Studies in Multiphase Reactions
(Kinetics of Reactive Absorption of Carbon Dioxide with Solutions of Amines in Aqueous and Nonaqueous Solvents; Epoxidation of Vegetable Oils)

In recent years, sustainable development has become the focus of research throughout the world. It includes, along many other things, development of environmentally friendly processes and products. The present research was undertaken on the same line, i.e., to develop greener routes and greener products from low cost and renewable raw materials. It is needless to say that the heterogeneous reactions play the pivotal role in any process or product development activity.

The whole work has been divided into two parts. First part of the work deals with the use of carbon dioxide, a green house gas, to produce commercially important products and the developed process is more environmentally friendly than the traditional ones. The second part of the present work is concerned with the development of processes for the environment-friendly product, epoxidised vegetable oil, from locally available renewable raw materials. Accordingly, the major findings of the study are discussed below under two separate headings.

PART I: Kinetics of Reactive Absorption of Carbon Dioxide into Solutions of Amines in Aqueous and Nonaqueous Solvents

Traditionally, organic isocyanates are manufactured by the reaction of an amine with phosgene ($COCl_2$), and the intermediate is converted to isocyanate in the presence of a nonaqueous aprotic solvent. Recently, carbon dioxide is attracting serious attention of research workers in the synthetic chemistry, particularly from the viewpoint of Green Technology. Carbon dioxide is environmentally friendly as compared to phosgene, because of its nontoxic, nonhazardous, and nonflammable nature. Carbon dioxide has a potential to act as a reactant in many chemical reactions for the synthesis of high value products such as organic carbamates, isocyanates, and urethanes. The major demand for isocyanates is for the production of polyurethanes, and carbamates are mainly used for the preparation of insecticides and pesticides. The first step for the production of isocyanates / carbamates from amines and carbon dioxide is the reactive absorption of carbon dioxide with amine solutions. However, the commercial utilisation of this process requires systematic kinetic study, because for rational design of gas absorbers, where a reacting gas is absorbed in liquid reactant(s), knowledge of kinetic data is essential. Moreover, there are very few published reports about the kinetics of the reactive absorption of carbon dioxide in nonaqueous solutions of amines; most of the published work deals with aqueous alkanolamines.

In the present work, the kinetics of reactive absorption of carbon dioxide with mono– and diamines, namely, aniline and 1,6–hexamethylenediamine have been studied. Commercially available nonaqueous solvents such as acetonitrile, methyl ethyl ketone, toluene, *m*–xylene, chloroform, carbon tetrachloride, and methanol have been used. The specific rates of absorption were analysed using the theory of gas absorption with chemical reaction.

Most the experiments were conducted in a glass stirred cell (6.4 cm i.d, 500 mL capacity) and a few runs were taken in a model stirred contactor (93 cm i.d., 1.25 L capacity) at 303±1K and atmospheric pressure. In the stirred cell, the specific rate of absorption of pure carbon dioxide was measured using soap film meter and in the case of model stirred contactor, the specific rates were determined based on the liquid phase carbamate analysis by chemical method.

In the case of reactive absorption of carbon dioxide with solutions of aniline in nonaqueous aprotic solvents such as acetonitrile, methyl ethyl ketone (MEK), toluene, *m*–xylene, carbon tetrachloride, and chloroform, the concentration of aniline was varied from 0.75 to 5 kmol m^{-3}, and the partial pressure of carbon dioxide was varied from 0.42 to 0.99 atm.

The absorption of carbon dioxide with aniline dissolved in acetonitrile, appears to conform to the fast pseudo–first order reaction regime where the dissolved carbon dioxide reacts completely within the diffusion film. The reaction was found to be first order with respect to carbon dioxide and the apparent reaction order with respect to aniline was found to be −1. The average value of intrinsic kinetic rate constant ($k_{1,-1}$), at 303±1 K, was estimated to be 5.6 x 10^1 (kmol m^{-3}) s^{-1}.

The absorption of CO_2 with aniline dissolved in MEK appears to conform to the fast pseudo–first order reaction regime or to the intermediate reaction regime where part of the carbon dioxide reacts in the diffusion film and the rest reacts in the bulk liquid. The reaction was found to be first order with respect to both carbon dioxide and aniline. The average value of intrinsic kinetic rate constant ($k_{1,1}$), at 303±1 K, was estimated to be 8.03 x 10^{-2} (kmol $m^{-3})^{-1}$ s^{-1}.

The absorption of CO_2 with aniline dissolved in toluene and *m*–xylene, appears to conform to the intermediate reaction regime between fast pseudo–first order and slow reaction regime where part of the CO_2 reacts in the diffusion film and the rest reacts in the bulk liquid. In both these solvents, the reaction was found to be first order with respect to carbon dioxide and the apparent reaction orders with respect to aniline were found to be 2 and 2.5 in the case of toluene and *m*–xylene, respectively. The average values of intrinsic kinetic rate constants at 303±1 K, were estimated to be 5.01 x 10^{-2} $(\text{kmol m}^{-3})^{-2}$ s^{-1} and 1.06 x 10^{-2} $(\text{kmol m}^{-3})^{-2.5}$ s^{-1} in the case of toluene and *m*–xylene, respectively.

The reactive absorption of carbon dioxide with aniline dissolved in carbon tetrachloride, and in chloroform, appears to conform to the intermediate regime between very slow, slow and fast reaction regime. Here, the dissolved carbon dioxide reacts partly in the film and partly in the bulk and yet there may be a finite quantity of dissolved carbon dioxide in the bulk liquid. In both these chlorinated solvents, the reaction was found to be first order with respect to carbon dioxide and the apparent reaction orders with respect to aniline were found to be 0.26 and −0.17 in the case of carbon tetrachloride and chloroform, respectively. The average values of intrinsic kinetic rate constants at 303±1 K, were estimated to be 8.09 x 10^{-4} $(\text{kmol m}^{-3})^{-0.26}$ s^{-1} and 1.28 x 10^{-3} $(\text{kmol m}^{-3})^{0.17}$ s^{-1} in the case of carbon tetrachloride and chloroform, respectively.

The reactive absorption of carbon dioxide was also studied with solutions of 1,6–hexamethylenediamine (HMDA) in polar protic solvents such as water and methanol, in a stirred cell, and a model stirred contactor, at 303±1 K operated at atmospheric pressure. The concentration of 1,6–hexamethylenediamine was varied from 0.5 to 3 kmol m^{-3}. For HMDA concentrations less than or equal to 2.5 kmol m^{-3}, the reactive absorption of CO_2 in methanolic HMDA appears to conform to the instantaneous reaction regime, but at higher HMDA concentrations, the reaction shifted towards the intermediate regime between fast and instantaneous reactions regime. The specific rate of absorption was found to be almost independent of partial pressure of solute gas. The absorption of carbon dioxide with HMDA dissolved in water, appears to conform to the intermediate regime between very fast and fast reactions regime. The reaction was found to be first order with respect to carbon dioxide and the apparent reaction orders with respect to HMDA were found to be 0.84. The average value of intrinsic kinetic rate constant ($k_{1,\,0.84}$), at 303±1 K, was found to be 2.9 x 10^{2} $(\text{kmol m}^{-3})^{-0.84}$ s^{-1}.

In addition, attempt was also made to establish a correlation between the rate constants and the solubility parameters of the solvents. It has been observed that, the order of reaction increased as the solvent polarity and relative dielectric constant of the solvents decreased. The value of $k_{1,\,n}$ increased with the increase of both Hildebrand solubility parameter and relative dielectric constant of the solvents.

PART II: Epoxidation of Vegetable Oils

Epoxidation of long chain olefins, and unsaturated fatty acid derivatives such as vegetable oils is an important reaction for the synthesis of high value commercial products. The epoxides obtained from the vegetable oils and from their methyl esters, have wide applications as plasticisers, polymer stabilizers and can acts as replacement for materials derived from petroleum. Due to the high reactivity of the oxirane (epoxy) ring, epoxides can also act as raw materials for synthesis of a variety of chemicals, such as alcohols, glycols, alkanolamines, carbonyl compounds, olefinic compounds, and polymers like polyesters, polyurethanes, and epoxy resin. However, the cost effectiveness of the route greatly depends upon the local and cheap availability of the raw material. The objective of the present work was to study the epoxidation of vegetable oils with *in situ* generated peroxyacetic acid, with a view of obtaining value–added products from locally available renewable natural resources. The focus was on heterogeneous liquid–liquid and liquid–liquid–solid reaction systems. The main areas of interest were producing better quality epoxidised oil with higher oxirane value and lower iodine value, finding out product distribution by varying the reaction parameters, fitting a reaction mechanism for the different reactions encountered, and proposing an appropriate kinetic model and kinetic parameters.

There are four known technologies to produce epoxides from olefinic / unsaturated type of molecules. However, for the clean and efficient epoxidation of vegetable oils, the most widely used technologies are: (i) epoxidation with percarboxylic acids, an (ii) epoxidation with organic and inorganic peroxides. The present work is focused on the *in situ* epoxidation of cottonseed oil with peroxyacetic / peroxyformic acids as the epoxidising agents in the presence of sulfuric / nitric / phosphoric / hydrochloric acid / acidic ion exchange resin Amberlite IR–120) as the acidic catalysts.

All the experiments were conducted in a fully baffled mechanically agitated batch contactor made of glass (6.5 cm i.d, 250 mL capacity), at atmospheric pressure. Reaction products were then analysed by chemical methods for oxirane oxygen (epoxy) content, α–glycol content, and iodine value.

The kinetics of liquid–liquid epoxidation of cottonseed oil was studied with 50% aqueous hydrogen peroxide as oxygen donor and acetic acid / formic acid as active oxygen carriers in the presence of catalytic amount of a liquid inorganic acid catalyst. The order of effectiveness of catalysts was found to be sulphuric acid > phosphoric acid > nitric acid > hydrochloric acid. Acetic acid was found to be superior to formic acid for the *in situ* cottonseed oil epoxidation. It was possible to obtain up to 78% relative conversion to oxirane with very less oxirane cleavage by *in situ* technique at 60^0C. The rate constants for sulphuric acid catalysed epoxidation of cottonseed oil were in the range 0.39–5.4 × 10^{-6} (mol $L^{-1})^{-1}$ s^{-1} and the activation energy was found to be 11.7 kcal mol^{-1}. Some thermodynamic parameters such as enthalpy, entropy, and free energy of activation were determined to be of 11.0 kcal mol^{-1}, –51.4 cal mol^{-1} K^{-1} and 28.1 kcal mol^{-1}, respectively.

The heterogeneous multiphase (liquid–liquid–solid) process of epoxidation of cottonseed oil with acidic ion exchange resin (Amberlite IR–120) consisted of a consecutive reaction, that is, the acidic ion exchange resin catalysed peroxyacid formation followed by the epoxidation reaction. Moreover, the solid acid catalysed epoxidation was found to be more selective, as compared to the sulfuric acid catalysed epoxidation. It was possible to obtain about 65% relative conversion with more than 90% selectivity to oxirane oxygen at 75^0C.

All the experiments were conducted at a stirring speed of about 2400 rev/min to ensure that there was no diffusional resistance present at any existing solid–liquid and liquid–liquid interfaces. To check the intraparticle diffusional resistance, the reaction was carried out with two different size catalyst particles and was confirmed that there was no intraparticle diffusional resistance. In these kinetic studies, the Langmuir-Hinshelwood-Hougen-Watson surface reaction model was found to interpret the kinetics reasonably well. The kinetic parameters were estimated using the Marquardt's routine. From the estimated kinetic constants, the activation energy of the reaction was determined to be 9.42 kcal mol^{-1}.

The epoxidation of neem oil was carried out with *in situ* generated peroxyacetic acid as oxygen carrier in the presence of catalytic amounts of liquid inorganic acids (sulphuric/ nitric/phosphoric acid) or a solid acidic ion exchange resin (AIER) as catalysts. For the two-phase epoxidation of neem oil catalysed by sulphuric acid, about 30% oxirane conversion with less than 75% selectivity was achieved after 10 h at 30^0C. Out of all the liquid inorganic acid catalysts studied, H_2SO_4 was found to be comparatively more effective than other two. It was observed that the oxirane conversion decreased with the increase of temperature, with corresponding increase in the glycol formation. For the triphase epoxidation of neem oil catalysed by Amberlite IR 120, about 20% oxirane conversion was possible even after 10 h at 30^0C with 20% catalyst loading. Moreover, it was observed that, even in presence of AIER, the oxirane conversion decreased with temperature, with corresponding increase in the glycol formation. The maximum yield obtained was very poor (about 30%) for commercial utilisation, and hence, further experiments were not conducted.