ABSTRACT

Aromatic nitration by mixed acid (a mixture of concentrated nitric and sulfuric acids) is one of the most widely used reactions in the organic chemical industries. Aromatic nitro compounds find wide use in the manufacture of dyes and explosives. It is a heterogeneous liquid–liquid reaction which occurs almost-exclusively in the aqueous phase. The organic compound diffuses into the aqueous mixed-acid phase and reacts with the nitronium ion $\left(NO_2^+\right)$ generated by the reaction between concentrated sulfuric acid and nitric acid. In this thesis, nitration of nitrobenzene using high-concentrations of sulfuric acid (i.e., between 14 kmol/m^3 and 17.2 kmol/m^3) was studied in a batch reactor at room temperature and at moderately higher temperatures.

Nitration of nitrobenzene is a very slow reaction at room temperature when sulfuric acid concentration is 14.9 kmol/m^3 or below, due to the deactivating nitro group in the benzene ring. But at high-concentrations of sulfuric acid (≥ 16.6 kmol/m^3) and at high temperatures, the reaction is fast enough to obtain high conversion and yield. The advantage of this reaction is the absence of sulfonation reaction. The behavior of each aromatic nitration system is unique in terms of the physicochemical properties of the heterogeneous organic–acid mixture. Various physicochemical properties of the nitrobenzene, sulfuric acid and nitric acid system were measured, which include solubility of nitrobenzene in the sulfuric and nitric acids, and the density of the aqueous sulfuric acid phase equilibrated with nitrobenzene. We have noticed unique interfacial phenomena that occur when nitrobenzene is brought in contact with concentrated sulfuric acid. A dispersion of nitrobenzene droplets in sulfuric acid forms which resembles a microemulsion. The dispersion is thermodynamically stable. It results in high solubilization of nitrobenzene into sulfuric acid and generates large interfacial area exposed for the nitration reaction.

The mass transfer coefficient of nitrobenzene in aqueous sulfuric acid at different concentrations of sulfuric acid was measured at 298 K and 313 K under flat-interface condition employing the batch dynamic process. The change in the volume of the aqueous phase, especially at the high-concentrations of sulfuric acid has been taken into account in the determination of the mass transfer coefficient. The effect of stirring speed on mass transfer coefficient was also investigated. At high-concentration of sulfuric acid, the mass transfer coefficient increased significantly with increase in stirring speed. The kinetics of nitration under homogenized conditions was studied at different sulfuric acid concentrations at 298 K, 313 K and 323 K. The reaction rate constants were determined at these temperatures. The variation of rate constant with sulfuric acid concentration was explained by the M_c activity coefficient function. The activation energies of the reactions were determined from the Arrhenius plots. The regimes of the reactions were determined using the values of the mass transfer coefficients and the reaction rate constants.

Two-phase nitration of nitrobenzene was carried out in the batch reactor, and the concentration profiles of the reactants and the products in the reactor were determined. A model was developed for simultaneous mass transfer and chemical reaction in the aqueous phase. The yields of the three isomers of dinitrobenzene were determined. The variation of isomer distribution with sulfuric acid concentration and temperature was analyzed. This work demonstrates that more than 90% conversion of nitrobenzene can be achieved at high-concentrations of sulfuric acid at moderate temperatures and at low speeds of stirring.