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Ionic liquids as novel quartz collectors: Insights from experiments and theory

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HIGHLIGHTS

- Quaternary ammonium based IL's attempted as collectors for quartz flotation.
- Effect of alkyl chain length assessed through XPS and molecular modelling.
- IL–quartz interaction governed by van der Waals and electrostatic forces.
- IL with 6 carbon in alkyl chains gives the maximum coverage and floatability.
- IL's are found to be better than conventional quartz collectors.

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ABSTRACT

Application of quaternary ammonium based ionic liquids (IL's) as flotation collectors of quartz has been investigated. Effect of number of carbon atoms in the four identical alkyl chains of the IL's has been studied. The adsorption behaviour of the IL's on the quartz surface is ascertained through FTIR, XPS and molecular modelling. The FTIR peak at 2900 cm^{-1} indicates the adsorption of the IL's onto the quartz surface, which is further substantiated by the appearance of the N (1S) peak in the X-ray photoelectron spectra (XPS). Curve splitting data of C (1S) suggests the maximum adsorption for the IL tetrahexylammonium iodide (THEX). Flotation results of pure quartz using ionic liquids are found to be better compared to the conventional collectors such as dodecylamine (DDA) or cetyltrimethylammonium bromide (CTAB). It is possible to float 92–100% quartz by using a THEX concentration of 4.8×10^{-5} M. IL collectors are further applied in the flotation of a low grade banded hematite quartzite (BHQ) iron ore with ~38% Fe. It is possible to achieve an iron concentrate of 63.6% Fe at 63.2% recovery by using THEX as the collector. Molecular simulations using the COMPASS forcefield explains the IL–quartz adsorption mechanism comprising of both electrostatic and van der Waals forces. Floatability of quartz has been correlated with the surface coverage and adsorption energy calculations. The IL's used here are found to be better quartz collectors than the conventional ones as they show better collecting efficiency in lower dosages. Flotation using these IL's does not require frothers which is an added advantage compared to the conventional collectors.

1. Introduction

Quartz is a naturally occurring mineral associated with almost all the ores. It needs to be separated from the ore in order to achieve a suitable concentrate of the valuable mineral leading to an economic extraction of the metal values. Froth flotation is a process by which the hydrophobic particles of a finely divided ore are separated from the hydrophilic particles. The addition of selective reagents induces hydrophobicity in the desired mineral particles, which get attached to air bubbles and report in the froth phase. In quartz flotation, primary monoamines and their corresponding acetate or chloride derivatives have been long used as the cationic collectors. However, there is always a need of developing highly selective collectors to reduce the overall cost of the process with an enhanced quartz recovery.

Primary amines such as dodecylamine (DDA) and its salts are generally used in the reverse cationic flotation for the separation of quartz and silicates from the associated minerals. In this context, Filiipov et al. have done an extensive review of cationic reverse

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flotation of quartz with regards to various collectors [1]. In search of new and alternate reagents, the commonly used fatty amines which have low solubility in water are now being replaced by more soluble ether and ester amines. Ether amines, which are otherwise cheaper and less pH sensitive compared to primary amines, have been more effective than DDA [2,3]. Several other studies relevant to ether amines and diamines have shown high adsorption and high flotation recovery of quartz [4,5]. Quaternary ammonium surfactants containing ester functional group have displayed better collecting capacity and selectivity with quartz particles in comparison to dodecylamine [6–8]. A Gemini surfactant containing two quaternary ammonium groups has been found to be a better quartz collector compared to dodecylammonium chloride [9].

Application of ionic liquids in froth flotation was not explored until we came up with the study of Aliquat-336 [10] and TOMAS [11] as collectors of quartz. Aliquat-336 and TOMAS are quaternary ammonium based ionic liquids, where the ammonium head is responsible for getting attached to the quartz surface electrostatically and the bulky alkyl groups cause the hydrophobicity. Generally ionic liquids are composed of ionic species and they remain solely as liquid near 100 °C or even below that temperature [12]. These compounds possess low volatility due to the presence of bulky groups. Ionic liquids are easier to handle as ionic species even at room temperature unlike the molten salts which ionise only at elevated temperatures. They are generally used as phase transfer catalysts in organic synthesis and as solvent extractants replacing the conventional organic solvents. Task specific ionic liquids can be designed by different combinations of anions and cations. Substitution of ionic liquids by conventional organic solvents can be done due to their low vapour pressure, wide temperature range, high thermal and chemical stability [13–18].

Introducing new collectors into the flotation system needs to be backed by a proper explanation of the mechanism governing the mineral-collector interaction. Typical characterization studies such as infrared spectroscopy (IR), zeta potential and XPS have helped the researchers to learn different aspects of the interaction mechanisms. However, molecular modelling techniques involving density functional theory (DFT), molecular dynamics (MD), and semi-empirical approaches are quite efficient to predict the collector-mineral adsorption configuration and energy associated with it. Recently, density functional calculations have been used to establish the optimum geometric configuration of long chain amines and its ether and ester derivatives on the surface of quartz [19]. Different design aspects such as variation in alkyl chain length and position of the functional groups in the reagents were considered and the corresponding adsorption energies were calculated. DFT has also been employed in developing a deep understanding of the adsorption mechanism of oleate on different cleavage planes of the three major iron oxides namely hematite, magnetite and goethite [20]. Similarly, molecular mechanics calculations with universal force field were used in designing specific reagents for different minerals [21–24]. Other than DFT and forcefield calculations, HOMO–LUMO studies using semi-empirical methods were exploited to study the interaction of different fatty acids and xanthates with the iron and copper atoms respectively [25,26]. Apart from the static energy minimization calculations, molecular dynamic simulation was also incorporated in several reagent-mineral mechanistic studies. Rai and Pradip modelled a self assembled monolayer (SAM) of oleate on calcium mineral surfaces [27]. UFF based molecular dynamics (MD) simulations were done to model SAM's of different coverage of oleates in terms of site occupancy. Later on, contact angle with water was calculated for the oleate adsorbed mineral surfaces [28]. Molecular dynamics was also used to model complex alumino-silicate surfaces and the adsorption of different chemisorbing and physiosorbing collectors on them [29]. Recently, Fa et al. used a similar strategy to study the interaction of calcium dioleate collector colloids with calcite and fluorite surfaces [30].

As an extension to our previous work [10,11], herein we intend to look into the quartz collecting capabilities of a series of quaternary ammonium based ionic liquids having a variation in the alkyl chain length. Characterization studies and molecular modelling calculations using COMPASS force field have been applied to support the flotation of quartz using these IL's. Further, reverse flotation of a low grade BHQ iron ore was conducted to confirm the applicability of the ionic liquid collectors for floating quartz from low grade iron ores.

2. Materials and methods

2.1. Experimental

Quartz sample (99% pure) was collected from a quartz mines in Odisha, India. The sample was used in the flotation studies after grinding it to below 100 μm in a laboratory ball mill and the size analysis is given in Fig. 1. A pulverizer was used to reduce its size to below 5 μm for characterization studies such as FTIR and XPS. Pellets for XPS and FTIR were made with PVA and KBr binder respectively using a mortar. The ground quartz particles were washed with dilute HCl in order to remove the impurities. The naturally occurring low grade banded hematite quartzite (BHQ) ore; containing around 38% Fe and 42% silica as the major constituents was collected from one of the iron ore mines of India. The BHQ ore was ground to below 100 μm and the particle size distribution is given in Fig. 1. XRD study shown in Fig. 2 indicates that BHQ is mainly composed of hematite and quartz. A detailed

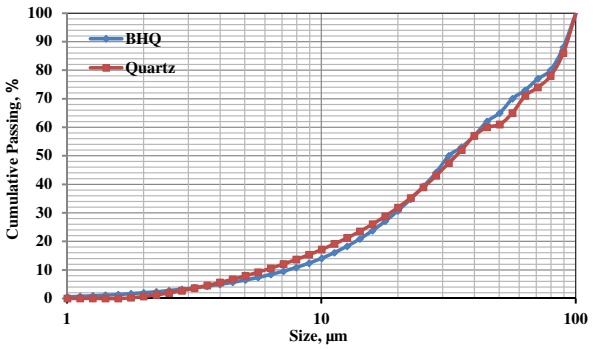

Fig. 1. Particle size distribution of the quartz and BHQ used for flotation studies.

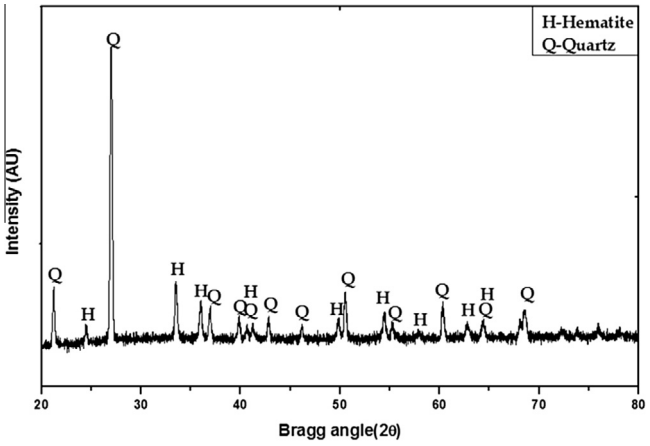

Fig. 2. XRD spectra of BHQ sample.