorption and improve flotation recovery at low temperature during KCl flotation

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ABSTRACT

Understanding the adsorption process of collectors and the interaction between bubbles and mineral particles during KCl froth flotation are still weaknesses in our interpretation of the mechanism of flotation. In this study, we investigated in detail the adsorption kinetics and adsorption isotherm of a commonly used collector, octadecylamine hydrochloride (ODA), at the surface of KCl crystals. The effects of bubbling and temperature are discussed systematically. Our results indicated that the adsorption of ODA onto the surface of KCl crystals can be facilitated by bubbles, and that the adsorption kinetics of this process can be interpreted according to a pseudo-second order model. Both the Langmuir and Freundlich isotherm models were found to fit the adsorption isotherm of ODA on KCl crystal surface inappropriately, implying that the adsorption of ODA upon KCl crystal surfaces is a more complex process than typical monolayer, or multilayer, adsorption. This might be because the adsorption of ODA on KCl crystal surfaces takes place through an aggregated intermediate, rather than through the direct interaction of dispersed molecules. We note that the quantity of ODA adsorbed at $0\,°C$ increased markedly with increasing numbers of bubbles. Micro-flotation tests suggested that increasing the gas flow rate effectively improved flotation recovery at $0\,°C$, consistent with the adsorption behavior. These results provide complementary information on the adsorption behavior of ODA at the surface of KCl crystals and on the effect of bubbles during froth flotation, which could help to design new flotation process and improve flotation recovery of KCl at low temperatures.

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1. Introduction

Froth flotation, an efficient means of separating heterogeneous mixtures of finely subdivided solids, is still widely used within the primary mineral and chemical industries (Du et al., 2014; Esmaeili et al., 2015; Fuerstenau et al., 2007; Hernáinz and Calero, 2001; Park and Wang, 2015; Xia et al., 2016). Potash is an essential raw material that most notably finds use as an agricultural fertilizer (Li et al., 2015). Currently, over 80% of the world's potash is produced by froth flotation from other more complex salts (Du et al., 2014; Hernáinz et al., 2003; Wang et al., 2014).

However, in northwestern China, especially within the Qaidam basin salt lake area, the effects of low temperature reduce flotation recovery and force a break in sylvite production during the winter months. A better understanding of the mechanisms underlying flotation might allow recovery at low temperatures to be improved, increasing yield and avoiding the annual shut-down.

Octadecylamine hydrochloride (ODA) is an efficient collector commonly used, in KCl flotation. Typically, during the process of froth flotation, the hydrophilic head groups of ODA become adsorbed onto the surface of KCl crystals, while the hydrophobic hydrocarbon tails are recruited to bubbles. The KCl crystal then floats to the surface with the rising bubble. The adsorption of ODA on the surface of KCl crystals is therefore one of fundamental determinants of the efficacy of the flotation process. Many previous studies have investigated the selective adsorption of collectors on the surfaces of KCl crystals, in preference

to NaCl or other crystals, and several different models have been proposed (Fuerstenau and Fuerstenau, 1956; Hancer et al., 2001; Rogers, 1957). The details of the adsorption process of ODA on the surface of KCl crystals, however, including the calculation of adsorption kinetics and adsorption isotherm models, remain poorly understood. Understanding the adsorption behavior of ODA during its interaction with the surfaces of KCl crystals is critical for the optimization of the adsorption mechanism and the effective control of adsorption systems (Foo and Hameed, 2010; Xu et al., 2015).

The presence of bubbles is indispensable during froth flotation (Painmanakul et al., 2010; Shahbazi et al., 2010). When bubbles are introduced into the flotation system, much more of the collector becomes adsorbed preferentially at the air/liquid interface (Smolders, 1961). Leja and Schulman (1954) suggested that the collectors adsorbed upon bubbles will be transferred to the solid/liquid interface during collisions with the main surface. This collector transfer process was conclusively demonstrated by Burdukova and Laskowski (2009). In addition, Laskowski (2013) proposed that the amines adsorbed upon the surface of bubbles could spread into a molecular film; these bubbles with an amine molecular film were considered 'active bubbles', which easily pick up KCl particles. In summary, the transfer of collectors indicates that the presence of bubbles can effectively facilitate the adsorption of collectors on KCl crystal surfaces.

In order to obtain more information on the effects of bubbles on the adsorption behavior of ODA upon the surfaces of KCl crystals, and to shed light on the relationship between the flotation mechanism and this adsorption behavior, we have investigated the adsorption kinetics and adsorption isotherm model through the comparison of systems with or without bubbles. The effects of changes in temperature are also discussed for all systems, with a special focus on adsorption behavior at low temperature. Micro-flotation tests are conducted with different levels of bubbling at low temperature to interpret the effect of bubbles on ODA adsorption behavior. This work constitutes a substantial step forwards in our understanding of the froth flotation of KCl and provides new insights into means by which flotation recovery at low temperature may be improved.

2. Experimental

2.1. Materials

Octadecylamine hydrochloride (ODA) was purchased from Tokyo Chemical Industry Co., Ltd. Potassium chloride, sodium acetate, acetic acid, and chloroform were obtained from Tianjin Hengxing Chemical Industry. Acid orange II was produced by the Tianjin Institute of Chemicals. All reagents were analytical-reagent grade, and were used without further purification. Millipore water (Milli Q, Millipore Corp., 18.2 MΩ cm) was used for all experiments.

A saturated KCl solution was prepared by dissolving an excess of KCl in water at 0 °C, 15 °C and 25 °C, respectively, which is consistent to the temperature for adsorption process. The mixture was agitated for 12 h and allowed to equilibrate for 24 h to achieve saturation and then filtered to remove all insoluble impurities and residual salt particles. All glassware was soaked in chromic acid, rinsed with purified water and dried prior to use.

2.2. Adsorption experiments

Firstly, ODA was dispersed into 100 mL of saturated KCl solution to the reported concentration. Then 10 g of KCl particles (80 × 100 mesh) was added and the resulting mixture stirred for the reported time. For experiments incorporating bubbling, 10 mL/min nitrogen was introduced into the system during the adsorption process to investigate the effect of bubbles

on adsorption behavior. The temperature of the adsorption process was controlled by using a thermostat circulating, water/ethyl alcohol bath.

2.3. Measurement of the concentration of ODA in saturated KCl solutions

In order to estimate the quantity of ODA adsorbed on KCl crystals, the concentration of residual ODA in the saturated KCl solution has to be measured first. After the adsorption process, 20 mL of liquid was transferred to a separating funnel followed by the addition of 1 mL of acid orange II [2%(w/w)] and 2 mL of HAC-NaAC buffer solution (pH 5.0). After five minutes agitation, 20 mL of chloroform was added to extract the complex of ODA and acid orange II. The concentration of the lower layer was measured by using UV–vis spectrophotometer (UV-1601, Beijing Beifen-Ruili Analytical Instrument Co., Ltd.) which can measure the concentration of organic chemicals in solutions with high ionic strength simply and accurately. For this measurement, the wavelength was set to 485 nm, at which the ODA-acid orange II complex adsorbs maximally.

The resulting value is the concentration of ODA in saturated KCl solution at time t, C_t (mol/L). The adsorption quantity (q_t, mol/g) was then calculated according to:

$$q_t = \frac{C_0 - C_t}{m} \tag{1}$$

where C_0 is the initial concentration of ODA (mol/L) and m is the amount of KCl (g).

It is noted that the calibration curve of ODA in saturated KCl solution needs to be conducted first before the samples test by using the UV–vis spectrophotometer.

2.4. Micro-flotation tests

Micro-flotation tests were conducted using a micro-flotation column developed on the basis of a previous study (Hancer, 2000). For each flotation test, ODA was dispersed in 120 mL of saturated KCl solution of the desired concentration for 5 min, before the addition of 3 g of KCl particles (80 × 100 mesh), followed by another 5 min of stirring. The mixture was then transferred into the micro-flotation column and the sample floated at 0 °C for 1 min with 10 mL/min nitrogen. The temperature was controlled using a connected thermostat, circulating water/ethyl alcohol bath. The flotation concentrate and tailings were collected by filtration and dried at 110 °C for 4 h in an oven.

3. Results and discussion

3.1. Adsorption equilibrium time

Adsorption equilibrium is the state in which the adsorbate concentration in the bulk solution is in a dynamic equilibrium with the solution/adsorbent interface concentration after the adsorbate-containing phase has been in contact with the adsorbent for a sufficient time period (Foo and Hameed, 2010; Gedam and Dongre, 2015; Ghiaci et al., 2004; Hu et al., 2014; Kumar and Sivanesan, 2007). Adsorption equilibrium time corresponds to the time at which the adsorbate cannot be adsorbed on the adsorbent any further. The relationship between the amount of ODA adsorbed upon the surface of KCl crystals and the adsorption time with or without bubbles