Abstract

This study focuses on utilization of hydrogen sulfide (H_2S) in the synthesis of fine chemicals such as dibenzyl sulfide (DBS), benzyl mercaptan (BM) and aromatic amines. This involves first absorption of H_2S in either aqueous ammonia or alkanolamine and then reaction of this H_2S-rich aqueous solution with organic reactants, benzyl chloride (to synthesize DBS or BM) and nitroarenes (to synthesize anilines). To carry out this biphasic reaction, phase transfer catalyst has been used. Tetra-n-butylammonium bromide (TBAB) has been chosen as phase transfer catalyst (PTC) in all cases because of its ease of availability, faster reaction rate in comparison to some other nitrogenous PTCs, more selectivity for desired product and high mutual solubility in both the phases. The overall objective of this study is to maximize conversion of reactant, maximize selectivity of desired product, searching for mechanism and optimization. Three reaction systems have been studied in the present work – first being the reaction of benzyl chloride with aqueous ammonium sulfide in the presence and absence of catalyst and in the presence and absence of an organic solvent. Kinetic modeling, mechanistic investigation and statistical optimization studies have been performed. Then the reaction of benzyl chloride with H_2S-loaded monoethanolamine (MEA) has been carried out. Parametric studies and statistical optimization studies have been performed. In the final system, parachloronitrobenzene has been reduced by H_2S-loaded MEA to get parachloroaniline selectively. Here also parametric study has been done along with kinetic modeling. In all the systems under study, desirable products were obtained with 100% selectivity at some level of process parameters. Reaction time, temperature, catalyst loading, stirring speed, reactants concentration and solvent concentration were chosen as parameters. They were optimized by both one-variable-at-a-time method and statistical method to get maximum conversion and selectivity. In statistical optimization study, response surface methodology (RSM) with central composite rotatable design (CCRD) has been used to optimize the process variable and analyze the process. Desirability function is then used to dual-optimize conversion and selectivity.

Keywords: Hydrogen sulfide; dibenzyl sulfide; parachloronitrobenzene; ammonium sulfide; phase transfer catalyst; selectivity; optimization; response surface methodology; central composite rotatable design.