Influence of surfactant upon SO$_2$ absorption with and without chemical reaction

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The influence of surfactants upon sulfur dioxide chemical absorption in a bubble column reactor has been analysed. This kind of substances (surfactants) can cause important influences over mass transfer processes due the amphiphilic behaviour of these compounds. This kind of behaviour produces the accumulation of surfactants at the gas-liquid interface influencing upon mass transfer processes. Different alkalis have been used to enhance sulfur dioxide transfer by the chemical reaction with absorbed gas in the liquid phase. The high gas solubility and gas absorption rate causes the surfactant presence to have a low influence upon sulfur dioxide absorption under some experimental conditions.

Keywords: Surfactant, Absorption, Bubble column, Chemical absorption.

Gas-liquid absorption processes using different types of contactors and also several liquid phases have been the aim of numerous research studies mainly centered on the carbon dioxide capture or separation. This increase in the number of this kind of studies about absorption of acidic gases is highly related with the aims of carbon capture and storage (CCS) processes. It has produced an important advance upon post-combustion treatments with the aim of to obtain a high purity carbon dioxide from separation processes to store it or to use in other kind of processes (e. g. food industry). More specifically the SO$_x$ limits have been reduced and some process were modified to comply the regulations because it gas has serious hazards to the environment and human health due to acid rain and other phenomena.

Previous studies have shown the important influence of superficial pollutants upon the absorption processes efficiency. Surfactants are compounds that can cause important effects upon mass transfer operations and these effects are generally undesired even though the surfactant concentration in the liquid phase is low. The main influence of this kind of substances upon absorption processes is a decrease in mass transfer rate caused by the accumulation of surfactant molecules at gas-liquid interface. But also, an small number of studies have observed an enhancement in mass transfer rate produced by the existence of surface tension gradients near the interface that enhances liquid elements renewal by means of an increase in interfacial turbulence.

This research work analyses the effect of different surfactants upon sulfur dioxide absorption with and without chemical reaction in the liquid phase. In this way the aim of this work is to study the effect of these substances upon several operation conditions present in a bubble column reactor for sulfur dioxide capture.

Experimental Section

Several surfactants have been used in present work to modify liquid phase characteristics, more specifically hexyl-(HTAB) [CAS nº: 2650-53-5] and decyl-trimethylammonium bromide (DTAB) [CAS nº: 2082-84-0], supplied by Fluka and with a purity of 98% in all cases. Sodium [CAS nº: 1310-73-2] and calcium hydroxide [CAS nº: 1305-62-0] have been supplied by Sigma-Aldrich with a purity >99%. Commercial grade sulfur dioxide [CAS nº: 7446-09-5], supplied by Carburos Metálicos (Spain), was used in this research work. Bi-distilled water has been employed to prepare the absorbent liquid phases. Sulfurdioxide physical and chemical absorption experiments were carried out using the experimental device used in a previous work related to carbon dioxide absorption processes. The gas-liquid reactor was a cylindrical bubble column (internal diameter = 7 cm; height = 100 cm), made in methacrylate with a volume of 2.4 litres. The gas sparger has been a glass capillary with only one orifice (internal diameter: 1.6 mm) to produce a small number of bubbles, which allows us a careful analysis of the surfactant influence on the bubbles size.

The gas to be absorbed, pure sulfur dioxide, was passed through two “humidifiers” at 25°C to prepare the gas phase. This procedure removed the resistance to the mass transfer in the gas phase, and it only allowed us the evaluation of the liquid phase resistance to the gas transfer. Bi-distilled water was
placed into the “humidifiers”. The gas flow-rate was measured and controlled with two mass flow controllers (Alicat Scientific). The mass flow controllers employed in the present study for the gas flow-rate and pressures were calibrated by the supplier. The operation regime was continuous in relation to the gas phase and batch as regards the absorbent liquid. The alkalis concentration was varied depending the solubility because calcium hydroxide solubility is lower than sodium hydroxide.

**Results and Discussion**

The first study was performed using water and aqueous solutions of sodium hydroxide and calcium hydroxide for sulfur dioxide absorption in the bubble column reactor. Figure 1 shows the absorption kinetics during sulfur dioxide absorption until liquid phase saturation. These data show an increase in the quantity of sulfur dioxide when a chemical reaction in the liquid phase takes place. Calcium hydroxide solution shows the best results in relation to the sulfur dioxide loading due to the higher concentration of hydroxide ions than for sodium hydroxide solution. The first part of the experiments shows a plateau with a constant absorption rate value. This behaviour is observed because the absorption rate at the beginning of the experiment is very high and the absorption is complete (the outlet gas flow-rate is null). On the other hand the differences between the sulfur dioxide loading corresponding to water and alkalis solutions are low. This behaviour is very different than the corresponding ones using other gases such as carbon dioxide\(^1\). This fact is due to the high sulfur dioxide solubility in water that allows to reach high sulfur dioxide loadings with and without chemical reaction.

In relation with the influence of reagent concentration upon sulfur dioxide absorption kinetics experimental results are shown in Fig. 2 for calcium hydroxide aqueous solutions. The observed behaviour consists in a clear increase in the sulfur dioxide loading when calcium hydroxide concentration increases in the liquid phase. This behaviour is in agreement with previous studies analyzing this kind of systems for carbon dioxide separation\(^15\).

Figure 3 shows the influence of surfactant nature upon absorption rate using sodium hydroxide aqueous solutions. A similar behaviour has been observed for all systems with and without surfactant presence. The surfactant influence can be centred on mass transfer coefficient and interfacial area. The presence of surfactant in the liquid phase generally causes an increase in interfacial area but a decrease in mass transfer coefficient\(^16\). The first effect is produced by the decrease on surface tension and the effect of this physical property upon bubble diameter. On the other hand surfactants generally produce a decrease in gas diffusivity close the interface\(^17\). A previous work has concluded that the negative influence of HTAB is lower than for DTAB aqueous solutions\(^10\) but in Fig. 3 a non-influence of surfactant upon absorption rate is observed. This fact is due to the high reaction rate between sulphur dioxide and sodium hydroxide because the base concentration in the liquid phase is high. Then the negative influence of surfactant upon gas diffusivity is negligible in comparison with the positive effect caused by the chemical reaction.

![Fig. 1 — Sulfur dioxide absorption kinetics using different alkalis aqueous solutions. (○) water, (●) \([\text{NaOH}] = 0.02 \text{ M}\), (□) \([\text{Ca(OH)}_2] = 0.02 \text{ M}\)](image_url)

![Fig. 2 — Influence of calcium hydroxide concentration upon sulfur dioxide absorption. (○) water, (●) \([\text{Ca(OH)}_2] = 0.01 \text{ M}\), (□) \([\text{Ca(OH)}_2] = 0.02 \text{ M}\)](image_url)
A different behaviour is observed in Fig. 4 using calcium hydroxide aqueous solutions with and without DTAB. This figure shows different effects: (i) the presence of a chemical reaction produces an increase in sulfur dioxide loading previously commented in Fig. 1, (ii) an increase in DTAB concentration produces a significant decrease in mass transfer rate. This behaviour is produced because the surfactant difficult the gas transfer to the liquid phase by the existence of a barrier due to surfactant accumulation in the gas-liquid interface.

**References**