NITRATION OF NITROBENZENE AT HIGH-CONCENTRATIONS OF SULFURIC ACID

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Nitration of Nitrobenzene at High-Concentrations of Sulfuric Acid

Thesis

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requirements for the degree of

DOCTOR OF PHILOSOPHY

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Dedication

To My Parents and Family

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CERTIFICATE

It is certified that the work contained in the thesis entitled **"Nitration of Nitrobenzene at High-Concentrations of Sulfuric Acid"**, by *Mehabub Rahaman* has been carried out under our guidance and supervision. The work documented in this thesis has not been submitted to any other University or Institute for the award of any other degree or diploma.

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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 ($\geq$ 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.

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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.

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RESEARCH PUBLICATIONS

Journal

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CHAPTER 1

INTRODUCTION TO AROMATIC NITRATION

This chapter presents an introductory discussion on nitration in different organic chemical processes. It describes the importance of nitration of aromatic compounds. It also discusses the various features of different approaches by which the nitration process can be carried out.

1.1 Introduction

Nitration is one of the oldest and probably the most widely used reactions in organic process industry. Nitration is defined as the reaction between an organic compound and a nitrating agent, generally nitric acid or its derivatives, to introduce one or more nitro functional groups ($-NO_2$) to an atom in the organic compound [1]. The nitro functional group consists of a nitrogen atom joined to two oxygen atoms. From the resonating structure of the nitro group as shown in the Figure 1.1, it can be observed that the nitrogen atom is positively charged and each oxygen atom has a partial negative charge. For this reason, the nitro group has a powerful attraction for electrons, and it is indeed an important electron-withdrawing functional group. The nitro group, whether attached to an aliphatic or aromatic carbon (or to an oxygen or a nitrogen atom), is the most widely studied functional groups.

With respect to the chemical structure of the compounds resulting from the nitration process, three types of nitration reactions are distinguished as shown in Figure 1.2.

(i) ***C-nitration***: In this nitration process, the nitro group is attached to a carbon atom and leads

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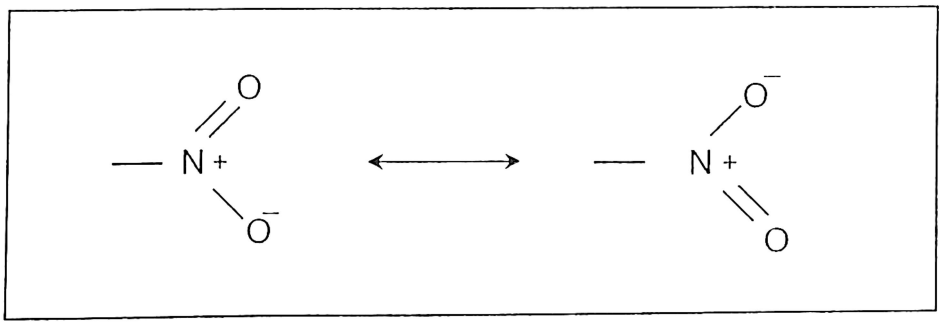


Figure 1.1 Resonating structure of the nitro group.

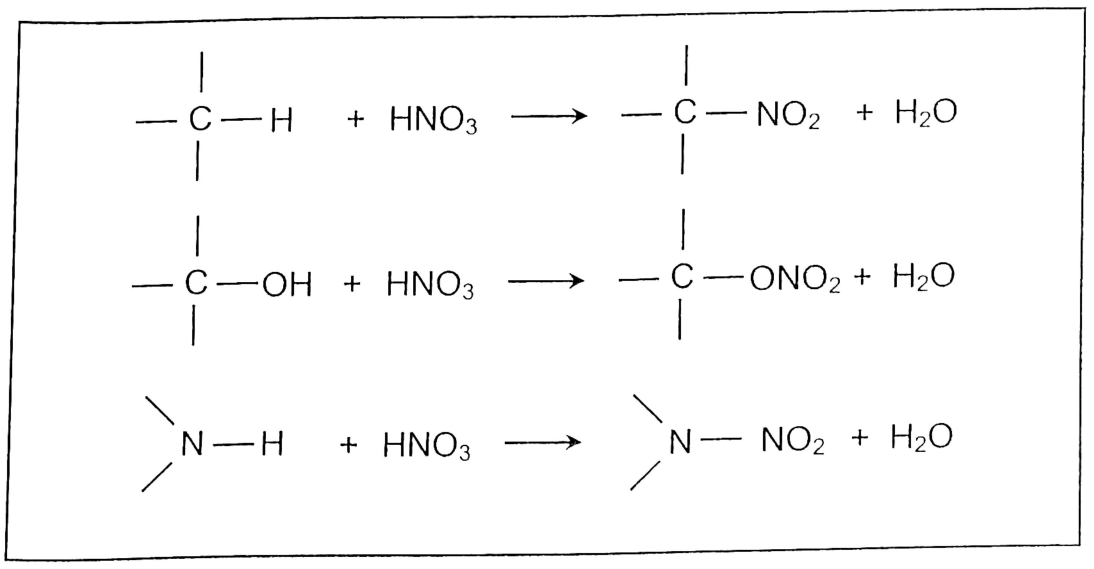


Figure 1.2 Various types of nitration in organic chemical processes.

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to the formation of nitro compounds.

(ii) ***O-nitration***: In this nitration process, the nitro group is introduced to an oxygen atom and an ester is formed during this kind of nitration process.

(iii) ***N-nitration***: In this process, the nitro group is bonded to a nitrogen atom and leads to the formation of nitramines.

The nitro functional group most frequently substitutes a hydrogen atom and water is produced as a by-product of the reaction. However, in general, the nitro group may substitute any other atom or groups of atoms. For example, in Victor Meyer reaction, which uses silver nitrite, the nitro group replaces a halogen atom, e.g., I or Br [2].

1.2 History of aromatic nitration

Nitration has been an active area of research in industrial chemistry for over a century. Nitration of benzene was the first nitration process reported in the literature. In 1834, German chemist Eilhardt Mitscherlich prepared nitrobenzene by reacting benzene with nitric acid [3]. Soon afterwards, Charles Mansfield (1845) augmented the nitration reaction by adding sulfuric acid, and made large quantities of the nitro product. In this way, nitration with a mixture of nitric and sulfuric acids (i.e., *mixed acid*) became the most common method for the nitration of aromatic compounds. It was first applied in an industrial scale in 1847 by Mansfield [3]. It eventually turned out to be a gateway into the vast area of aromatic chemistry. Nitration of aliphatic compounds was reported in the later part of 19th century. The nitration of aliphatic hydrocarbons gained importance after the advent of the petrochemicals industry in which nitroalkanes were primarily used as solvents. The versatility of nitro compounds in organic synthesis is largely due to their easy availability and transformation into a variety of compounds.

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1.3 Importance of aromatic nitration

Nitration of aromatic compounds is important mainly for two reasons: (i) it is the most general process for the preparation of aromatic nitro compounds and has many significant industrial applications, and (ii) it has played an important role in the development of research activities in the theoretical organic chemistry.

1.3.1 Industrial applications of nitro compounds

Nitration is an immensely important industrial process for synthesis of different nitro compounds. There is a wide range of use of nitro compounds, both as intermediates and as end products. The nitration processes of aromatic and aliphatic compounds are similar. However, the former are industrially prevalent. A large number of basic organic intermediates are produced from the nitro compounds. The nitro aromatic compounds are used as explosives and act as key substrates for the preparation of useful materials such as dyes, drugs, agrochemicals, polymers, solvents, perfumes and plastics. They are also used for the synthesis of other industrially important chemicals such as amines, isocyanates and polynitro aromatic compounds. Some of the industrially important nitration processes, the products of nitration and their use are described below [4–7].

(i) Nitration of benzene and its derivatives

The mononitration of benzene gives nitrobenzene. The use of nitrobenzene as a processing solvent in chemical reactions is minor but important. Most (95 % or more) of nitrobenzene manufactured is converted to aniline, which has hundreds of downstream products. Further nitration of nitrobenzene produces dinitrobenzene isomers. 1,3-dinitrobenzene has been used in the formulation of explosives, lubricants, polymerization

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inhibitors and corrosion inhibitors. The other isomers find use in dye intermediates and in various organic syntheses. Nitration of 1,3-dinitrobenzene gives 1,3,5-trinitrobenzene. Although trinitrobenzene has more explosive power than trinitrotoluene (TNT), it is much more expensive.

(ii) Nitration of toluene and its derivatives

All three isomeric mononitrotoluenes, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene (TNT) are industrially important products obtained from the sequential nitration of toluene. Mononitrotoluene derivatives are used principally as colorant intermediates and some other related products. Most of the 2,4-dinitrotoluene produced is hydrogenated for conversion to toluene diisocyanate (TDI), which is a component of the monomer of polyurethane. A much smaller amount is used in explosives and for further nitration to TNT, which has use in the making of explosives.

(iii) Nitration of xylene and its derivatives

All three xylenes isomers (i.e., 1,2-dimethylbenzene, 1,3-dimethylbenzene and 1,4-dimethylbenzene) can be nitrated easily to produce mononitroxylenes. The nitroxylenes are readily reduced to the corresponding aminoxylenes (xylidines), which find use in the production of riboflavin, agrochemicals, and used as colorant intermediates. Mixtures of xylidines can be used for some colorants.

(iv) Nitration of naphthalene and its derivatives

Under moderate conditions, naphthalene is nitrated to give 1-nitronaphthalene and a small amount of 2-nitronaphthalene. 1-nitronaphthalene is catalytically reduced to 1-naphthylamine, which is used as a deblooming agent for petroleum oils, and as a component in the formulation of explosives to decrease the burning rate.

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(v) Nitration of halobenzenes and their derivatives

a) ***Chloronitrobenzene:*** Successive nitration of chlorobenzene will produce three isomeric chloronitrobenzenes (i.e., 2-chloronitrobenzene, 3-chloronitrobenzene and 4-chloronitrobenzene), and 2,4-dinitrochlorobenzene, respectively. They are industrially very important compounds. Dinitrochlorobenzenes have been used to produce sulfur dyes. Other nitrochlorobenzenes find their use in the synthesis of colorants, and act as intermediates of many significant chemicals.

b) ***Dichloro and polychloronitrobenzenes:*** Both 1,2- and 1,4-dichlorobenzene are nitrated on a large scale to give important intermediates for colorants, agrochemicals and diazo compounds. Pentachloronitrobenzene is produced by the nitration of pentachlorobenzene, which is used as a fungicide known as terrachlor. It has led to a series of nitro-containing agrochemicals.

(vi) Nitration of aniline and its derivatives

The sequential nitration of aniline produces isomeric mononitroanilines (i.e., 2-nitroaniline, 3-nitroaniline and 4-nitroaniline), and 2,4,6-trinitroaniline. These compounds are industrially important as colorant intermediates. Nearly all the primary nitroanilines are used as diazo compounds in azo dyes and pigments, and as intermediates for vat or disperse dyes.

(vii) Nitration of sulfonic acids and their derivatives

Most of the sulfonic acids derived from nitrobenzene, nitrotoluenes, chloronitrobenzenes and related products are reduced to yield anilinesulfonic acids for use in the synthesis of water-soluble dyes or pigments. 3-nitrobenzenesulfonic acid is used primarily as a mild oxidizing agent or as a precursor for colorant intermediates. Amination of 2-chloro-5-nitrobenzenesulfonic acid gives 4-nitroaniline-2-sulfonic acid, which is used as a diazo

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compound or reduced to the colorant intermediate. Some of the derived sulfonamides and sulfones are important intermediates for colorants and fine chemicals.

(viii) Nitration of other aromatic compounds

Aromatic compounds such as ethylbenzene and cumene can be readily nitrated. Complete nitration of ethylbenzene gives 2,4-dinitroethylbenzene, which is a component of the energetic plasticizer known as K-10 (which is a 2:1 mixture of 2,4-dinitroethylbenzene and 2,4,6-trinitroethylbenzene). Nitro derivatives of cumene (i.e., 2-nitrocumene and 4-nitrocumene) are very important chemicals. Their hydrogenation produces the corresponding cumidines. Cumidines are used as important intermediates for azo solvent dyes (i.e., 2-cumidine) and in the manufacture of herbicides such as isoproturon (i.e., 4-cumidine). Compounds produced from the nitration of polyalkylbenzenes (e.g., mesitylene and durene) are used as explosives and intermediates of colorants. Nitration of phenol gives 2-nitrophenol which on catalytic hydrogenation produces 2-aminophenol. It is used as a photographic developer and in larger amounts, as an intermediate for dyes and fine chemicals. Other nitrophenol isomers are used as important intermediates for fine chemicals which have large industrial uses.

1.3.2 Development of research in theoretical organic chemistry

Aromatic nitration has played an important role in the progress of theoretical organic chemistry [8,9]. Nitration can be carried out under various operating conditions. However, it invariably proceeds through the electrophilic species, the nitronium ion $\left(NO_2^+\right)$. Aromatic nitration has numerous advantages in terms of studying the reaction mechanism. After introduction of a nitro group in the molecule, the system becomes deactivated. Thus, further

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nitration does not take place readily, and it can be stopped after the first step. Furthermore, the products are generally easy to separate and analyze. With the establishment of structural organic chemistry, the first major landmark in its development was in the area of orientation in aromatic substitution [10]. The nitration has played an important role in the establishment of the electrophilic substitution mechanism. The most extensive data were on nitration for the establishment of the aromatic electrophilic substitution mechanism, and classification of the orienting substituents as *ortho*-, *para*- or *meta*-directing. The electronic theory of organic chemistry which describes the course of organic reactions in terms of movement of electrons has developed mainly through the studies on aromatic nitration and related substituent effects. Other developments such as resonance theory, nature of inductive effect and developments in molecular orbital theory relating to aromatic reactivity have extensively involved aromatic nitration. Aromatic nitration has therefore played a scholastic role both in academic and industrial research.

1.4 Reagents and methods of aromatic nitration

The nitration reactions can be carried out under a wide variety of conditions. Numerous nitrating agents have been used for nitration, but not all of the methods are commonly used in industry or even laboratory. The following nitrating agents are most frequently used for the introduction of a nitro group to an aromatic compound.

1.4.1 Nitration in nitric acid

Nitric acid can be an effective nitrating agent [9–12]. Anhydrous HNO_3 undergoes appreciable self-dehydration according to the following scheme.

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (1.1)$$

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Aromatic hydrocarbons as well as their nitrated derivatives have appreciable solubility in 100% nitric acid and thus, the nitration in nitric acid proceeds homogeneously. Dilute nitric acid is useful for nitrating reactive substances such as phenol, but the oxidizing properties of nitric acid can be disadvantageous. The major drawback of using 100% HNO_3 is that its reactivity drops considerably as water is produced during nitration. The regeneration of spent HNO_3 is also a matter of concern for using anhydrous nitric acid. In practice, nitroaromatics are soluble in the concentrated nitric acid which makes them difficult to recover [10]. The intercalation of nitric acid with graphite gives graphite nitrate $\left[(C_{12}HNO_3)_n\right]$ which is a nitrating and oxidizing agent under heterogeneous conditions. Graphite nitrates are less stable and nitration takes place at the surface of the compound. Alkylbenzenes, anisole and phenol are nitrated in moderate yields giving products with usual isomer distribution [13,14].

1.4.2 Nitration in nitric acid with acid catalyst

Nitration of aromatic compounds with the mixture of nitric and sulfuric acids (i.e., the *mixed acid*) is the most frequently used nitrating agent in the industrial practice [9,10]. Sulfuric acid facilitates the ionization of nitric acid to the nitronium ion by the following equilibrium.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (1.2)$$

Sulfuric acid also binds the water formed in the reaction. Solutions of nitric acid in sulfuric acid of various concentrations generate a wide range of reactivity towards the aromatic compounds. Sulfuric acid is also used in the making of solid acidic catalysts to nitrate aromatic compounds with nitric acid [15–17].

Nitric acid in oleum produces the nitronium ion in the following manner [4].

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$$HNO_3 + 2H_2S_2O_7 \rightleftharpoons NO_2^+ + HS_2O_7^- + 2H_2SO_4 \quad (1.3)$$

It is an extremely active nitrating agent. However, its use is limited to the nitration of highly deactivated aromatics since oleum can also cause sulfonation and oxidation of the reactive aromatics.

Phosphoric acid is a weaker acid than H_2SO_4 and thus, a high concentration of phosphoric acid solution is needed to carry out the nitration. The rate constants for the nitration reactions are lower. High concentrations of H_3PO_4 solutions are generally prepared by adding P_2O_5 to H_3PO_4. These are known as polyphosphoric acids (PPA). PPA is a syrupy viscous liquid, which does not form a homogeneous phase with HNO_3. Use of phosphoric acid in nitric acid solutions may be useful in some cases where a different isomer distribution of products is necessary from that formed in sulfuric acid. The regioselectivity of the nitration of toluene can be altered by using increasingly stronger H_3PO_4. It results in decreasing ortho product over the para product as compared with H_2SO_4 [18]. Recently, phosphoric acid has been frequently used as a solid supported acidic catalyst [19–22].

Nitric acid and concentrated perchloric acid have played a significant role in the development of knowledge on acid catalyzed nitration. A disadvantage of using perchloric acid in concentration greater than 72% is the increasing risk of explosion [10]. The anhydrous HNO_3–$HClO_4$ mixtures are also strong oxidizing agents for some organic compounds. But they have never achieved wide use in nitration, and have limited use in industry [23,24]. An extreme caution is needed for handling the mixtures of nitric and perchloric acids.

Nitric acid in anhydrous hydrogen fluoride ionizes to give nitronium ion $\left(NO_2^+\right)$ [10]. Benzene has been nitrated by HNO_3 in anhydrous HF with a yield of 83% nitrobenzene at 273 K [25]. But, nitrobenzene was not nitrated further at this condition. Olah et al. [26] have

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introduced HNO_3–anhydrous HF–BF_3 as an efficient and safe nitrating agent. HNO_3 gives NO_2^+ with HF–BF_3 mixture according to the following scheme.

$$HNO_3 + HF + 2BF_3 \longrightarrow NO_2^+BF_4^- + BF_3H_2O \qquad (1.4)$$

Nitronium tetrafluoroborate $\left(NO_2^+BF_4^-\right)$ can be removed as a stable salt and used as a nitrating agent for the nitration of aromatics. BF_3 can be readily regenerated from the hydrate by distillation.

Mixture of nitric acid and boron trifluoride is also an active nitrating agent. The combining property of BF_3 with water makes this nitrating agent very valuable. Thomas et al. [27] first nitrated aromatics (including nitrobenzene) using HNO_3 and BF_3. The reaction proceeds as follow.

$$ArH + HNO_3 + BF_3 \longrightarrow ArNO_2 + BF_3.H_2O \qquad (1.5)$$

At the completion of reaction, sufficient water is added to convert $BF_3.H_2O$ to $BF_3.2H_2O$. The latter is distilled out under vacuum as a heavy, water-soluble white liquid. Boron trifluoride may be recovered from the dehydrate in various ways. In the nitrating mixture, BF_3 does not directly ionize in HNO_3: it is $BF_3.H_2O$ or $BF_3.2H_2O$ which protonates HNO_3 to produce NO_2^+ ion, similar to other strong protic acids.

Trifluoroacetic acid gives a reactive nitrating mixture with HNO_3 for many aromatics [28,29]. The acidity of nitric acid and trifluoroacetic acid are comparable. Trifluoroacetic acid is a good solvent for many aromatic compounds as well. Due to its low boiling point (345 K), it can be easily recovered from the nitration mixture. Despite these advantages, the trifluoroacetate ion depresses the rate constant for nitration. It has rarely been used as a nitrating medium due to these properties.

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Nitric acid in methanesulfonic acid is an active nitrating agent of limited use [24,30,31]. Aqueous methanesulfonic acid is weaker than sulfuric acid of the same concentration. When nitric acid is used with methanesulfonic acid, the rate constant decreases with the increasing concentration of nitric acid. The equilibrium between nitric acid and nitronium ion is favored at the low concentration of the nitric acid [9]. But, it has the advantage as a nitrating medium in which the aromatic compounds are generally well-soluble, and no sulfonation or oxidation occurs as side reaction.

Trifluoromethanesulfonic acid (triflic acid) is one of the strongest known Bronsted acids. The main advantage of CF_3SO_3H is that it does not cause oxidation or sulfonation of the aromatic compounds, and can be useful for polynitration of the deactivated aromatic substrates. It is therefore an important strong acid for nitration with nitric acid. Coon et al. [32] found that two equivalents of CF_3SO_3H react with 100% HNO_3 to give a white crystalline solid, which is a mixture of nitronium trifluoromethanesulfonate and hydronium trifluoromethanesulfonate.

$$2CF_3SO_3H + HNO_3 \longrightarrow NO_2^+CF_3SO_3^- + H_3O^+CF_3SO_3^- \qquad (1.6)$$

The nitronium trifluoromethanesulfonate $\left(NO_2^+CF_3SO_3^-\right)$ is a more powerful nitrating agent than the mixed acid, and the rate of reaction can be extremely high [33]. Methylene chloride or other halogenated hydrocarbons can be used as co-solvents, which also facilitate the substrate solubility in nitration process.

Nitric acid in combination with fluorosulfuric acid (FSO_3H) acts as an excellent nitrating agent. Olah et al. [34] found that a mixture of HNO_3 and FSO_3H allows the trinitration of benzene to 1,3,5-trinitrobenzene at a temperature of 368 K. Water formed in the ionization of HNO_3 to NO_2^+ ion reacts with FSO_3H and thus, the nitrating system maintains

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high acidity. HNO_3–FSO_3H is also very suitable for other deactivated aromatics. Fluorosulfuric acid can lead to side-reactions resulting in oxidation and sulfonation.

Lewis acid fluorides such as antimony, tantalum or niobium pentafluoride greatly enhance the acidity of FSO_3H. FSO_3H–SbF_5 (known as *magic acid*) is one of the strongest known superacids [10].

$$2FSO_3H + 2SbF_5 \rightleftharpoons H_2SO_3F^+ + Sb_2F_{10}(SO_3F)^- \qquad (1.7)$$

SbF_5 stabilizes the fluorosulfate which is the deprotonated form of fluorosulfuric acid. Therefore, the presence of SbF_5 shifts the equilibrium in equation (1.7) to the right. $H_2SO_3F^+$ is an exceptionally strong acid and readily protonates in the presence of nitric acid. Thus, the nitric–magic acid combination is an extremely effective nitrating agent for the polynitration of aromatic compounds.

Nitration with HNO_3 in the presence of strong acids requires subsequent separation of the spent acid and neutralization of the acid left in the product. Most of the problems can be overcome by using a solid acid catalyst. Wright et al. [35] reported the use of polystyrene resin with 90% HNO_3 as the nitrating agent for nitration of toluene. However, this method is of limited use because the catalyst degrades during the reaction due to the benzylic hydrogens of polystyrene that can be abstracted easily by the highly reactive species such as NO_2^+ present in the medium. Thus, the polymer readily undergoes oxidative degradation. In addition, the polymer can also undergo nitration or sulfonation under the reaction conditions. In view of these limitations of polystyrene resin, various solid acid catalysts have been used such as zeolites [36–38], clay supported metal nitrates [39] and silica gel supported catalysts [15–17]. The majority of these approaches have alleviated the problem of increased para-

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selectivity in the nitration of substituted aromatics. These methods, however, are acceptable for the production of small quantities of chemicals and unsuitable for large scale manufacture.

1.4.3 Nitration using alkyl nitrates with acid catalyst

Nitration of aromatics can be carried out with alkyl nitrates ($RONO_2$). The alkyl nitrates themselves do not act as nitrating agents. However, they become nitrating agents in the presence of acids. The alkyl nitrates are the alkyl esters of nitric acid. The catalyzing acids are supposed to form NO_2^+ from the alkyl nitrates. Sulfuric acid was first used with the alkyl nitrates and has been the most widely used protic acid [10].

$$RONO_2 + H_2SO_4 \longrightarrow NO_2^+HSO_4^- + ROH \qquad (1.8)$$

Alkyl nitrates have also been used with polyphosphoric acid [40]. The most frequently used alkyl nitrates are methyl nitrate and ethyl nitrate. Several Lewis acids are used as effective catalysts for nitration with alkyl nitrates. $AlCl_3$ was first used with ethyl nitrate [9].

$$RONO_2 + AlCl_3 \longrightarrow NO_2^+AlCl_3OR^- \qquad (1.9)$$

The reactions proceed through the formation of a complex of the alkyl nitrate. Methyl nitrate is a very effective nitrating agent in the presence of BF_3 as catalyst [41]. The other Lewis acids such as $SnCl_4$, $SbCl_5$ and $FeCl_3$ can also be used with the alkyl nitrates to carry out nitration. Nafion-H was found active in catalyzing nitration with alkyl nitrates. Benzene and alkylbenzenes are nitrated with excellent yields using *n*-butyl nitrate at around 353 K in the presence of solid Nafion-H acid catalyst [42]. The reactions were found useful as a selective and mild nitration method. Alkyl nitrates must be prepared and stored with care, because they can become explosives in the presence of a trace amount of acid. Acetone cyanohydrin nitrate was found to have enhanced reactivity compared to methyl nitrate in the preparation of many

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substituted nitro compounds [42,43]. It is more stable and can be stored for a longer period of time.

1.4.4 Nitration using acyl nitrates

Acyl nitrates $[RC(O)ONO_2]$ are the mixed anhydrides of nitric and carboxylic acids. They are considered to be powerful nitrating agents.

$$ArH + RC(O)ONO_2 \longrightarrow ArNO_2 + RCOOH \qquad (1.10)$$

They can be extremely explosive at high temperature. Therefore, they must be handled with great care. They are safely generated *in situ*. Acetyl nitrate (CH_3COONO_2) is the most-used acyl nitrate. It can be readily prepared in pure state from dinitrogen pentaoxide (prepared by distilling HNO_3 from P_2O_5) in acetic anhydride. Nitration with nitric acid in acetic anhydride is the most widely studied process [9,44,45]. Benzoyl nitrate also finds wide use in nitration together with other aroyl nitrates [46]. It is prepared in a manner similar to acetyl nitrate from benzoyl chloride and silver nitrate.

1.4.5 Nitration by nitryl halides with acid catalyst

The nitryl halides (i.e., nitryl chloride, fluoride and bromide) can nitrate aromatic compounds. Nitryl chloride (NO_2Cl) acts as a chlorinating agent for aromatics giving minor amounts of nitro compounds in polar solvents [10]. It becomes a more active nitrating agent in presence of the Lewis acids [47,48]. Titanium tetrachloride has been found to be the most satisfactory Lewis acid. $AlCl_3$, $FeCl_3$, $ZrCl_4$ and $AlBr_3$ are also effective, but the reactions are more difficult. Deactivated aromatics are nitrated with difficulty, and thus this method is of limited use. Nitration with nitryl fluoride can be satisfactorily carried out at low temperatures

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in the presence of Lewis acid fluorides. The fluoride reagent is a more reactive nitrating agent than the chloride, but it is more difficult to handle. The reactions need to be carried out at low temperatures. Benzotrifluoride has been nitrated at 223 K with 90% yield using BF_3 as catalyst [47]. Nitryl bromide is quite unstable as compared to its chloride and fluoride counterparts. Therefore, it has a very limited use.

1.4.6 Nitration by nitrogen oxides with acid catalyst

The oxides of nitrogen are important nitrating agents. Dinitrogen trioxide (N_2O_3), the anhydride of nitrous acid, shows no nitrating ability towards aromatic compounds. But, interesting nitration capabilities have been found when dinitrogen trioxide was used with Lewis acids such as boron trifluoride (BF_3). With BF_3, it forms a complex which is a good nitrosating agent, and a weak nitrating agent [49].

$$3N_2O_3 + 8BF_3 \longrightarrow 6\left(NO^+\right)\left(BF_4^-\right) + B_2O_3 \qquad (1.11)$$

The complex is nitrosonium tetrafluoroborate, and the nitration proceeds via nitrosation followed by oxidation [50]. Dinitrogen tetroxide (N_2O_4) is also regarded as a nitrating agent in the presence of strong acids. N_2O_4 is the mixed anhydride of nitric and nitrous acids. Sulfuric acid has been commonly used with N_2O_4 for nitration purpose. Several aromatic compounds have been nitrated to give excellent conversion in the presence of this nitrating agent [10]. Nitration has also been carried out with the complexes from dinitrogen tetroxide and Lewis acids such as BF_3 [42,50]. Dinitrogen pentoxide (P_2O_5) is also used to nitrate aromatic compounds in carbon tetrachloride solution and several other organic solvents [10,51]. Nitration of aromatic compounds has been studied in the solution of N_2O_5 in nitric acid as well as in sulfuric acid [10]. Lewis acid (e.g., BF_3)-catalyzed nitration of aromatic compounds with N_2O_5 has also been reported [52].

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1.4.7 Nitration with nitronium salts

Aromatic compounds can be efficiently nitrated by using many stable nitronium salts. Nitronium salts are colorless, crystalline compounds and they are very hygroscopic. Some of them are very unstable (e.g., nitronium perchlorate and sulfate), which undergo spontaneous decomposition. On the other hand, nitronium tetrafluoroborate and other complex fluoro-salts are relatively more stable. Nitronium tetrafluoroborate was initially prepared by adding a mixture of anhydrous hydrofluoric acid and boron trifluoride to a solution of dinitrogen pentoxide. Nitric acid can be used in place of dinitrogen pentoxide as mentioned in Section 1.4.2. The byproduct of reaction (i.e., HF and BF_3) can be recycled, and thus the nitration can be made catalytic. As no water is produced during the nitration, this process is advantageous where substrates contain functional groups that are sensitive to hydrolysis. Therefore, aromatic arenes, haloarenes, haloalkanes, nitroarenes, esters and aromatic nitriles can be nitrated in high yield without any difficulty [10,30]. Deactivated aromatic compounds need higher temperatures and longer reaction times. They are preferably nitrated in strongly acidic solutions. The most serious limitation of the use of nitronium tetrafluoroborate is its low solubility in many solvents. The most convenient solvent is sulfolane in which the tetrafluoborate is soluble in about 7% [53]. Acetonitrile is also an appropriate solvent for nitration with nitronium salts but the nitrile group strongly interacts with NO_2^+ and causes acetonitrile to slowly oligomerize even at room temperature. Therefore, there is a significant need for more soluble nitronium salts that are stable at the same time. Nitronium hexafluorophosphate $\left(NO_2^+PF_6^-\right)$ is much more soluble in many organic solvents. Its solubility in nitromethane is more than 30%. Thus, it is recognized as a very useful nitrating agent for nitration [54]. It can be prepared by using HF and PF_5. The availability of PF_5 may

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be a limitation for using this nitronium salt. The nitronium salt formed in HNO_3–CF_3SO_3H system is known as *triflate*, which is also a strong nitrating agent as described in Section 1.4.2.

1.5 Thesis outline

From the discussion in the previous sections on nitration of organic compounds, especially the nitration of aromatic compounds, it is apparent that the nitration reaction has immense industrial significance and there is a huge scope of research work. The objective of the research work presented in this thesis is to study the mass transfer and kinetic phenomena involved in the nitration of nitrobenzene at high-concentrations of sulfuric acid. **CHAPTER 1** presents a preliminary discussion on the history and importance of nitration of aromatic compounds in organic chemical processes. It also described the various reagents and approaches of aromatic nitration. **CHAPTER 2** reviews the background, and the related work for the nitration of aromatic compounds that has been carried out with mixed acid at various concentrations of sulfuric acid. It also describes the importance of the nitration of nitrobenzene at high-concentrations of sulfuric acid and the objectives of the present work. **CHAPTER 3** describes the measurement of important physicochemical properties of the nitrobenzene, sulfuric acid and nitric acid system. **CHAPTER 4** presents the mass transfer and kinetic aspects of nitration of nitrobenzene at high-concentrations of sulfuric acid. In this chapter, the theory of mass transfer in this liquid–liquid system has been presented and the mass transfer coefficients have been determined at various temperatures with varying stirring speeds. A novel method was employed to determine the rate constants under homogenized conditions, and they were analyzed using the M_c function. Using the values of the mass transfer coefficients and the rate constants, the reaction regimes were also determined.

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CHAPTER 5 presents the study of heterogeneous two-phase nitration of nitrobenzene at high-concentrations of sulfuric acid. A model was developed for simultaneous mass transfer with chemical reaction in the aqueous phase using the values of the mass transfer coefficients and the rate constants in Chapter 4. The proposed model was validated by carrying out nitration reactions at high-concentrations sulfuric acid. This chapter also presents the determination of yield of the products obtained in the nitration of nitrobenzene at various sulfuric acid concentrations at different temperatures. In addition, this chapter reports the distribution of isomers in the product. **CHAPTER 6** presents a summary and conclusion, with suggestions for future research.

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CHAPTER 2

BACKGROUND AND OBJECTIVES OF THE PRESENT WORK

This chapter describes the background of the research work and subsequently presents a detailed literature review on the nitration of aromatic compounds in the mixed acid. Importance and objectives of the present work are also highlighted in this chapter.

2.1 Introduction

It has been mentioned in Chapter 1 that the nitration of aromatic compounds using a mixture of nitric and sulfuric acids is an effective and most widely used technique. The mixed acid has served as an excellent agent to study the nitration system and has produced different types of products which have extensive use. It is cost effective as well. Thus, it has been used for a long time in the nitration of aromatic compounds. A detailed literature survey on aromatic nitration using mixed acid is presented in the following sections to understand the phenomena taking place in the reaction media.

2.2 Background and related works

2.2.1 Physical properties of the nitric acid and sulfuric acid systems

The pure nitric acid is free of nitrogen dioxide, which is called *white fuming nitric acid*. It is a colorless liquid with a density of 1520 kg/m^3 at 298 K which solidifies at 231.4 K to form white crystals and boils at 355.6 K [1]. When boiling in presence of light, even at room

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temperature, there is a partial decomposition with the formation of nitrogen dioxide as per the following reaction.

$$4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2 \qquad (2.1)$$

Nitric acid is miscible with water and upon distillation, gives an azeotrope with a concentration of 68.5% HNO_3 and a normal boiling temperature of 395 K. It has a density of 1410 kg/m^3. Nitric acid acts on organic compounds both as nitrating and as oxidizing agents. The type of reaction depends upon the compound and the concentration of the nitric acid. As a general rule, concentrated nitric acid acts mostly as a nitrating agent. When diluted, its nitrating action diminishes, and finally gives way to an oxidizing action. The limiting concentration of the nitric acid in a nitration process depends solely on the nitrated compound. Some phenols, for example, can be nitrated with nitric acid in concentrations of below 5 %, while benzene does not nitrate at this concentration [1].

Sulfuric acid, on the other hand, is not encountered naturally due to its great affinity towards water. The 100% sulfuric acid is a clear, colorless, odorless oily liquid having a melting point of 283 K and a boiling point of 563 K. It is sometimes called *oil of vitriol*. Although nearly 100% sulfuric acid can be made, the 98% grade is more stable in storage. When heated, the pure 100% acid loses sulfur trioxide gas, until an azeotrope, containing about 98% H_2SO_4 is formed at 610 K. The 98% grade is the usual form of what is described as concentrated sulfuric acid. It is miscible with water in all proportions. The densities of aqueous sulfuric acid solutions are well-documented in the literature [2]. The viscosity of concentrated sulfuric acid has some interesting features which are shown in Figure 2.1. The viscosity of sulfuric acid increases with sulfuric acid concentration up to 15.9 kmol/m^3 and then decreases with increase in sulfuric acid concentration, passes through a minimum at 17.5

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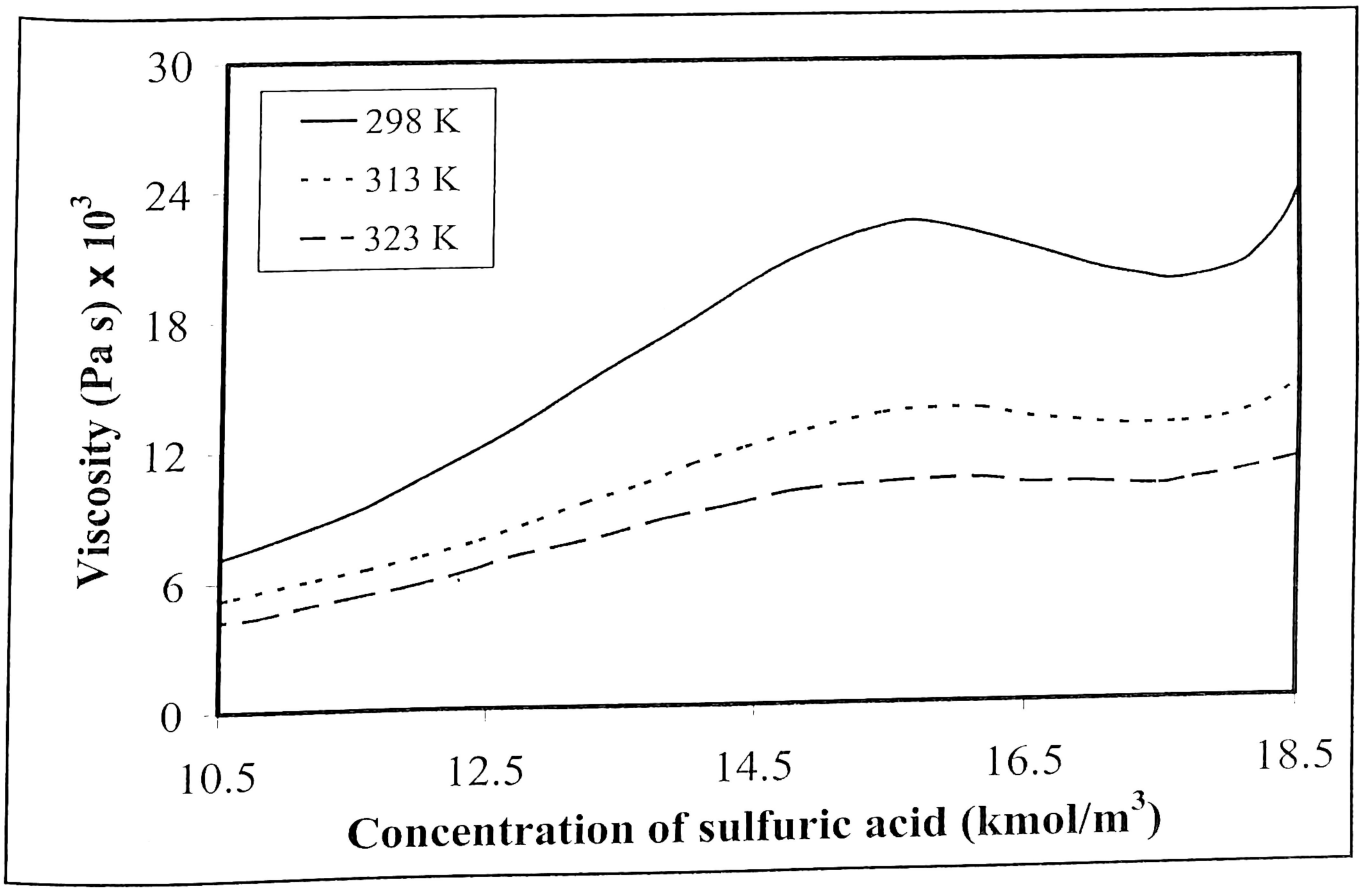


Figure 2.1 Variation of viscosity of aqueous sulfuric acid with its concentration [3–5].

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kmol/m^3, and then increases at the high sulfuric acid concentration. The failure of the oxygen atom of H_3O^+ to engage in hydrogen bonding with HSO_4^- results in the decrease in viscosity observed in sulfuric acid. The viscosity maximum results from the hydrogen bonded network developed with $H_3O^+ - HSO_4^-$ ion pairs [3].

Sulfuric acid is more acidic than nitric acid. The acidity of sulfuric acid changes by a large extent from the low concentrations to the high concentrations. The measurement scale of acidity in concentrated acids where pH is inappropriate was first realized by Hammett and Deyrup [6]. They used an acidity function, H_0, which is known as the *Hammett acidity function*. This function provides a measure of the tendency of the solution to transfer a proton to an uncharged base molecule. It is derived from the ionization equilibria of a particular class of indicators which behave as uncharged Brønsted-Lowry bases.

$$B + H^+ \rightleftharpoons BH^+ \tag{2.2}$$

The Hammett acidity function is defined as,

$$H_0 = pK_{BH^+} - \log\left(\frac{C_{BH^+}}{C_B}\right) \tag{2.3}$$

where pK_{BH^+} is equal to $-\log K_{BH^+}$, and K_{BH^+} is defined as the dissociation constant of the conjugate acid BH^+ of base B. C_B and C_{BH^+} are the concentrations of the base B and the BH^+ ion, respectively. An increasing order of negative values of the function corresponds to increasing acidity. The H_0 acidity scale has turned out to be useful for the measurement of strength of very weak uncharged bases, and also for the interpretation of the kinetics of certain classes of acid-catalyzed reactions. The value of H_0 for 100% sulfuric acid is -10.6 at 298 K. Afterwards, a different acidity function was proposed by Westheimer and Kharasch

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[7]. It has been further developed for sulfuric acid by several other investigators [8–11]. This function was designed to provide an acidity scale for secondary bases (ROH) whose ionization occurs according to the following relation.

$$ROH + H^+ \rightleftharpoons R^+ + H_2O \tag{2.4}$$

where R^+ is a carbonium ion. The new acidity function was defined as,

$$J_0 = -pK_{ROH} - \log\left(\frac{C_{R^+}}{C_{ROH}}\right) \tag{2.5}$$

where K_{ROH} represents the equilibrium constant for the equation (2.4). The usefulness of the new acidity function was much greater than the Hammett acidity function. As a result, the J_0 acidity function found wide use in various acid catalyzed reactions. The original idea of Hammett and Deyrup [6] has undergone modification since it has been shown that the Hammett's acidity function is generally not applicable to the protonation equilibria of all bases [12–14].

In attempting to overcome some uncertainties in the Hammett's method and to improve the acidity function J_0 further for determining the relative strengths of weak bases, Marziano et al. [15] proposed a new approach using a different criterion of the analysis of acidity of sulfuric acid. This is based on the observation that linear plots are formed between the logarithms of the C_{BH^+}/C_B values for the protonation equilibrium [i.e., equation (2.2)] of two overlapping indicators at the same acid concentration. This is valid for the entire acidity range. For indicator (X) whose protonation equilibrium, $X + H^+ \rightleftharpoons XH^+$, can be measured up to a concentration of 2 kmol/m^3, extrapolation to infinite dilution of a plot of the following equation against acid concentration (C_A) leads to the thermodynamic pK_{XH^+}

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values.

$$\log \frac{C_{XH^+}}{C_X} - \log C_{H^+} = -\log K_{app} \tag{2.6}$$

where K_{app} is the equilibrium constant which can be expressed as,

$$\log K_{app} = -pK_{XH^+} + bC_A \tag{2.7}$$

where b is constant. Thus, the plots of $\log K_{app}$ versus C_A will be linear. The quantities pK_{XH^+} and b are determined from these plots. The ratio of the activity coefficients of the following equation varies with C_A according to the following equation when the acid concentration is not too high.

$$-\log\left(\frac{\gamma_X \gamma_{H^+}}{\gamma_{XH^+}}\right) = bC_A \tag{2.8}$$

In equation (2.8), γ represents the activity coefficients for the respective species.

For two bases A and B, whose protonation occur as per the following equations,

$$A + H^+ \rightleftharpoons AH^+ \tag{2.9}$$

and

$$B + H^+ \rightleftharpoons BH^+ \tag{2.10}$$

we have,

$$\log K^A_{app} = -pK_{AH^+} + b_1 C_A \tag{2.11}$$

and

$$\log K^B_{app} = -pK_{BH^+} + b_2 C_A \tag{2.12}$$

The linear variation of the ratio of the activity coefficients with the acid concentration can be expressed as,

$$-\log\left(\frac{\gamma_A \gamma_{H^+}}{\gamma_{AH^+}}\right) = b_1 C_A \tag{2.13}$$

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and $$-\log\left(\frac{\gamma_B\gamma_{H^+}}{\gamma_{BH^+}}\right) = b_2 C_A \quad (2.14)$$

The following equation can be derived for the same acid concentration [15].

$$\log\left(\frac{\gamma_B\gamma_{H^+}}{\gamma_{BH^+}}\right) = n_B \log\left(\frac{\gamma_A\gamma_{H^+}}{\gamma_{AH^+}}\right) \quad (2.15)$$

where n_B is a constant which is equal to b_2/b_1. This equation shows that the log of the ratio of the activity coefficients corresponding to equilibrium (2.10) is the multiplie of that corresponding to equilibrium (2.9). Hence, equations (2.11) and (2.12) can be expressed as,

$$\log K_{app}^{A} = -pK_{AH^+} - \log\left(\frac{\gamma_A\gamma_{H^+}}{\gamma_{AH^+}}\right) \quad (2.16)$$

$$\log K_{app}^{B} = -pK_{BH^+} - \log\left(\frac{\gamma_B\gamma_{H^+}}{\gamma_{BH^+}}\right) \quad (2.17)$$

Substituting the value of $\log\left(\gamma_B\gamma_{H^+}/\gamma_{BH^+}\right)$ from equation (2.15) into equation (2.17) we get,

$$\log K_{app}^{B} = -pK_{BH^+} - n_B \log\left(\frac{\gamma_A\gamma_{H^+}}{\gamma_{AH^+}}\right) \quad (2.18)$$

Substituting the value of $\log\left(\gamma_A\gamma_{H^+}/\gamma_{AH^+}\right)$ from equation (2.16) into equation (2.18) we get,

$$\log K_{app}^{B} = n_B\left(\log K_{app}^{A} + pK_{AH^+}\right) - pK_{BH^+} \quad (2.19)$$

If base A is taken as the standard indicator whose parameters are known, then from the plot of $\log K_{app}^{B}$ versus $\log K_{app}^{A}$, the value of pK_{BH^+} can be calculated.

The protonation equilibria for weaker bases were studied at the higher acid concentrations. Let us consider two bases (e.g., C and D) which undergo protonation at the

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same range of acid concentration. From the protonation experiments, it was observed that a plot of $\log K_{app}$ of base C versus $\log K_{app}$ of base D was linear [15]. This experimental behavior for different series of basic indicators has been tested over the whole range of acidity. By extrapolation of the plots of $\log K_{app}^{D}$ versus $\log K_{app}^{C}$ to pure solvent which can be regarded as the standard state, the equilibrium constants of an indicator can be calculated by equation (2.19). The stepwise method allows the estimation of the equilibrium constant for a series of indicators of decreasing strength. Moreover the extension of equation (2.15) to the whole acidity range for any two overlapping weak bases leads to the following relation which connects all the indicators.

$$\log\left(\frac{\gamma_A\gamma_{H^+}}{\gamma_{AH^+}}\right)=\frac{1}{n_B}\log\left(\frac{\gamma_B\gamma_{H^+}}{\gamma_{BH^+}}\right)=\frac{1}{n_Bn_C}\log\left(\frac{\gamma_C\gamma_{H^+}}{\gamma_{CH^+}}\right)=\frac{1}{n_Bn_Cn_D}\log\left(\frac{\gamma_D\gamma_{H^+}}{\gamma_{DH^+}}\right)$$
$$=\ldots\frac{1}{n_Bn_Cn_D\ldots n_Z}\log\left(\frac{\gamma_Z\gamma_{H^+}}{\gamma_{ZH^+}}\right)$$
$$=\frac{1}{n_{Z^*}}\log\left(\frac{\gamma_Z\gamma_{H^+}}{\gamma_{ZH^+}}\right) \qquad (2.20)$$

This equation relates the ratio of the activity coefficients of the weaker base Z to that of the standard base by the corresponding n_{Z^*}. Equation (2.20) allows the calculation of a new function, M_c, for the whole range of acidity by use of a set of indicators chosen independently of the conditions formulated for the H_0 function. The M_c function is defined as,

$$M_c=-\log\left(\frac{\gamma_A\gamma_{H^+}}{\gamma_{AH^+}}\right) \qquad (2.21)$$

In this method, it is only necessary to select the first indicator and its properties should be

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known. Thus, based on the first indicator, the values of n_B, n_C, n_D,. . ., n_Z for each base can be calculated. Then the unknown value of pK_{XH^+} of base X can be calculated by the M_c function from the following equation.

$$\log\left(\frac{C_X C_{H^+}}{C_{XH^+}}\right) = -pK_{XH^+} - \log\left(\frac{\gamma_X \gamma_{H^+}}{\gamma_{XH^+}}\right)$$

$$= -pK_{XH^+} - n_X\left(\frac{\gamma_A \gamma_{H^+}}{\gamma_{AH^+}}\right) = -pK_{XH^+} + n_X M_c \qquad (2.22)$$

This approach is independent of the limitations of the H_0 function (e.g., the structure of the indicators) because the concentration of the acid is the only factor that affects the protonation equilibrium. The dissociation constant obtained for each base is independent of the structure of the indicators used.

The M_c function has been determined by the following equation given the values of pK_{XH^+}, $\log\left[C_X/C_{XH^+}\right]$ and n_X for various indicators (say, X), and of $\log C_{H^+}$ of each acid concentration [16].

$$M_c = -\log\left(\frac{\gamma_A \gamma_{H^+}}{\gamma_{AH^+}}\right) = \frac{1}{n_B}\left[\log\left(\frac{C_B}{C_{BH^+}}\right) + \log C_{H^+} + pK_{BH^+}\right]$$

$$= \frac{1}{n_B n_C}\left[\log\left(\frac{C_C}{C_{CH^+}}\right) + \log C_{H^+} + pK_{CH^+}\right]$$

$$\ldots\ldots = \frac{1}{n_B n_C \ldots n_Z}\left[\log\left(\frac{C_Z}{C_{ZH^+}}\right) + \log C_{H^+} + pK_{ZH^+}\right] \qquad (2.23)$$

The M_c function and the H_0 acidity function for aqueous sulfuric acid is shown in Figure 2.2.

The protonation equilibria of two weak bases in sulfuric acid have been extensively studied and the following relationship between the activity coefficients of any i and j

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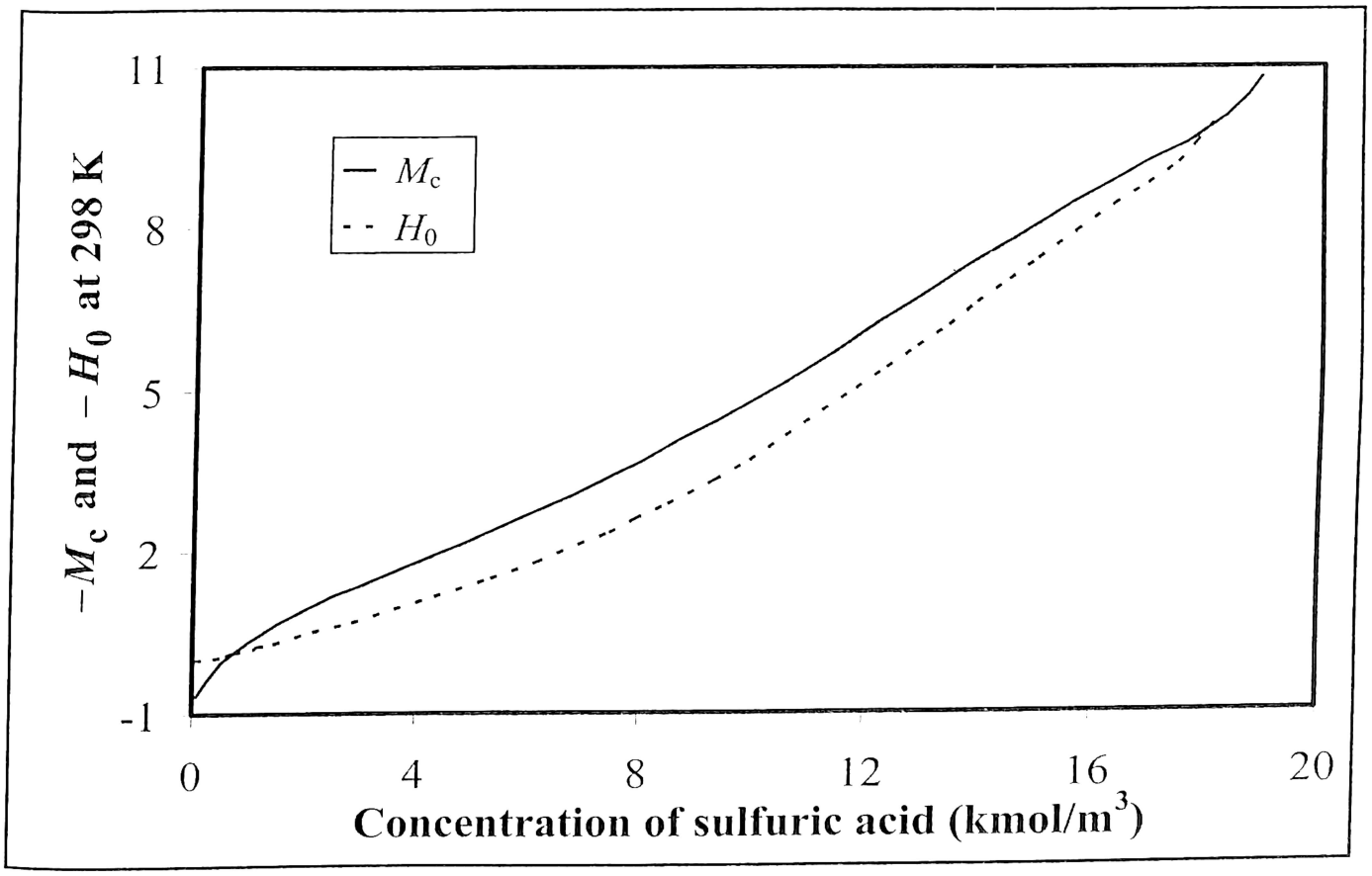


Figure 2.2 Plots of M_c and H_0 against the concentration of sulfuric acid at 298 K [6,15].

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indicators has been obtained [17].

$$-\log\left(\frac{\gamma_{Bi}\gamma_{H^+}}{\gamma_{BiH^+}}\right) = -n_{ij}\log\left(\frac{\gamma_{Bj}\gamma_{H^+}}{\gamma_{BjH^+}}\right) \tag{2.24}$$

Using equation (2.24), it is possible to define the M_c function in a generalized form as,

$$M_c = -\log\left(\frac{\gamma_{Bi}\gamma_{Ai}}{\gamma_{Ci}}\right) = -n_{ij}\log\left(\frac{\gamma_{Bj}\gamma_{Aj}}{\gamma_{Cj}}\right) \tag{2.25}$$

where B represents the base, A represents the acid and C represents the conjugated acid. The general validity of the above relationship has been tested using different weak bases involved in protonation, ionization and rate processes. Experimental values of the M_c activity coefficient function in aqueous sulfuric acid have been used simultaneously by a computational procedure different from the stepwise method described above [18]. The computational method has several advantages. This method enables many sets of data to be treated simultaneously. The concept of linearity of the activity coefficient ratio with the concentration of acid was tested and found to be valid for all cases [19]. The M_c function scale for sulfuric acid was calculated ensuring that the indicators have the same pK_{BH^+} value regardless of the medium. The values of M_c function for sulfuric acid at 298 K are shown in Figure 2.3. The values of M_c at higher temperatures were determined by the following equation given by Marziano et al. [20]. The variation of M_c function with temperature is given by,

$$M_c(T) = M_c(298\ \mathrm{K})\left[\frac{200}{T} + 0.3292\right] \tag{2.26}$$

The applicability of M_c activity coefficient function was compared with the Hammett acidity function H_0, and the J_0 acidity function, and it was found that equilibria between various

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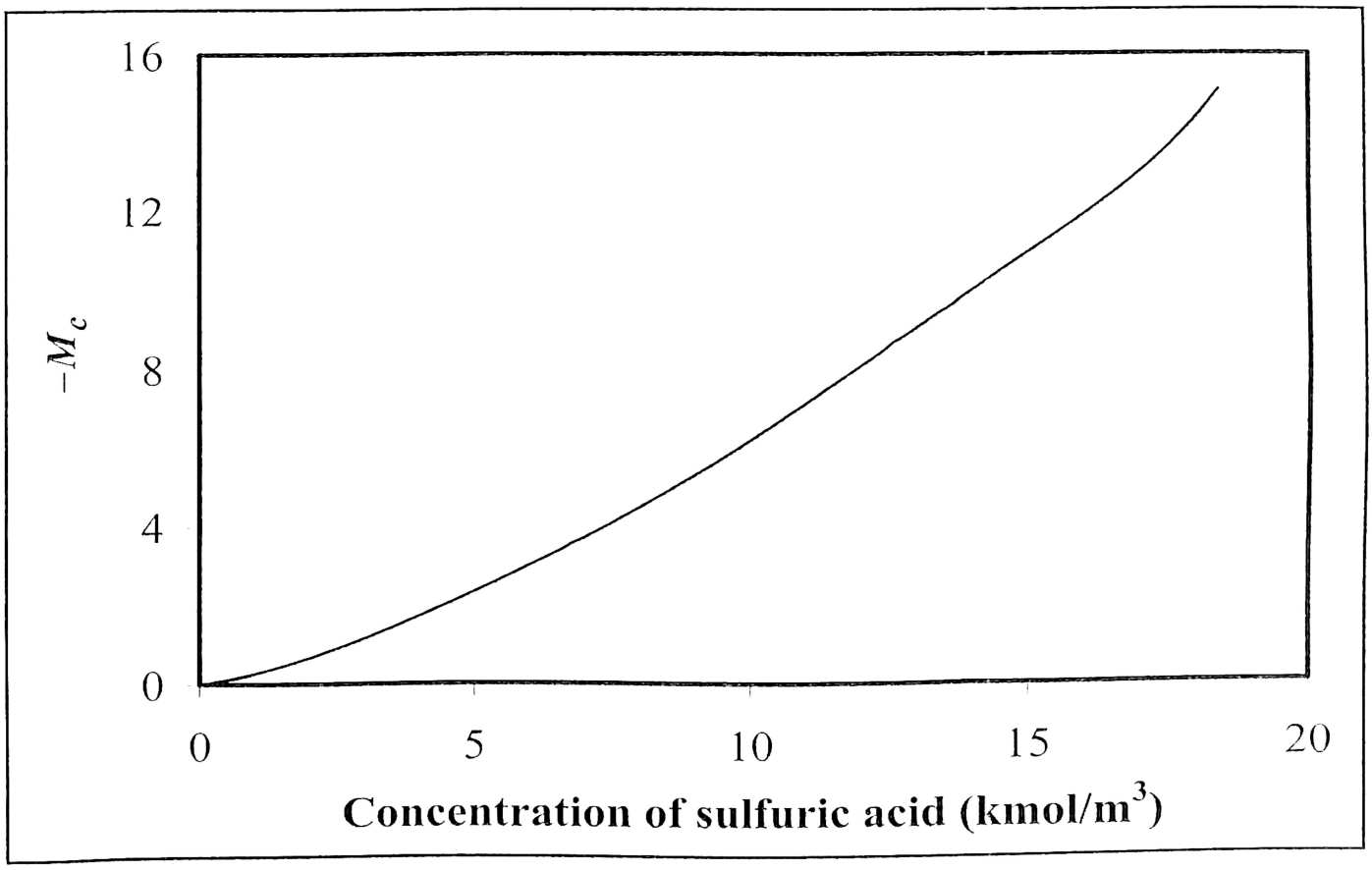


Figure 2.3 Variation of the M_c function with the concentration of sulfuric acid at 298 K [19].

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indicators and acid were compatible with the M_c activity coefficient function [21, 22]. This M_c function has been used to analyze results in reaction kinetics. It has also been used to investigate the mechanisms of a number of different reactions [14].

An interesting equilibrium was observed when nitric acid was treated with aqueous sulfuric acid solutions. The ionic species, which are present in the solution, are described by the following equilibria [23].

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \qquad (2.27)$$

and

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O \qquad (2.28)$$

These equilibria have been extensively studied by different techniques such as, Raman, UV, IR and NMR spectroscopy. These investigations have identified different molecular and ionic species present in the solutions. Deno et al. [24] examined the solutions of nitric acid in sulfuric acid (0 – 18.5 kmol/m^3) by Raman spectroscopy. They observed that equilibrium (2.27) exists for 2.3 – 9.2 kmol/m^3 sulfuric acid, and nitric acid exists as molecular nitric acid for 10.3 – 14.6 kmol/m^3 sulfuric acid. They also pointed out that the shift of equilibrium from HNO_3 to NO_2^+ was complete by 16.7 kmol/m^3 H_2SO_4, and from 17.1 to 18.5 kmol/m^3 H_2SO_4, the conversion to NO_2^+ was complete and remained constant. Marziano et al. [25] evaluated the ionization ratio, $C_{NO_2^+}/C_{HNO_3}$ of nitric acid in 14.1 – 17.9 kmol/m^3 sulfuric acid by Raman and UV spectroscopy at 298 K. Ross et al. [26] have used ^{14}N NMR studies of the $HNO_3 - NO_2^+$ equilibrium to determine the fractional conversions of nitric acid. They also obtained the rate constants for the formation and dehydration of the NO_2^+ ion. NMR spectra were recorded for HNO_3 in 14.1 – 18.4 kmol/m^3 aqueous sulfuric acid. The data obtained from the NMR studies showed good agreement with the data reported by Raman and UV

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spectroscopy. Later, Sampoli [27] studied extensively the equilibria of nitric acid in sulfuric acid (0 – 18.4 kmol/m^3) at 298 K by Raman and UV spectroscopy. The variations of $C_{HNO_3}/C_{NO_3^-}$ and $C_{NO_2^+}/C_{HNO_3}$ with sulfuric acid concentration were analyzed to evaluate the corresponding dissociation constants. Their extensive experiments have shown that nitric acid is dissociated to NO_3^- in sulfuric acid of concentrations up to 14.1 kmol/m^3, and at the higher concentrations of sulfuric acid, nitric acid is dissociated to NO_2^+ as reported by Deno et al. [24]. These equilibria were studied widely and well supported by the other works [28,29]. Marziano et al. [20] also studied the protonation-dehydration equilibrium of nitric acid [i.e., equilibrium (2.28)] in the range of 14.1 – 17.5 kmol/m^3 sulfuric acid as a function of temperature. The variation of $C_{NO_2^+}/C_{HNO_3}$ ratios has been analyzed to evaluate the dissociation constants $\left(pK_{NO_2^+}\right)$. The ionization ratio, $C_{NO_2^+}/C^0_{HNO_3}$, at different concentrations of sulfuric acid has been summarized in Figure 2.4.

The acidity dependence of the $HNO_3 - NO_3^- - NO_2^+$ equilibrium in aqueous sulfuric acid was described satisfactorily in terms of the M_c function [22,27,30–32]. The good description of the equilibria over a wide range of acidity strongly supports the M_c method. The definition of M_c function can be represented as [30,32],

$$M_c = -n' \log\left[\frac{\text{Product of activity coefficients of reactants}}{\text{Product of activity coefficients of products}}\right] \qquad (2.29)$$

where n' is a thermodynamic parameter which depends on a particular equilibrium. Equation (2.29) relates M_c to the ratio of activity coefficients of all species involved. This suggests that M_c could describe the dissociation of the acid itself within the solution.

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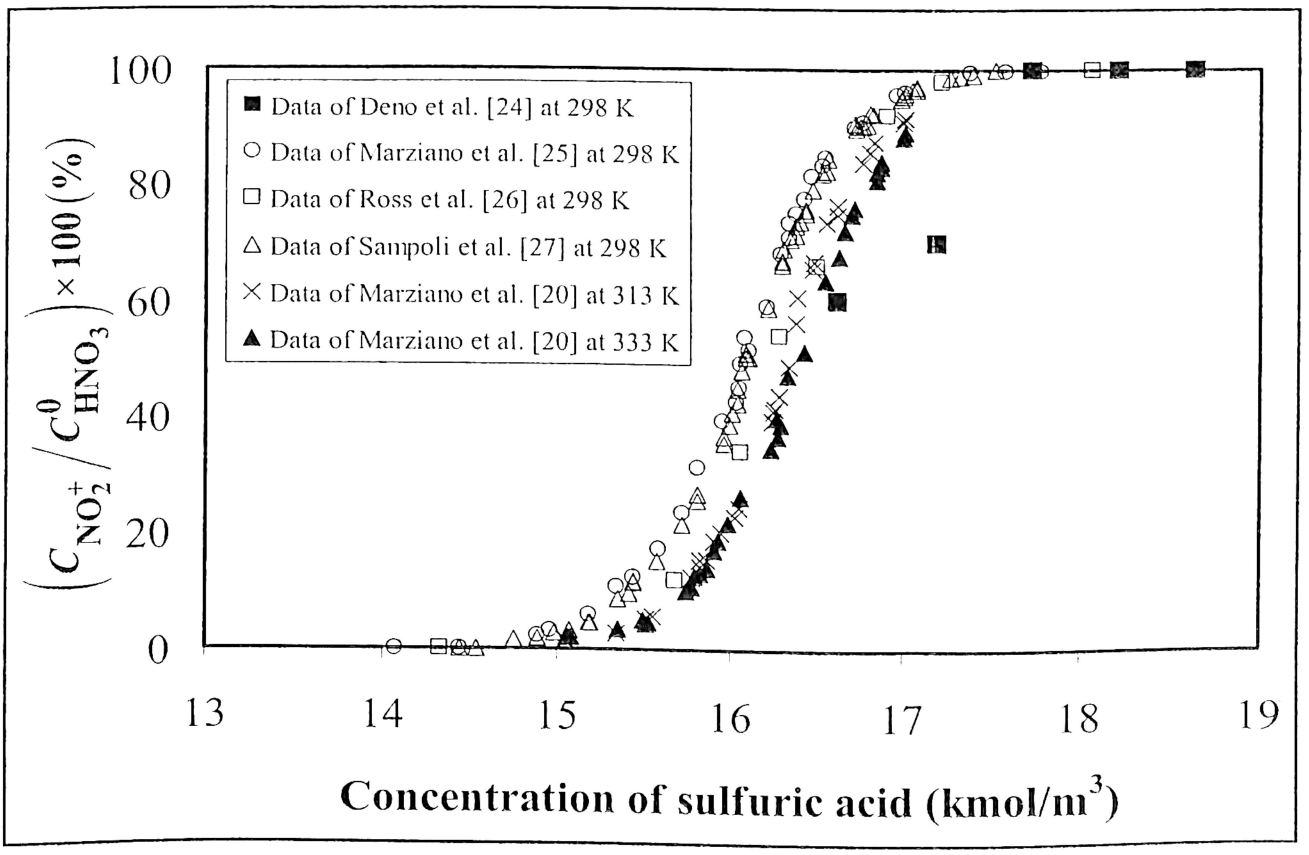


Figure 2.4 Percentage of HNO_3 converted to NO_2^+ in concentrated sulfuric acid at 298 K, 313 K and 333K.

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2.2.2 Mass transfer aspects of aromatic nitration

Aromatic nitration by mixed acid involves a heterogeneous liquid–liquid reaction. The rate of reaction depends upon the amount of aromatic compound transferred into the mixed acid phase from the organic phase. Because the nitration is industrially carried out with a large volume of sulfuric acid, the knowledge of solubility of aromatic compound in sulfuric acid is important. The equilibrium solubility is required to determine the mass transfer coefficient of the aromatic compound in sulfuric acid. Hammett and Chapman [33] determined the solubility of some organic oxygen compounds in a wide range of concentrations of sulfuric acid at 298 K. They found that most oxygen compounds were well-soluble in the concentrated sulfuric acid. Nitrobenzene was found to have the highest solubility in the concentrated sulfuric acid. They reported data on equilibrium solubility of nitrobenzene in sulfuric acid of concentration between 0 and 13.9 kmol/m^3. They found that the value of equilibrium solubility of nitrobenzene was 255 mol/m^3 at 13.9 kmol/m^3 sulfuric acid. Later, Modak and Juvekar [34] studied the solubility of nitrobenzene at sulfuric acid concentrations up to 15.6 kmol/m^3. Their data compared well with the data of Hammett and Chapman [33].

Active aromatic compounds undergo either spontaneous sulfonation or they have very low solubility in sulfuric acid. Benzene has very low solubility in aqueous sulfuric acid, and it is converted to benzenesulfonic acid at the high-concentrations of sulfuric acid. However, in presence of nitric acid, no sulfonation takes place until HNO_3 is exhausted. This is due to the fact that nitration is generally a much more rapid process than sulfonation. Toluene also shows very low solubility in the sulfuric acid solutions. The solubility of toluene in aqueous sulfuric acid has been reported by Cox and Strachan [35]. They studied the solubility at 11.6 kmol/m^3 sulfuric acid in the temperature range between 288 K and 308 K. The equilibrium

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solubility of toluene in 11.6 kmol/m^3 sulfuric acid at 298 K was 2.23 mol/m^3. They have also reported the solubility of toluene in the range of 9.8 to 13.8 kmol/m^3 sulfuric acid at 298 K [36,37]. The measurement of solubility of toluene in concentrated sulfuric acid is difficult because toluene gets sulfonated in the concentrated sulfuric acid medium [38]. Thus, the solubility data are unavailable in the literature at the high-concentrations of sulfuric acid. The solubility of chlorobenzene has been reported by Cox and Strachan [39]. They determined the solubility at 11.6 kmol/m^3 sulfuric acid at the temperature from 283 K to 323 K. The solubility of chlorobenzene at 298 K was found to be 4.4 mol/m^3.

Chapman et al. [37] reported the value of mass transfer coefficient of toluene at sulfuric acid concentrations between 13 kmol/m^3 and 13.8 kmol/m^3. They found the value of mass transfer coefficient to be 1.03×10^{-5} m/s at 298 K with a stirrer speed of 65 revolutions per minute. They used the technique of Danckwerts [40] to determine the mass transfer coefficient.

The following empirical correlation has been developed by Calderbank and Moo-Young [41] to determine the mass transfer coefficient in agitated liquid–liquid systems.

$$k_L = 0.13\left(\frac{P\mu_a}{V_a\rho_a^2}\right)^{1/4}\left(\frac{\mu_a}{\rho_a D_{ArH}}\right)^{-2/3} \tag{2.30}$$

where μ_a, ρ_a and V_a are the viscosity, density and volume of the continuous phase, respectively, and D_{ArH} is the diffusivity of the aromatic compound into the continuous phase. P is the power dissipated by the agitator which can be calculated by the following equation.

$$P = P_0\rho_{mix}N^3D_i \tag{2.31}$$

where P_0 is the power number (which is a constant), ρ_{mix} is the density of the mixture, N is stirrer speed and D_i is the diameter of the impeller. Although equation (2.30) was developed

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for non-reactive agitated system, it has been widely used in the systems where mass transfer with chemical reaction occurs simultaneously. This method has been extensively used in the mixed acid nitration of aromatic compounds [42–46]. This correlation is useful for predicting the value of k_L when the aromatic substrate has very low solubility, or undergoes sulfonation in the concentrated sulfuric acid medium. Using the correlation given by equation (2.30) and the experimental data of Chapman et al. [37], the value of mass transfer coefficient of toluene in sulfuric acid was found to be 1.1×10^{-5} m/s, which is in agreement with the value reported in the literature.

Direct experimental values of mass transfer coefficient of nitrobenzene in sulfuric acid solutions were measured by Modak and Juvekar [34]. They have measured the mass transfer coefficient by batch dynamic experiments in a glass reactor under the flat interface condition. Nitrobenzene was contacted with sulfuric acid of known concentration (in absence of any nitric acid). The build-up of concentration of nitrobenzene in the acid phase was measured as a function of time. The values of mass transfer coefficient were found to be 1.94×10^{-5} and 2.1×10^{-5} m/s at the impeller speeds of 50 and 80 revolutions per minute, respectively. The concentration of sulfuric acid was 14.5 kmol/m^3. Since the organic phase is almost pure nitrobenzene, the resistance to diffusion in that phase is practically absent. Hence, the measured value of mass transfer coefficient corresponds to the mass transfer coefficient in the aqueous film.

2.2.3 Mechanism and kinetics of aromatic nitration with mixed acid

In aromatic nitration, nitric acid may be used in a variety of media (see Section 1.3). It may be used in pure form, in aqueous media or in other acids. The mechanisms of the reaction in these different media have been studied extensively for a large number of aromatic

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compounds. The widespread experimental evidence has led to the conclusion that the nitration mechanism proceeds through the formation of the NO_2^+ ion, which acts as the electrophile.

Ingold and Hughes [47–49] first demonstrated that the NO_2^+ ion attacks the aromatic compound (ArH) to form an intermediate, $ArHNO_2^+$. Their mechanism consists of four steps, which are outlined below.

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^- \quad (2.32)$$

$$H_2NO_3^+ \rightleftharpoons NO_2^+ + H_2O \quad (2.33)$$

$$ArH + NO_2^+ \rightleftharpoons ArHNO_2^+ \quad (2.34)$$

$$ArHNO_2^+ + HSO_4^- \longrightarrow ArNO_2 + H_2SO_4 \quad (2.35)$$

The first two steps represent the acid-catalyzed transformation of nitric acid into the NO_2^+ ion. The NO_2^+ ion then reacts with the aromatic ring to give the Wheland intermediate (which is also known as σ *complex* or *arenium ion*) [50–52]. Deprotonation of the Wheland intermediate completes the reaction by regenerating the aromaticity of the molecule. The last step also regenerates the acid catalyst. This classical interpretation is known as the *Ingold-Hughes mechanism* of electrophilic aromatic nitration. As the linear NO_2^+ ion does not contain an empty bonding orbital, a gradual displacement of a π-electron pair to the more electronegative oxygen atom takes place when the NO_2^+ ion approaches the aromatic ring. Thus, NO_2^+ is a polarizable electrophile. Concurrent bending of the developing nitro group allows eventual bonding with the aromatic ring. In strong sulfuric acid media, steps represented by equations (2.32) and (2.33) are rapid and reversible, and quickly establish an

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equilibrium concentration of the NO_2^+ ion. Furthermore, limited solubility of the aromatic compound in the nitration medium and the presence of a sufficient quantity of water result in the forward of step represented by equation (2.34) much slower than the reverse of the step represented by equation (2.33). The Ingold mechanism readily accounts for the observed substituent effects. Electron-donating substituents on the benzene nucleus increase its reactivity and on the other hand, electron withdrawing substituents decrease it. These observations are in agreement with the electrophilic nature of the reaction. Furthermore, electron-donating groups generally direct the nitro group to the ortho and para positions in relation to the substituent, since they increase the electron density at these positions. Conversely, the electron-withdrawing groups lead to meta nitration due to the decrease in electron density in the ortho and para positions, and relatively higher electron density at the meta position. These explanations are based on electronic considerations of the aromatic compounds.

Bunton and co-workers [53,54] investigated the rate of ^{18}O exchange between HNO_3 and $^{18}OH_2$ for various concentrations of HNO_3, and compared with the rates of nitration of a number of aromatic substrates at these acidities. Bunton's investigation has provided a strong kinetic evidence for the involvement of the NO_2^+ ion. This finding was significant since the previous studies by Ingold on the kinetics of nitration were consistent with either protonated HNO_3 (i.e., $H_2NO_3^+$ ion), or the NO_2^+ ion as the reactive species. However, Ingold had presented a strong argument in favor of the NO_2^+ ion. A strong evidence for the involvement of the NO_2^+ ion was furnished by Westheimer and Kharasch [7]. It had been quantitatively recognized in their work that nitration rate increases with increasing acidity. Their observation

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was consistent with both NO_2^+ and $H_2NO_3^+$ ions as the possible nitrating agent. They carried out the ionization of nitric acid in the concentrated sulfuric acid parallel with the ionization of trinitrotriphenyl carbinol. The trinitrotriphenyl carbinol was chosen because it converts into a colored carbonium ion, and it has the ability to ionize in the same manner as the nitric acid in concentrated sulfuric acid to produce NO_2^+ ion. The ionization of nitric acid in the concentrated sulfuric acid is given below.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (2.36)$$

The increase of rate of nitration of nitrobenzene parallels the ionization of trinitrotriphenyl carbinol in the same sulfuric acid medium. Thus, it was evident that the two processes undergo the same type of ionization. Their study strongly suggests that NO_2^+ ion is the active nitrating agent.

The homogeneous nitration of aromatic compounds in dilute or concentrated sulfuric acid has long been known to exhibit second-order kinetics. The rate determining step is believed to be attack of the nitronium ion, NO_2^+, on the aromatic compound. The rate of nitration is therefore given by [23],

$$\text{Rate} = k_2^* C_{ArH} C_{NO_2^+} \qquad (2.37)$$

where k_2^* is the observed rate constant, and C_{ArH} and $C_{NO_2^+}$ are the concentrations of the aromatic compound and nitronium ion in the acid phase, respectively. The direct determination of $C_{NO_2^+}$ is very difficult in the nitration medium. Thus, the rate expression in terms of the concentrations of reacting compounds has been given by [23],

$$\text{Rate} = k_{2,exp} C_{ArH} C_{HNO_3} \qquad (2.38)$$

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where $k_{2,exp}$ is the observed or experimentally-determined second-order rate constant. C_{ArH} and C_{HNO_3} are the concentrations of the aromatic compound and nitric acid in the aqueous phase, respectively.

Results of experimental studies on nitration of benzene, toluene, *o*-xylene, chlorobenzene, nitrobenzene and many other aromatic compounds are available in the literature. Most of these works have performed kinetic studies at low concentrations of sulfuric acid and with a small reaction mass in a batch process. The major parameters which influence the rate of nitration are the concentration of sulfuric acid, temperature of reaction and the speed of stirring. Lewis and Suen [55] investigated the mononitration of benzene to find the effects of various independent variables. These variables were composition of nitrating acid, composition of the organic phase, relative volume of the two liquid phases and the degree of agitation. Out of these variables, they found that the composition of nitrating acid had the greatest influence on the rate of nitration. They employed continuous nitration where the composition of acids and the organic phase remained constant. Later, Kobe and Mills [56] reported an optimum condition for nitration of benzene to mononitrobenzene. They obtained yield of nitrobenzene greater than 98% in just 40 minutes at 333 K with sulfuric acid-benzene weight ratio of 1.2. The initial sulfuric acid concentration used in their work was 15.1 kmol/m^3 and an equimolar ratio of nitric acid and benzene was employed. The effect of changing process variables (such as composition of nitrating acid, composition of the organic phase and the degree of agitation) on the yield was also studied. Kobe and co-workers studied nitration of various aromatic compounds such as cumene [57], *p*-xylene [58], *o*-xylene [59] and toluene [60,61]. These works were mainly focused on the effects of concentration of sulfuric acid, stirring speed, and the distribution ratio of nitric acid in two phases on the rate

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of nitration to find an optimum condition to get high yield. Biggs and White [62] studied the rate of nitration of benzene with mixed acid in a continuous-flow, stirred reaction system in the temperature range 307 K to 327 K. They determined the reaction rate as a function of the phase composition, temperature, agitation speed and the volume fraction of the acid phase.

Kinetic studies to determine the observed rate constant were carried out for nitrobenzene and other aromatic compounds by Westheimer and Kharasch [7] at various temperatures. The homogeneous nitration of nitrobenzene was performed at high-concentrations of sulfuric acid (> 14.5 kmol/m^3) at 278 K, 298 K and 313 K. They measured the rate of nitration calorimetrically. A non-adiabatic calorimeter was used to measure the temperature rise as the reaction proceeded. The value of rate constant was obtained by using the method of Roseveare [63]. In this method, the rate constant and the final temperature rise are computed from the data of an individual experiment for a second-order reaction. This method is useful when the reactants are present in equal concentrations and the observations are made at equal time intervals. Westheimer and Kharasch [7] found the rate of nitration of nitrobenzene increased by a factor of about 3000 when the concentration of sulfuric acid was increased from 14.1 kmol/m^3 to 16.6 kmol/m^3. They also reported that the maximum rate of nitration occurred at 16.6 kmol/m^3 sulfuric acid concentration. Bonner et al. [64] extended this experimental procedure to the nitration of nitrobenzene, 4-nitrochlorobenzene and trimethylphenylammonium ion at 298 K. They have shown that the maximum value of second-order rate constant occurred at 16.7 kmol/m^3 concentration of sulfuric acid.

Deno and Stein [65] have studied the rates of nitration of anisole, benzene, chlorobenzene and other aromatic compounds. They conducted the experiments in a 1 cm silica cell filled with sulfuric acid of the desired concentration. The progress of the reactions

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was followed spectroscopically, and a wide range of data on the pseudo second-order rate constant was obtained for the respective aromatic compounds. Coombes et al. [66] carried out the nitration of benzene, toluene, naphthalene and mesitylene at moderately higher sulfuric acid concentrations (upto 14.0 kmol/m^3). They determined the second-order rate constant $\left(k_{2,\exp}\right)$ using the *stopped-flow* technique at 298 K. Equal volumes of mixed acid and the solution of the substrate in sulfuric acid were rapidly mixed. When the mixed solution was stationary, the change of UV transmission at a chosen wavelength was recorded against time on an oscilloscope. They also investigated the kinetics of nitration of the monohalogenobenzenes in sulfuric acid and perchloric acid, and nitration of many di-poly-halogenobenzenes in sulfuric acid [67].

Due to the limited solubility of aromatic compounds in sulfuric acid, acetic acid has been used to enhance the solubility of the compound in sulfuric acid. The influence of acetic acid on nitration was investigated by Marziano et al. [68]. They performed the kinetic study at 298 K with and without acetic acid under the same conditions and showed that addition of *ca.* 10^{-3} kmol/m^3 acetic acid increased the solubility of aromatic compounds appreciably, without affecting the reaction rate.

It has long been noted that the rate of nitration of many organic compounds increases with the acidity of the sulfuric acid in the mixed acid medium. It has also been observed that some aromatic compounds show a maximum value of rate constant around 16.7 kmol/m^3 sulfuric acid. A steep increase up to the maximum is sometimes observed in going from dilute sulfuric acid solutions to 16.7 kmol/m^3 sulfuric acid. A slight decrease in rate constant is observed in the range of 16.7 kmol/m^3 to 18.3 kmol/m^3 sulfuric acid, although nitric acid is completely converted to NO_2^+ ion in this concentration range. Different explanations have

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been expounded for the decrease in rate constant [7,23,52,64]. The decline in the rate constant above 16.7 kmol/m^3 sulfuric acid concentration may be explained by considering the effect of the medium. To gain insight into the problem, the variation of the rate constant with the acidity of the medium was analyzed by using the M_c activity coefficient function given by Marziano and co-workers (see Section 2.2.1). According to the transition state theory (Brønsted rate law), the rate of nitration can be expressed as [69],

$$\text{Rate} = k_2' C_{\text{ArH}} C_{NO_2^+} \frac{\gamma_{\text{ArH}}\ \gamma_{NO_2^+}}{\gamma^{\#}} \tag{2.39}$$

where k_2' is a thermodynamic parameter that depends on temperature, γ_{ArH} and $\gamma_{NO_2^+}$ are the activity coefficients of the aromatic substrate and nitronium ion, respectively, and $\gamma^{\#}$ is the activity coefficient of the transition-state intermediate. Since the NO_2^+ ion and the transition-state intermediate are both positively charged species, their activity coefficients are likely to vary in the same manner. Therefore, the ratio of these coefficients is expected to be constant. Thus, any dependence of the second-order rate constant on acidity beyond the point where all of the nitric acid has been converted to NO_2^+ ion is primarily a consequence of the changes in the activity coefficient of the aromatic compound. Based on the rate expression given by equation (2.39), a rate equation has been proposed by Marziano and co-authors employing the M_c function of sulfuric acid as [30,70],

$$\text{Rate} = k_2' C_{\text{ArH}} C_{NO_2^+} 10^{nM_c} \tag{2.40}$$

where n is another thermodynamic parameter which is unique for each aromatic compound. Account to be taken of the actual concentration rather than the stoichiometric concentration (i.e., 1:1) in the use of the M_c function. Equation (2.40) has been tested for many aromatic

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compounds such as nitrobenzene, methyl phenyl sulfone, benzene, toluene and many other aromatic compounds in concentrated sulfuric acid, perchloric acid and trifluomethanesulfonic acid [22,30,32,44]. The M_c function has been very useful for determining the thermodynamic rate constants.

So far, single phase homogeneous aromatic nitration has been extensively investigated and reported in the literature. But nitration on an industrial scale is usually a two-phase reaction with an organic phase and an aqueous phase present throughout the reaction. In the heterogeneous system, the reaction occurs solely in the acid phase. The aromatic species dissolves in the aqueous phase and reacts with the nitronium ions generated through the action of sulfuric acid with nitric acid. Although nitric acid distributes to an appreciable extent in the organic phase, the rate of nitration in the organic phase is negligible due to the fact that the concentration of H^+ ions in the organic phase is too low for nitronium ions to be generated to an appreciable extent [71].

Kinetics of heterogeneous two-phase nitration was first studied by Cox and Strachan [39]. They investigated nitration of chlorobenzene in 11.6 kmol/m^3 sulfuric acid in a round-bottom three-necked flask fitted with a paddle-type agitator. They proposed a simple kinetic model where the rate of transfer of aromatic compound to the acid phase is exactly equal to the rate of its removal by reaction. They have shown that with 11.6 kmol/m^3 sulfuric acid and low-concentrations of nitric acid, the two phase nitration of chlorobenzene is kinetically controlled. In these circumstances, the maximum kinetic rate was very much smaller than the maximum mass transfer rate. Cox and co-workers [35–37] studied two-phase nitration of toluene and showed that the nitration rates are very sensitive to the sulfuric acid concentration. They performed kinetic studies of nitration in sulfuric acid concentration in the

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range of 11.6 kmol/m^3 to 13.8 kmol/m^3. They observed that at the lower concentrations of sulfuric acid, the transition from kinetic to mass transfer control occurred, and at the higher concentrations, the transition from slow to fast reaction was observed. Later, Hanson and co-workers [72–74] demonstrated through the nitration of chlorobenzene, toluene and benzene that under heterogeneous conditions, diffusional resistance plays an important role in determining the overall rate of nitration of aromatic hydrocarbons at the acid concentration of industrial importance, even when a high degree of agitation was employed.

Zaldivar and co-workers [42,44,75,76] have carried out a series of studies where they employed an extensive experimental programme using adiabatic and heat-flow calorimetry, and pilot reactor, supported by chemical analysis. A series of nitration experiments were carried out to study the influences of different operating conditions such as temperature, stirring speed, sulfuric acid concentration, feed rate, interfacial area and overall mass transfer coefficient. Furthermore, the effect of phase inversion on the overall reaction rate has been studied. They developed a mathematical model to predict the overall conversion rate for the validation of the kinetically-controlled regime for the mononitration of benzene, toluene and chlorobenzene, and the mass transfer control regime as well. Quadros and co-workers [46,77] have used the film and penetration theories to model the nitration of benzene. Their models were compared with the experimental results showing good prediction in the intermediate reaction regime.

Modak and Juvekar [34] have proposed an alternative mechanism for the heterogeneous aromatic nitration. As per their mechanism, nitration occurs at two locations: in the bulk acid phase, and in the interfacial monolayer (i.e., a thin region a few molecular diameters thick separating the bulk organic and acid phases). Therefore, the total rate of nitration can be

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expressed as,

$$R_N = R_a + R_i \tag{2.41}$$

where R_N is the total rate of nitration, R_a is the rate of bulk nitration and R_i is the rate of interfacial reaction. R_a and R_i can be written as,

$$R_a = k_2 V_a C^a_{ArH} C^a_{NO_2^+} \tag{2.42}$$

$$R_i = k_2^i A^i C^i_{ArH} C^i_{NO_2^+} \tag{2.43}$$

where k_2 and k_2^i are the second-order rate constants for the bulk and the interfacial reactions, respectively. C^a_{ArH} and C^i_{ArH} are the concentrations of the aromatic compound in the bulk and at the interface, respectively. $C^a_{NO_2^+}$ and $C^i_{NO_2^+}$ are the concentrations of the nitronium ion in the bulk and at the interface, respectively. V_a is the volume of the acid phase and A^i is the area of the interface. Their model was supported by the results of the experiments on nitration of nitrobenzene conducted in a batch reactor with a low stirring speed. Relative magnitude of the bulk and interfacial rates during the nitration of nitrobenzene was determined with 14.0 kmol/m^3 to 15.6 kmol/m^3 concentrations of sulfuric acid at 300 K. The effects of interfacial area, concentration of sulfuric and nitric acids, and addition of surfactant and inert diluent in the organic phase on the rate of nitration were also studied.

2.3 Importance and objectives of the present work

From the preceding sections, it is evident that both experimental and theoretical studies of aromatic nitration with mixed acid have great industrial significance. This is the present industrial method practiced all over the world. It is a heterogeneous liquid–liquid reaction

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which occurs almost-exclusively in the aqueous phase. The organic compound diffuses into the aqueous mixed-acid-phase and reacts with the nitronium ion generated by the reaction between concentrated sulfuric acid and nitric acid. From the review of literatures, it has been observed that at the low-concentrations of sulfuric acid (i.e., ~10 kmol/m^3), the reaction is first-order with respect to both nitric acid and the organic compound (overall second-order). The reaction proceeds in the slow regime. When the sulfuric acid concentration is high, the rate of reaction depends on the interfacial area and the mass transfer coefficient, and the reaction proceeds in the fast regime. Some of the major parameters identified to be crucial in this heterogeneous reaction with respect to yield and selectivity are the concentration of sulfuric acid, the temperature of reaction and the speed of stirring. The first two parameters significantly affect the kinetics of the reaction. The rate of transfer of the organic compound into the aqueous phase mainly depends on the concentration of the acid phase and the speed of stirring. The latter parameter varies between 1,000 and 5,000 revolutions per minute in the industrial reactors. High-speed stirring generates a dispersion of the organic phase into the aqueous phase. The present work on the nitration of nitrobenzene using mixed acid was undertaken to study the effects of aforementioned important parameters.

Despite the industrial importance of the product of nitration of nitrobenzene (see Section 1.2.1), only a few investigations on the nitration of nitrobenzene have been reported. Being a deactivated aromatic compound, nitration of nitrobenzene is slow and can be studied easily in laboratory. So far, studies on various physical properties of the reaction system and the mass transfer studies have been restricted up to 15.6 kmol/m^3 sulfuric acid concentration and at room temperature. The reaction rate constants have been reported at the high-sulfuric acid concentrations at 298 K and 313 K in small cuvettes, and in a calorimeter. The yield of

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reaction and the distribution of the product isomers at different sulfuric acid concentrations and at different temperatures under reactor conditions have not been determined so far. These parameters are essential for the rational design of the nitration process.

The present research work has been undertaken to study the nitration of nitrobenzene in reaction media constituted with concentrated sulfuric acid with the following objectives:

- Determination of the physicochemical properties of the system such as the solubility of nitrobenzene in sulfuric acid (and vice versa), density of the aqueous phase equilibrated with nitrobenzene, and study of interfacial phenomena that occur when the nitrobenzene is brought in contact with concentrated sulfuric acid
- Determination of mass transfer coefficient at different concentrations of sulfuric acid at different temperatures employing various stirring speeds
- Studies of kinetics of the homogeneous nitration of nitrobenzene in a batch reactor, which include the determination of rate constants at various sulfuric acid concentrations, the effect of temperature on the rate constants, analysis of kinetic results using the M_c function, determination of activation energy of the reaction, and determination of reaction regime using the mass transfer coefficients and the rate constants
- Investigation of two-phase nitration of nitrobenzene to determine the concentration profiles of the reactants and the products in the reactor, and development of a model for mass transfer with chemical reaction for the heterogeneous nitration system
- Determination of yield of the dinitrobenzene isomers at different sulfuric acid concentrations at different temperatures, and measurement of the distribution of dinitrobenzene isomers in the product

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Notation

A	base
A^i	interfacial area (m^2)
b	constant defined in equation (2.7)
b_1	constant defined in equation (2.11)
b_2	constant defined in equation (2.12)
B	base
C	base
C_A	concentration of acid (mol/m^3)
C_{ArH}	concentration of aromatic compound (mol/m^3)
C_B	concentration of B (mol/m^3)
C_{BH^+}	concentration of BH^+ ion (mol/m^3)
C_C	concentration of C (mol/m^3)
C_{CH^+}	concentration of CH^+ ion (mol/m^3)
C_{H^+}	concentration of H^+ ion (mol/m^3)
C_{HNO_3}	concentration of HNO_3 (mol/m^3)
$C_{NO_2^+}$	concentration of NO_2^+ ion (mol/m^3)
$C_{NO_3^-}$	concentration of NO_3^- ion (mol/m^3)
C_{R^+}	concentration of carbonium ion (mol/m^3)
C_{ROH}	concentration of secondary base (mol/m^3)
C_X	concentration of X (mol/m^3)
C_{XH^+}	concentration of XH^+ ion (mol/m^3)
C_Z	concentration of Z (mol/m^3)
C_{ZH^+}	concentration of ZH^+ ion (mol/m^3)
C^a_{ArH}	concentration of aromatic compound in the aqueous phase (mol/m^3)

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C^{i}_{ArH}	concentration of aromatic compound at the interface (mol/m^2)
$C^{0}_{HNO_3}$	initial concentration of nitric acid (mol/m^3)
$C^{a}_{NO_2^+}$	concentration of NO_2^+ in the aqueous phase (mol/m^3)
$C^{i}_{NO_2^+}$	concentration of NO_2^+ at the interface (mol/m^2)
D	base
D_{ArH}	diffusivity of aromatic compound (m^2/s)
D_i	diameter of impeller (m)
H_0	Hammett acidity function
J_0	acidity function defined in equation (2.5)
k_2	second-order rate constant for bulk nitration (m^3 mol^{-1} s^{-1})
$k_{2,exp}$	observed second-order rate constant (m^3 mol^{-1} s^{-1})
K_{app}	apparent dissociation constant
k_2'	thermodynamic parameter defined in equation (2.39)
k_2^*	observed second-order rate constant with respect to actual nitrating agent, NO_2^+ (m^3 mol^{-1} s^{-1})
k_2^i	second-order rate constant for interface nitration (m^2 mol^{-1} s^{-1})
K_{AH^+}	dissociation constant of AH^+ ion
K_{BH^+}	dissociation constant of BH^+ ion
K_{CH^+}	dissociation constant of CH^+ ion
k_L	mass transfer coefficient (m/s)
$K_{NO_2^+}$	equilibrium constant of the NO_2^+ ion formation equilibrium
K_{ROH}	equilibrium constant of dissociation of secondary base, ROH
K_{XH^+}	dissociation constant of XH^+ ion

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K_{ZH^+}	dissociation constant of ZH^+ ion
K_{app}^{A}	apparent dissociation constant of base, A
K_{app}^{B}	apparent dissociation constant of base, B
K_{app}^{C}	apparent dissociation constant of base, C
K_{app}^{D}	apparent dissociation constant of base, D
M_c	activity coefficient function
n	thermodynamic parameter defined in equation (2.40)
N	stirring speed (rad/s)
n'	thermodynamic parameter defined in equation (2.29)
n_{ij}	constant defined in equation (2.24)
n_B	constant defined in equation (2.15)
n_C	constant defined in equation (2.20)
n_D	constant defined in equation (2.20)
n_X	constant defined in equation (2.22)
n_Z	constant defined in equation (2.20)
n_{Z^*}	constant defined in equation (2.20)
P	power dissipated by the agitator (W)
P_0	power number
ROH	secondary base
Rate	rate of nitration (mol m^{-3} s^{-1})
R_a	rate of bulk nitration (mol/s)
R_i	rate of interfacial nitration (mol/s)
R_N	total rate of nitration (mol/s)
V_a	volume of aqueous phase (m^3)
X	indicator
Z	indicator

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Greek letters

γ_A	activity coefficient of base, A
γ_{AH^+}	activity coefficient of AH^+ ion
γ_{Ai}	activity coefficient of base, A, with respect to indicator, *i*
γ_{Aj}	activity coefficient of base, A, with respect to indicator, *j*
γ_{ArH}	activity coefficient of aromatic compound
γ_B	activity coefficient of base, B
γ_{BH^+}	activity coefficient of BH^+ ion
γ_{Bi}	activity coefficient of base, B, with respect to indicator, *i*
γ_{BiH^+}	activity coefficient of BiH^+ ion
γ_{Bj}	activity coefficient of base, B, with respect to indicator, *j*
γ_{BjH^+}	activity coefficient of BjH^+ ion
γ_C	activity coefficient of base, C
γ_{CH^+}	activity coefficient of CH^+ ion
γ_{Ci}	activity coefficient of base, C, with respect to indicator, *i*
γ_{Cj}	activity coefficient of base, C, with respect to indicator, *j*
γ_D	activity coefficient of base, D
γ_{DH^+}	activity coefficient of DH^+ ion
γ_{H^+}	activity coefficient of H^+ ion
$\gamma_{NO_2^+}$	activity coefficient of nitronium ion
γ_X	activity coefficient of indicator, X
γ_{XH^+}	activity coefficient of XH^+ ion
γ_Z	activity coefficient of base, Z
γ_{ZH^+}	activity coefficient of ZH^+ ion
$\gamma^{\#}$	activity coefficient of transition-state intermediate

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μ_a viscosity of aqueous phase (Pa s)

ρ_a density of aqueous phase (kg/m^3)

ρ_{mix} density of reacting mixture (kg/m^3)

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CHAPTER 3

PHYSICOCHEMICAL PROPERTIES OF NITROBENZENE, SULFURIC ACID AND NITRIC ACID SYSTEM AND THEIR ROLE IN NITRATION OF NITROBENZENE

This chapter describes the measurement of some important physicochemical properties of nitrobenzene and the aqueous sulfuric acid solutions of high concentrations. The physicochemical properties include: solubility of nitrobenzene in sulfuric acid (and vice versa), solubility of nitrobenzene in nitric acid (and vice versa), density of the aqueous phase equilibrated with nitrobenzene, and interfacial tension between nitrobenzene and sulfuric acid. The droplet size distribution of nitrobenzene in the sulfuric acid was also determined. Another important aspect studied is the possibility of formation of any sulfonic acid derivative of nitrobenzene in the aqueous phase.

3.1 Introduction

The rational design and operation of the batch reactor for the heterogeneous reaction between nitrobenzene and mixed acid using high-concentrations of sulfuric acid requires detailed knowledge of the mass transfer phenomena as well as the kinetics of the reaction. An accurate interpretation of the mass transfer and the kinetic data requires the knowledge of the various physical properties of the nitrobenzene, sulfuric acid and nitric acid system. The solubility of nitrobenzene in sulfuric acid is the most important property required to determine the mass transfer coefficient of nitrobenzene in sulfuric acid. The solubility of nitrobenzene in

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nitric acid and vice versa is also an important physical property. Although the amount of nitric acid is much smaller than sulfuric acid in the reaction medium, this information provides an idea about how much effect the nitric acid in the reaction medium can have on the transfer of nitrobenzene in the aqueous phase. The other properties such as the density of the aqueous phase are useful in the verification of the mathematical model for the heterogeneous reaction. The interfacial tension between nitrobenzene and sulfuric acid gives a good indication of the interaction between nitrobenzene and sulfuric acid. The formation of stable droplets of nitrobenzene in concentrated sulfuric acid increases the interfacial area. It not only provides a driving force for the solubilization of nitrobenzene into sulfuric acid, but also has direct effect on the enhancement of the reaction rate. The occurrence of dispersion of nitrobenzene in the aqueous phase is a rare phenomenon, which in many ways, is similar to the microemulsions. However, this dispersion forms in absence of any surface-active agent. The data on the physicochemical properties obtained in the present work are likely to provide a very useful database for process design and research work in the nitration of nitrobenzene at high-concentrations of sulfuric acid.

3.2 Experimental

3.2.1 Materials

Nitrobenzene (99% purity), sulfuric acid (18.3 kmol/m^3) and nitric acid (15.5 kmol/m^3) were procured from Merck (India). Standard organic sample 3-nitrobenzenesulfonic acid (sodium salt, 98% purity) was procured from Alfa Aesar (India). Pellets of sodium hydroxide (98% purity) and oxalic acid dihydrate (99% purity) were obtained from Merck (India). HPLC-grade methanol, water, acetonitrile and ethyl acetate were procured from Merck (India). Deuterated chloroform ($CDCl_3$) used for NMR spectroscopy was obtained from

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Sigma Aldrich (USA). Sulfuric acid solutions of lower concentrations were prepared by diluting the concentrated acid (18.3 kmol/m^3) with water. The water used in this study was purified from a Millipore® water purification system. Its conductivity and surface tension were $1\times10^{-7}\,\Omega^{-1}\,cm^{-1}$ and 72 mN/m (at 298 K), respectively.

3.2.2 Apparatus and procedure

3.2.2.1 Measurement of mutual solubility of nitrobenzene in sulfuric and nitric acids

For determining the equilibrium solubility of nitrobenzene in the sulfuric and nitric acids, a heterogeneous mixture of nitrobenzene and acid was prepared by adding an excess amount of nitrobenzene to the acid solutions. The amount of nitrobenzene in the mixture was approximately twice its amount that could be dissolved in the acids under equilibrium conditions. The mixture was stirred for 4–5 hours using a magnetic stirrer in a sealed glass vessel placed inside a water bath. The temperature of the bath was maintained within ±0.2 K using a thermostatic water circulator (make of the instrument: Jeio Tech, model: RW 2025G). The equilibrated mixture was allowed to separate into two phases for one day inside the bath. Samples from the aqueous phase were collected by inserting a pipette through the organic phase. About one gram of sample from the aqueous phase was collected, dissolved in methanol and then analyzed. The amount of nitrobenzene present in the sample was determined by UV-Visible spectrophotometry (make of the spectrophotometer: Perkin-Elmer, model: Lambda 35). A sample curve of absorbance versus wavelength in UV-Visible spectrophotometer is shown in Figure 3.1. It is seen from the spectrum that the maximum absorption of nitrobenzene in methanol occurs at 260 nm (λ_{max}).

Solutions of pure nitrobenzene at various concentrations were prepared in methanol and their absorption were measured at 260 nm for calibration purpose. The resulting calibration

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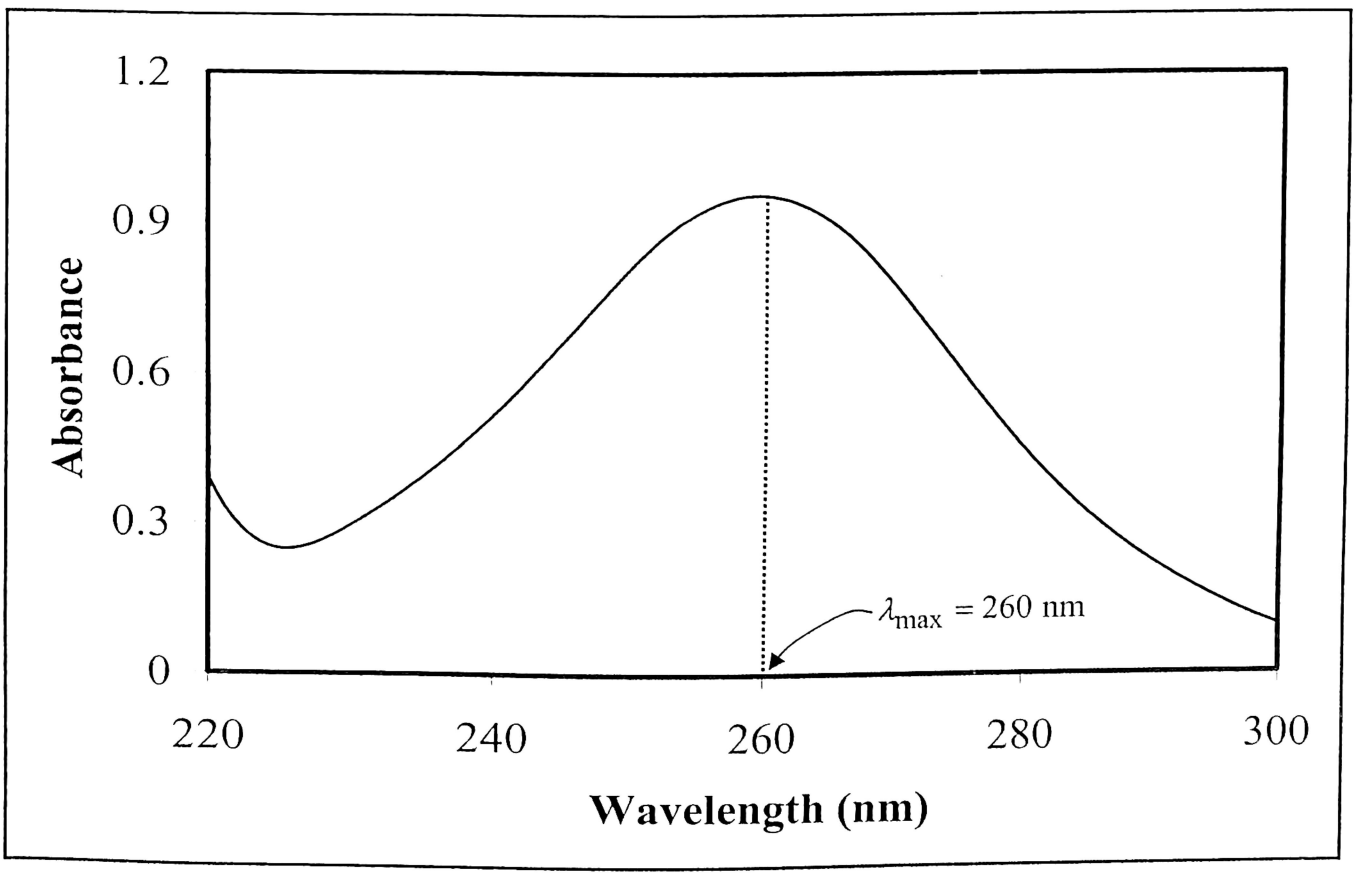


Figure 3.1 UV-Visible spectrum of nitrobenzene.

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plot is shown in Figure 3.2. An excellent linear plot was observed in the concentration range of 0 to 35 mg/dm^3. This plot was used to determine the equilibrium solubility of nitrobenzene in the acids. This technique was very efficient because the average absolute deviation (AAD), as defined below, in calculating the concentration of nitrobenzene from the calibration chart was within ±2%.

$$\text{Absolute deviation} = \left(\frac{C_{obs} - C_{true}}{C_{true}} \right) \times 100 \qquad (3.1)$$

where C_{obs} is the observed concentration of nitrobenzene from the calibration plot and C_{true} is the true concentration of nitrobenzene.

Samples from the organic phase were collected and dissolved in water so that the acid was easily transferred into the aqueous phase. The amount of acid dissolved in the sample was determined by acid–base titration using aqueous NaOH, which was standardized with a standard oxalic acid solution in water.

The range of acid concentrations for sulfuric acid was 14 kmol/m^3 to 17.5 kmol/m^3, and the same for nitric acid was from zero to 15.5 kmol/m^3. The experiments were carried out at two temperatures, viz. 298 K and 313 K. All these experiments were repeated thrice to check the reproducibility. The results were found to be highly reproducible. A typical calculation of solubility of nitrobenzene in the sulfuric acid (and vice versa) is shown in Section A.1 of Appendix A.

3.2.2.2 Investigation of the formation of sulfonic acid derivative of nitrobenzene

When nitrobenzene was treated with aqueous sulfuric acid (in the absence of any nitric acid), the possibility of formation of the sulfonic acid derivative of nitrobenzene was investigated. The aqueous and organic phases in the equilibrated mixture of nitrobenzene and

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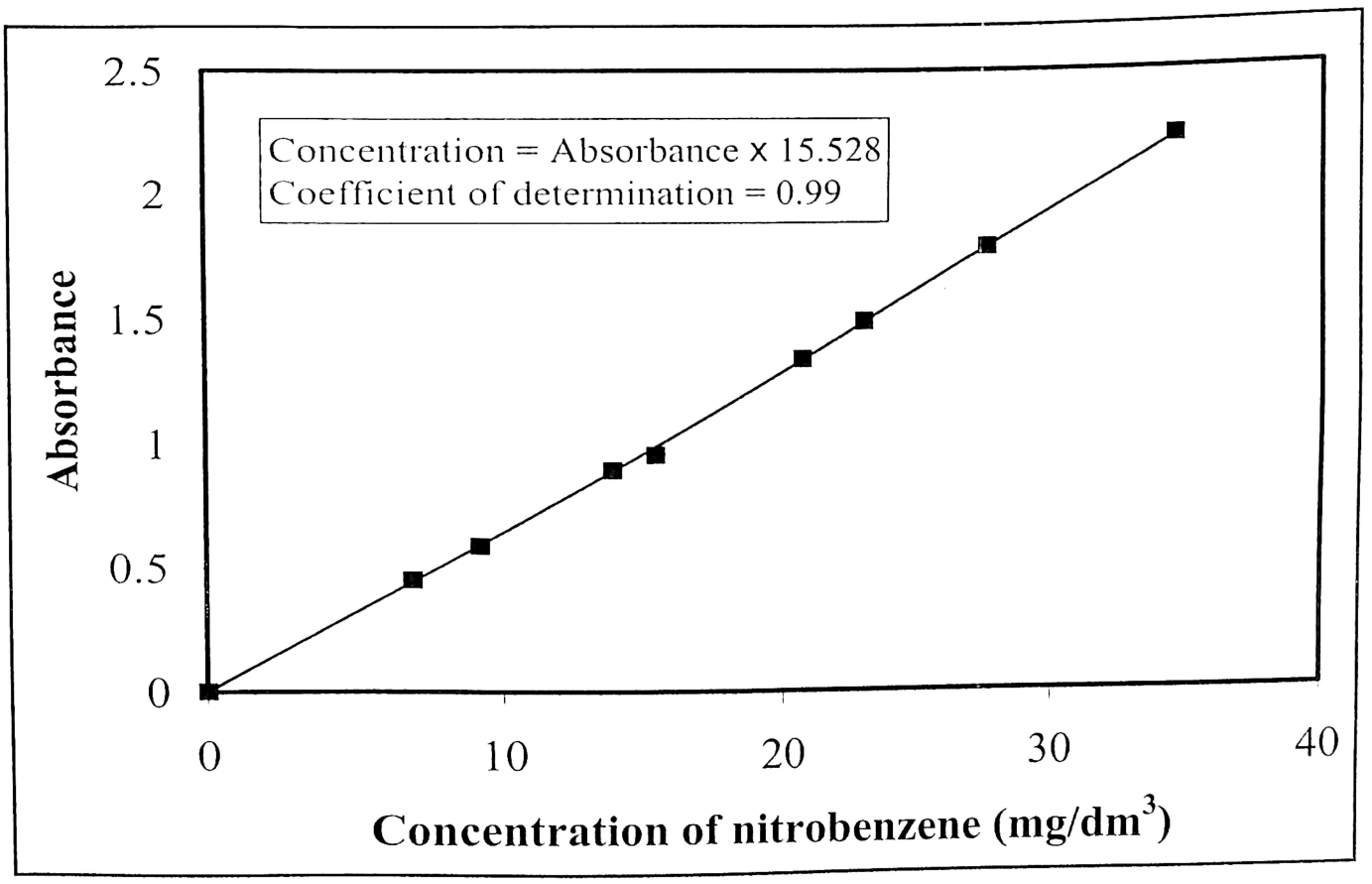


Figure 3.2 Calibration curve for nitrobenzene in the UV-Visible spectrophotometer.

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sulfuric acid were analyzed in HPLC (make of the instrument: Perkin-Elmer, model: Series 200, column: Hibar-Purospher-STAR RP-18 (Merck), detector: UV, $\lambda = 254$ nm). The mobile phase constituted of acetonitrile and water in 4:1 volumetric ratio.

The possibility of formation of 3-nitrobenzenesulfonic acid was also investigated with NMR spectroscopy. The organic compounds present in the equilibrated aqueous sulfuric acid phase were extracted with ethyl acetate. The ethyl acetate was evaporated *in vacuo* in a rotary evaporator. Sample collected from the residue was dissolved in $CDCl_3$ and its ^1H NMR was measured at 400 MHz (make of the instrument: Varian, model: Mercury Plus 400).

3.2.2.3 Measurement of density of the sulfuric acid solutions equilibrated with nitrobenzene

The density of the aqueous phase equilibrated with nitrobenzene was determined by gravimetric method. The equilibrated mixture of nitrobenzene and sulfuric acid was prepared at various sulfuric acid concentrations as stated in the Section 3.2.2.1 and allowed to separate into two phases. One cm^3 sample was collected from the bottom of the aqueous phase and its mass was determined using an electronic analytical balance (make of the instrument: A & D, model: GR-300). All these measurements were repeated thrice to check the reproducibility.

3.2.2.4 Measurement of interfacial tension between nitrobenzene and sulfuric acid

The interfacial tension between the aqueous sulfuric acid and nitrobenzene phases was measured by a digital tensiometer (make of the instrument: Krüss, model: K9). The du Noüy ring method was used to measure the interfacial tension. As described in the Section 3.2.2.1, the equilibrated mixture of nitrobenzene and sulfuric acid was prepared for various sulfuric acid concentrations and allowed to separate into two phases for one day at the room temperature. The two phases were isolated from the equilibrated mixture and collected

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separately. At first, the heavier aqueous phase was placed in the sample vessel of the tensiometer and the platinum-iridium ring was dipped inside it. Then the lighter organic phase was poured very carefully on top of the aqueous phase. The system was allowed to stabilize for one hour. The ring was pulled at a very slow speed (~200 μm/s) until it pierced through the aqueous–organic interface. The interfacial tension was measured for the system at 298 K.

3.2.2.5 Determination of droplet size distribution of nitrobenzene in sulfuric acid

The droplet size distribution of nitrobenzene in the sulfuric acid phase was measured by dynamic light scattering (make of the instrument: Horiba, model: LB-550). The equilibrated mixture of nitrobenzene and sulfuric acid was prepared at various sulfuric acid concentrations as mentioned before and allowed to separate into two phases. The aqueous phase from the bottom was collected and put in the size analyzer for measurement of distribution of particle diameter in the aqueous phase. The droplet size distribution of nitrobenzene in the aqueous sulfuric acid phase was measured at 298 K.

3.3 Results and discussion

The aromatic nitration reaction takes place mainly in the aqueous phase [1]. Therefore, the rate of reaction depends on the amount of nitrobenzene present in the aqueous phase. Thus, it is important to study the equilibrium solubility of nitrobenzene in the acid phase, which is required for the determination of mass transfer coefficient of nitrobenzene into the sulfuric acid. The data on equilibrium solubility of nitrobenzene in sulfuric acid and vice versa at 298 K and 313 K are shown in Figure 3.3. Solubility of nitrobenzene was found to depend strongly on the concentration of sulfuric acid. As the concentration of acid was increased, the solubility increased tremendously. A sharp increase in solubility was observed

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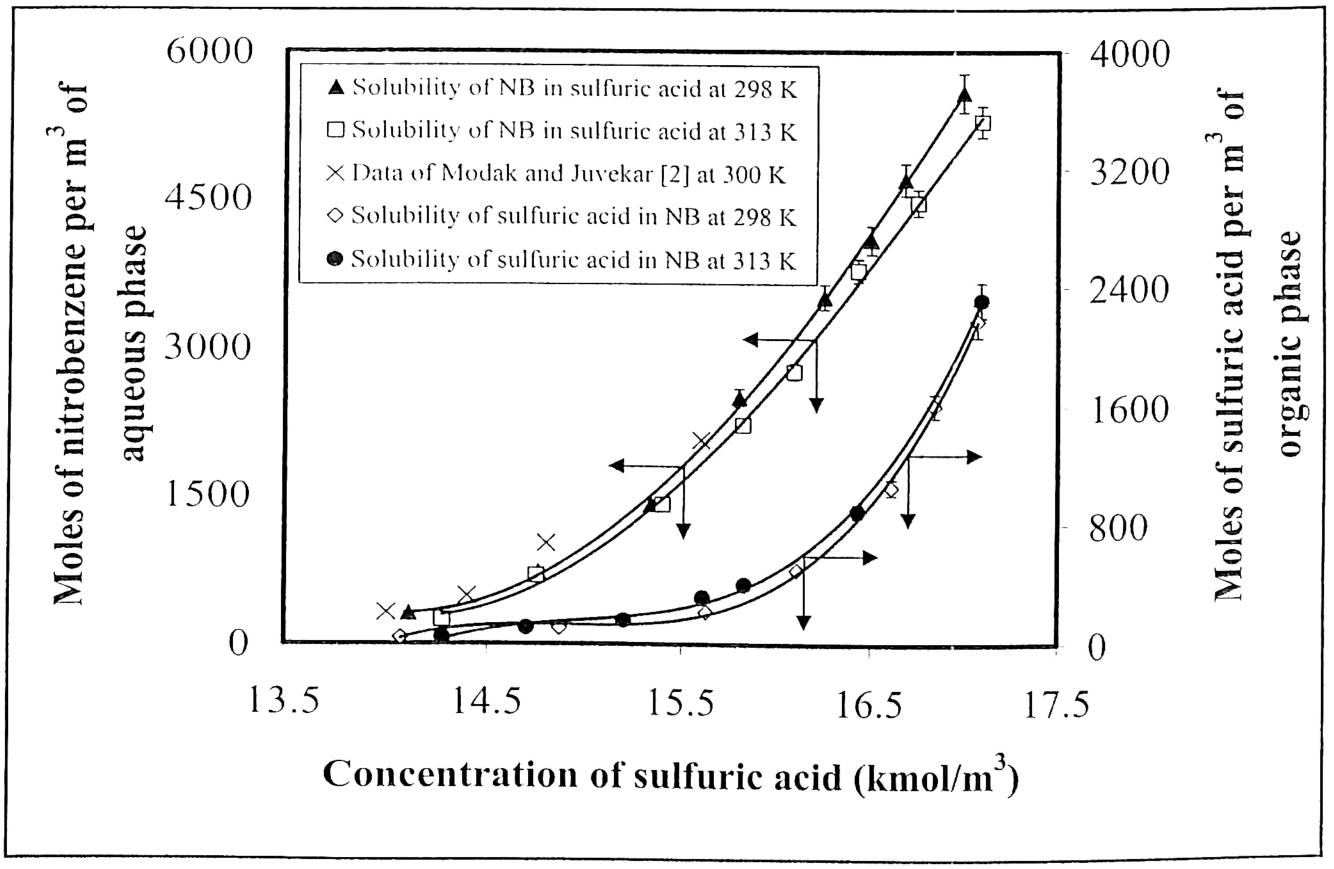


Figure 3.3 Variation of solubility of nitrobenzene in sulfuric acid (and vice versa) with the concentration of sulfuric acid at different temperatures.

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around 16.5 kmol/m^3 concentration of the sulfuric acid at both the temperatures. The solubility of sulfuric acid in the nitrobenzene phase also increased in a similar manner, which is depicted in Figure 3.3. The data on equilibrium solubility of nitrobenzene in the sulfuric acid by Modak and Juvekar [2] are also shown in Figure 3.3 for comparison.

The solubility of nitrobenzene in nitric acid also depends strongly upon the concentration of nitric acid at 298 K (Figure 3.4). It is seen from the figure that a significant increase in solubility occurred after 9 kmol/m^3 nitric acid concentration. The solubility of nitric acid in nitrobenzene also increased as seen from this figure. It is observed from the figure that the solubility of nitrobenzene in nitric acid was much less as compared to the solubility of nitric acid in the organic phase at the same nitric acid concentration.

To understand the phenomena behind this significant increase in solubility of nitrobenzene in sulfuric acid, the aqueous phase was analyzed by dynamic light scattering. These experiments showed that a fine dispersion of the nitrobenzene droplets was developed in the aqueous phase at 298 K, which resembled microemulsion. The droplet size distributions are shown in Figure 3.5. These distributions were obtained after equilibrating the aqueous and organic phases for one day. It is likely that this dispersion is thermodynamically stable similar to the standard surfactant-stabilized microemulsions [3]. The droplet size distributions were of unimodal and bimodal types as shown in Figure 3.5. As the concentration of sulfuric acid was increased, the size of the droplets reduced. At 14.9 kmol/m^3 concentration of sulfuric acid, a large fraction of the droplets had a diameter of a few hundred nanometers, whereas at 17.1 kmol/m^3 concentration, the droplets were very small (<10 nm). This reduction in size occurred due to the decrease in the interfacial tension between nitrobenzene and sulfuric acid. The variation of interfacial tension with increase in the concentration of sulfuric acid is shown

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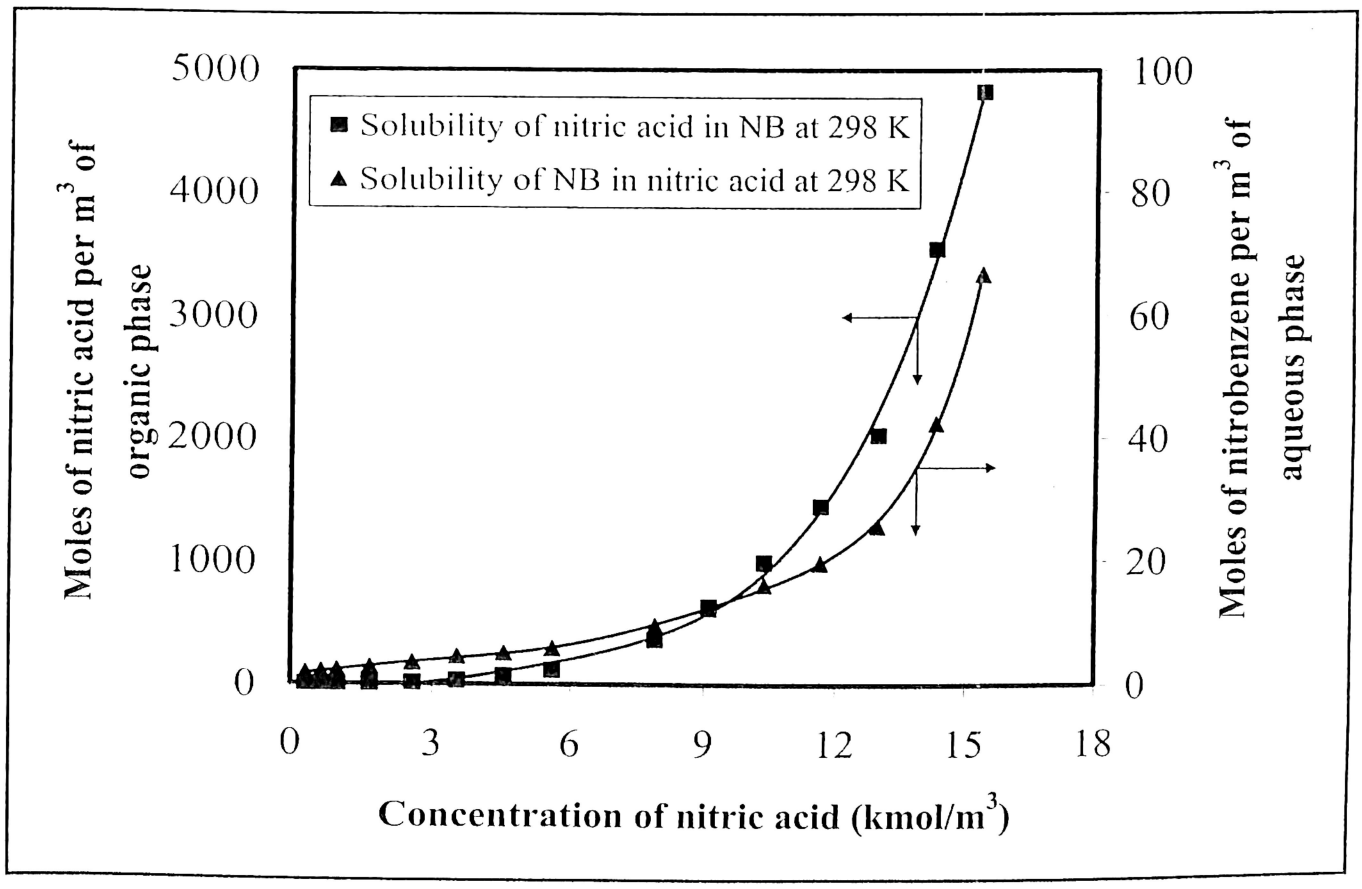


Figure 3.4 Variation of solubility of nitrobenzene in nitric acid (and vice versa) with the concentration of nitric acid at 298 K.

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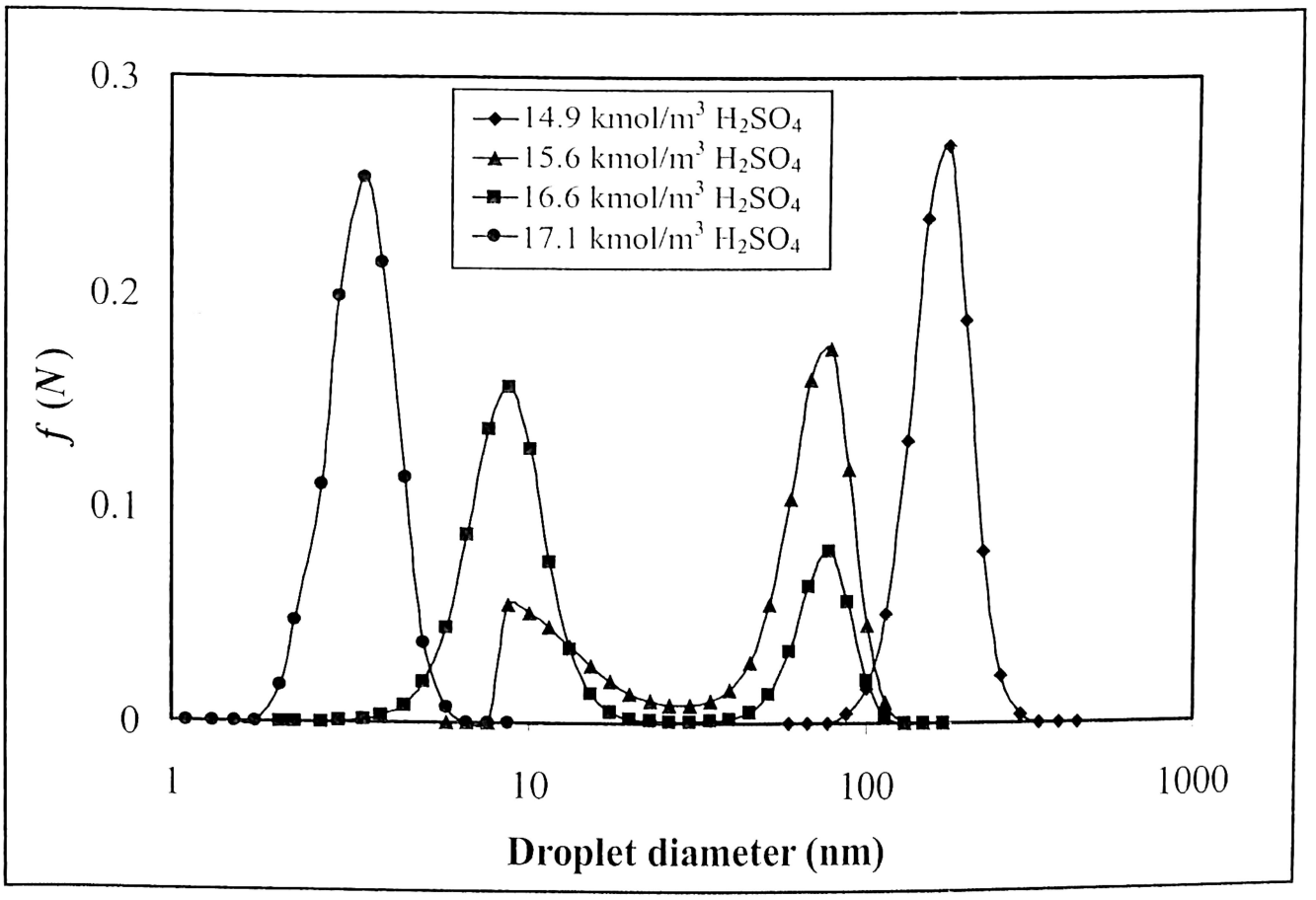


Figure 3.5 Droplet size distribution of nitrobenzene at different concentrations of sulfuric acid at 298 K. $f(N)$ represents the number fraction of the nitrobenzene droplets having size within a small droplet-size interval.

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in Figure 3.6. The interfacial tension, however, did not reach the near-zero values usually observed in the surfactant-stabilized microemulsions. The minimum of the interfacial tension curve was attained when the acid concentration was 17.2 kmol/m^3. The size of the droplets increased with time due to the coalescence between the droplets. In the bimodal distributions shown in Figure 3.5, the larger droplets (50–100 nm) were formed by the coalescence of the smaller droplets. The nitrobenzene molecules, however, were chemically free to participate in the nitration reaction, as we will discuss later. The size of the droplets and the number of droplets (which depends on the amount of the organic compound dissolved in the aqueous phase) present in the aqueous phase determine the total interfacial area. It is likely that a hydrogen-bonded network developed between the sulfuric acid and nitrobenzene molecules, which stabilized the microemulsion for days and even weeks. The rupture of these hydrogen bonds at the higher temperature (i.e., at 313 K) is believed to be the reason behind the decrease in equilibrium solubility of nitrobenzene in the sulfuric acid (Figure 3.3). The experiments on solubility at temperatures higher than 313 K were not carried out due to the sulfonation of nitrobenzene. The solubility of sulfuric acid in the organic phase increased with the concentration of sulfuric acid. However, the effect of temperature on the solubility of sulfuric acid in the organic phase was small.

The data on the density of the aqueous sulfuric acid phase equilibrated with nitrobenzene are shown in Figure 3.7. The data on density of aqueous sulfuric acid reported in the literature [4] are also shown in this figure. It is seen from the figure that the density decreased with increase in sulfuric acid concentration. The increase in the solubility of nitrobenzene (which increases the amount of nitrobenzene into the sulfuric acid) reduces the density of the aqueous phase.

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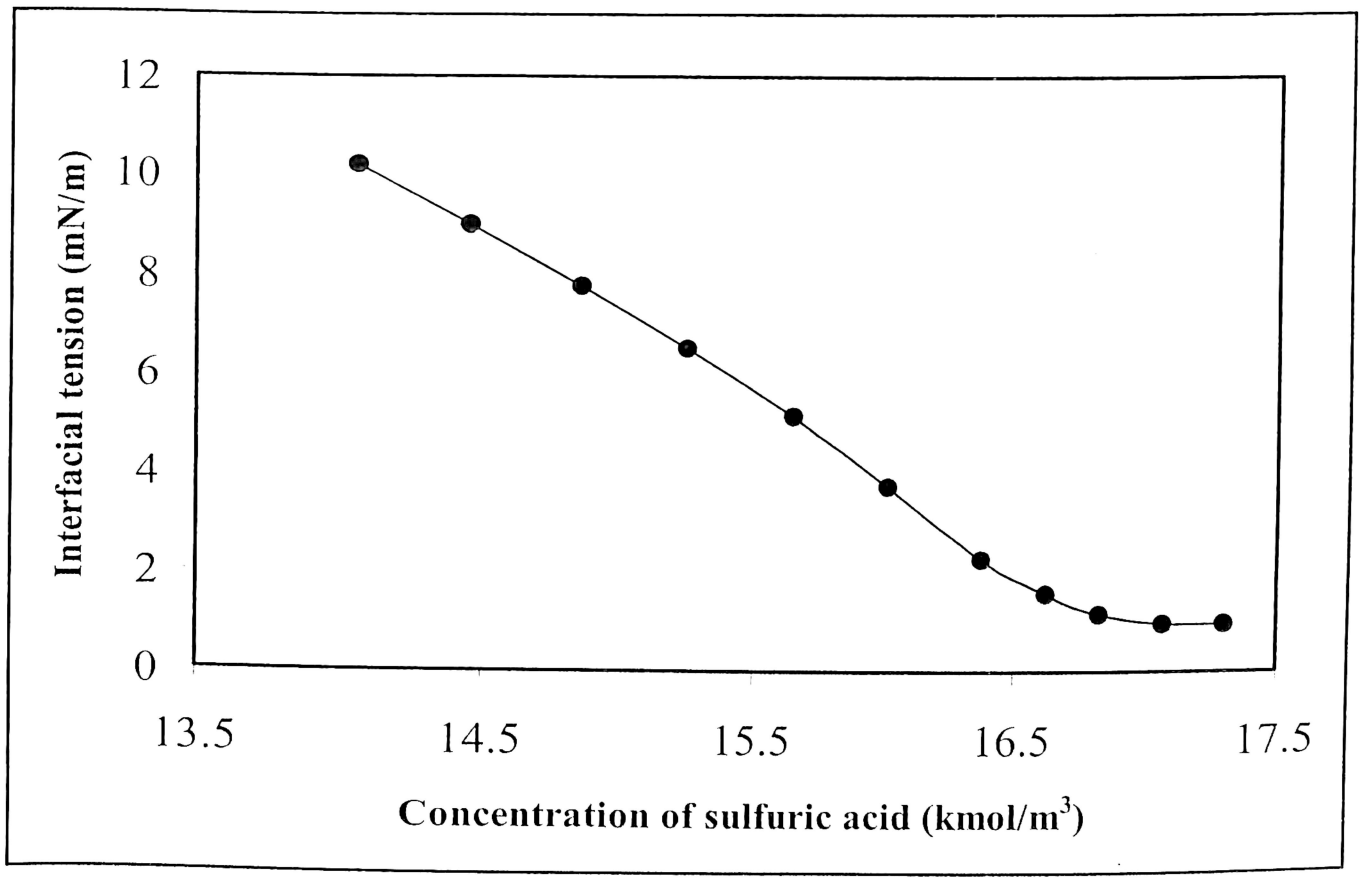


Figure 3.6 Variation of interfacial tension of the nitrobenzene–sulfuric acid system with the concentration of sulfuric acid at 298 K.

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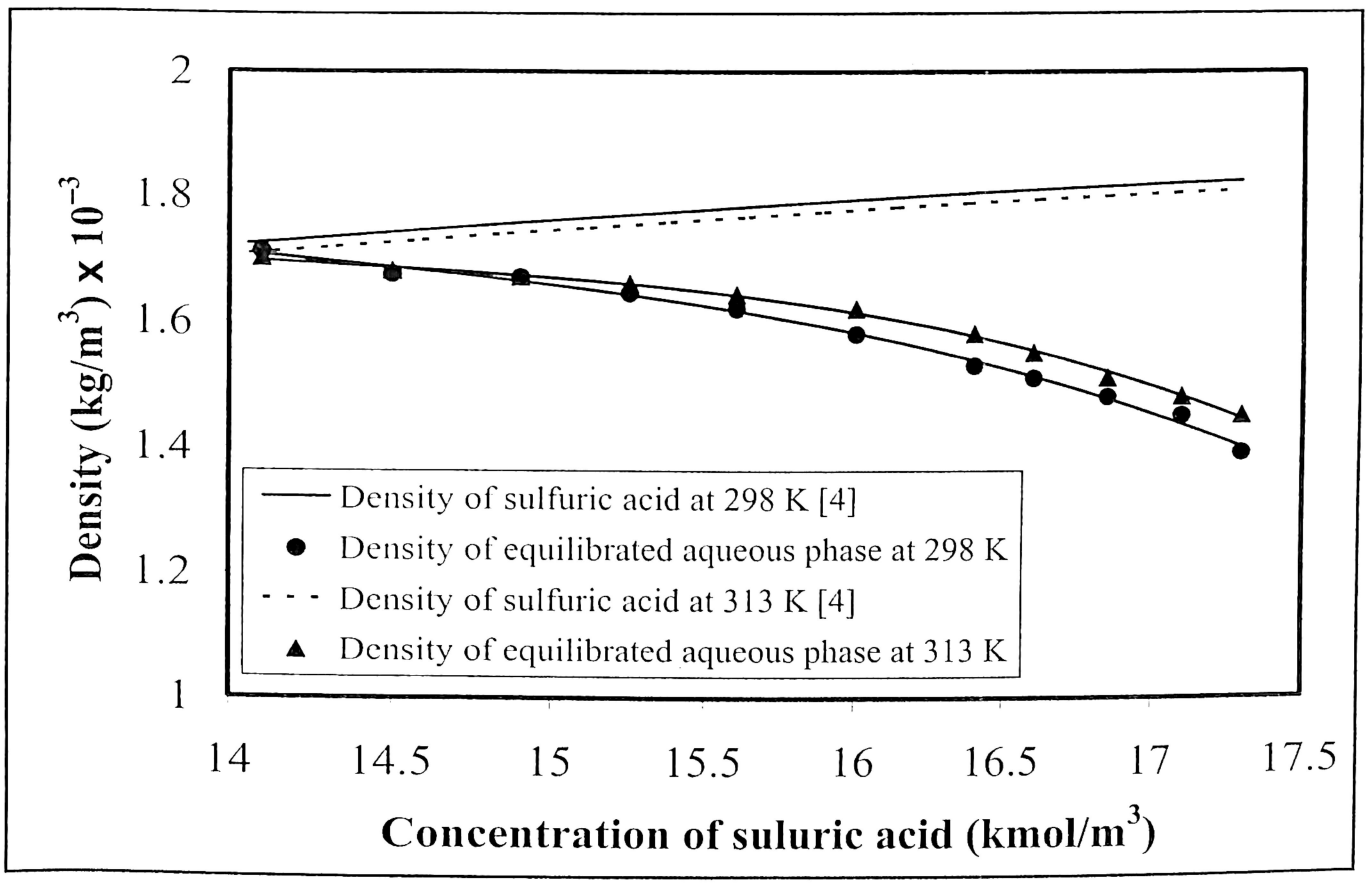


Figure 3.7 Variation of density of the aqueous phase equilibrated with nitrobenzene with the concentration of sulfuric acid.

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To check whether any significant sulfonation took place in the concentrated sulfuric acid medium in the temperature range of 298 K – 323 K, the organic and aqueous phases were analyzed by high performance liquid chromatography (HPLC) as described in Section 3.2.2.2. There was no peak of 3-nitrobenzenesulfonic acid in the chromatogram at 298 K and 313 K. But, it was observed that a significant amount of 3-nitrobenzenesulfonic acid was formed at 323 K. To confirm that no sulfonic acid forms in the range of 298 K to 313 K, the aqueous phases at these temperatures were further analyzed by ^{1}H-NMR spectroscopy. The NMR spectrum is shown in Figure 3.8 (a). The extended spectrum is shown in Figure 3.8 (b). The ^{1}H-NMR spectrum exhibited the signals at δ = 7.53 (t, J = 7.2 Hz, 2H, ArH), 7.68 (t, J = 7.2 Hz, 1H, ArH), 8.21 (d, J = 7.6 Hz, 2H, ArH), where δ is the chemical shift signal position for ^{1}H-NMR and J is the internuclear coupling constant. The values of δ obtained from the NMR study were similar to the values obtained for aromatic protons, and these signals are quite similar to the spectrum of nitrobenzene reported in the literature [5]. There was no additional peak (or signal) for 3-nitrobenzenesulfonic acid in the NMR spectrum. Thus, it is confirmed from the HPLC and NMR analyses that no sulfonation took place at 298 K and 313 K. This is expected since it is well-known that sulfonation of nitrobenzene proceeds extreme slowly due to the presence of the deactivating nitro group in the benzene ring. At these concentrations of sulfuric acid, however, sulfonation is significant in more active aromatic compounds, such as toluene or benzene even at 298 K.

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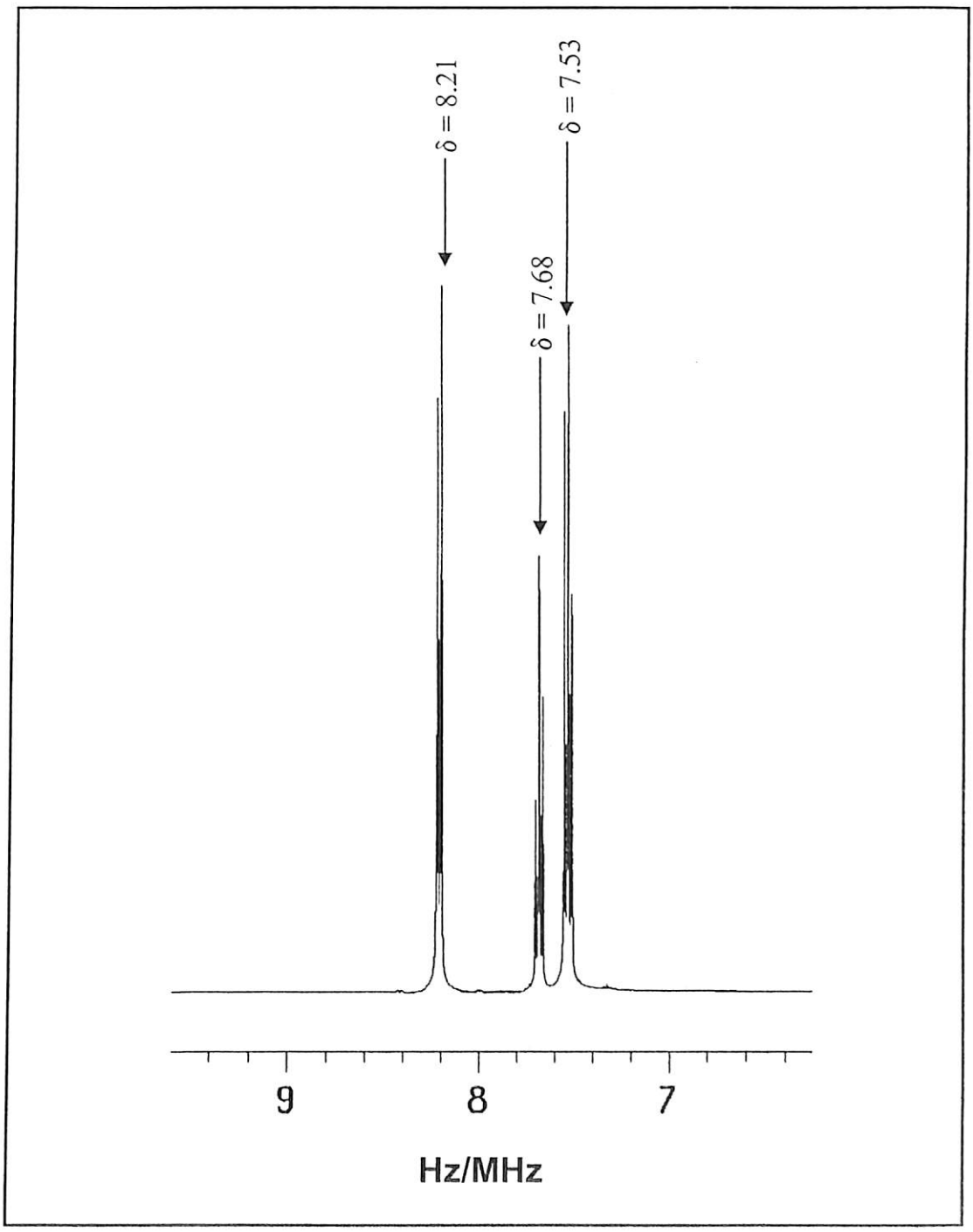


Figure 3.8 (a) ^{1}H-NMR spectrum of the organic compound present in the aqueous phase.

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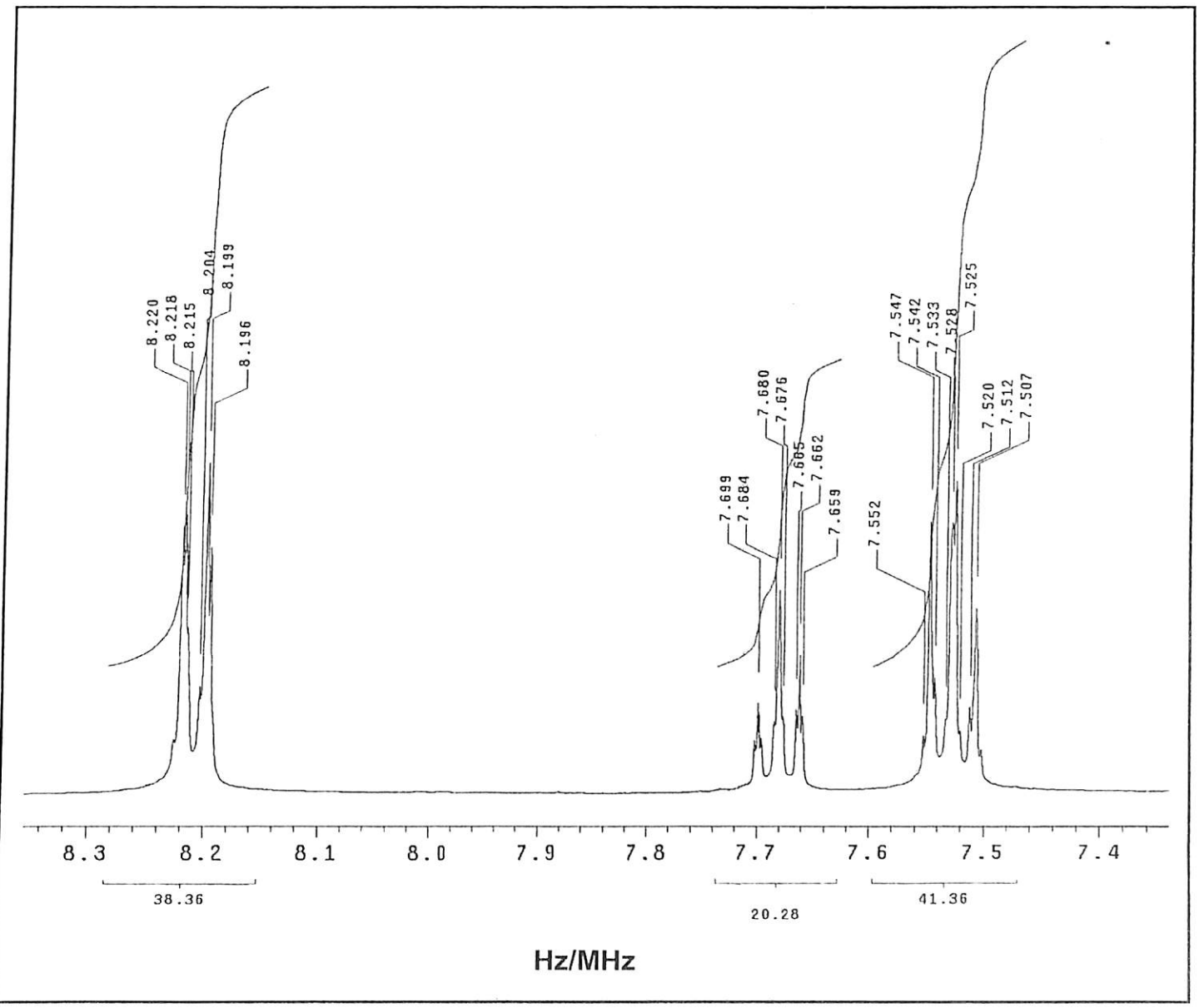


Figure 3.8 (b) Expanded ^{1}H-NMR spectrum of the organic compound present in the aqueous phase.

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Notation

ArH	aromatic compound
C_{obs}	observed concentration of nitrobenzene (mg/dm^3)
C_{true}	true concentration of nitrobenzene (mg/dm^3)
d	doublet (NMR signal multiplicity)
H	hydrogen atom
J	internuclear coupling constant (Hz)
t	triplet (NMR signal multiplicity)

Greek letters

δ	chemical shift of ^{1}H NMR (Hz/MHz)
λ	wavelength of detection in HPLC (nm)
λ_{max}	wavelength at which the maximum absorption occur (nm)

Abbreviation

NB	nitrobenzene

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1 Olah, G. A., Malhotra, R. and Narang, S. C., *Nitration: Methods and Mechanisms*, Wiley–VCH, New York (1989).

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CHAPTER 4

INDEPENDENT STUDIES OF MASS TRANSFER AND KINETICS OF NITRATION OF NITROBENZENE AT HIGH-CONCENTRATIONS OF SULFURIC ACID

This chapter presents the mass transfer and the kinetics of the nitration of nitrobenzene in concentrated sulfuric acid. The mass transfer coefficients of nitrobenzene in different sulfuric acid concentrations were measured at various stirring speeds. The homogeneous reaction rate constants were determined at high-concentrations of sulfuric acid at room temperature and at moderately higher temperatures. The kinetic results were analyzed using the M_c activity coefficient function. The activation energies were determined from the Arrhenius plots. Using the values of mass transfer coefficients and the rate constants, the reaction regimes were determined.

4.1 Introduction

In Chapter 3, it has been mentioned that aromatic nitration is a heterogeneous liquid–liquid reaction, which occurs almost exclusively in the aqueous phase. Therefore, detailed knowledge of the mass transfer phenomena between the aqueous and organic phases, and the kinetics of the reaction is important to deal with the nitration process in a batch reactor. To meet specific requirements, quantification of the parameters is very essential for the rational design of the nitrator. These parameters are mass transfer coefficient, rate constant and the activation energy of the reaction. The major factors which influence the rate of mass transfer are the concentration of sulfuric acid, the temperature and the speed of stirring. In an

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industrial reactor, the speed of stirring is more than 1000 revolutions per minute. High-speed stirring creates dispersion of the organic phase into the aqueous phase. The kinetics of the reaction is significantly affected by the temperature of the reaction and the concentration of sulfuric acid. In this chapter, the mass transfer and kinetic aspects of nitration of nitrobenzene in a batch reactor using concentrated sulfuric acid are presented.

4.2 Experimental

4.2.1 Materials

Nitrobenzene (99% purity), sulfuric acid (18.3 kmol/m^3) and nitric acid (15.5 kmol/m^3) were procured from Merck (India). Standard organic samples, 1,2-dinitrobenzene (99% purity), 1,3-dinitrobenzene (97% purity) and 1,4-dinitrobenzene (98% purity) were procured from Alfa Aesar (India). HPLC-grade methanol, water and acetonitrile were procured from Merck (India). Sulfuric acid solutions of lower concentrations were prepared by diluting the concentrated acid (18.3 kmol/m^3) with water. The concentrations of the sulfuric acid solutions were determined by acid–base titration using aqueous NaOH, which was standardized with oxalic acid. The water used in this study was purified from a Millipore® water purification system.

4.2.2 Apparatus and procedure

4.2.2.1 Measurement of mass transfer coefficient of nitrobenzene in sulfuric acid

The experiments to determine the mass transfer coefficient of nitrobenzene in sulfuric acid were carried out under flat-interface conditions employing the batch dynamic process. Nitrobenzene was contacted with sulfuric acid (without any nitric acid) of different concentrations in an apparatus shown in Figure 4.1. An unbaffled glass reactor with a working

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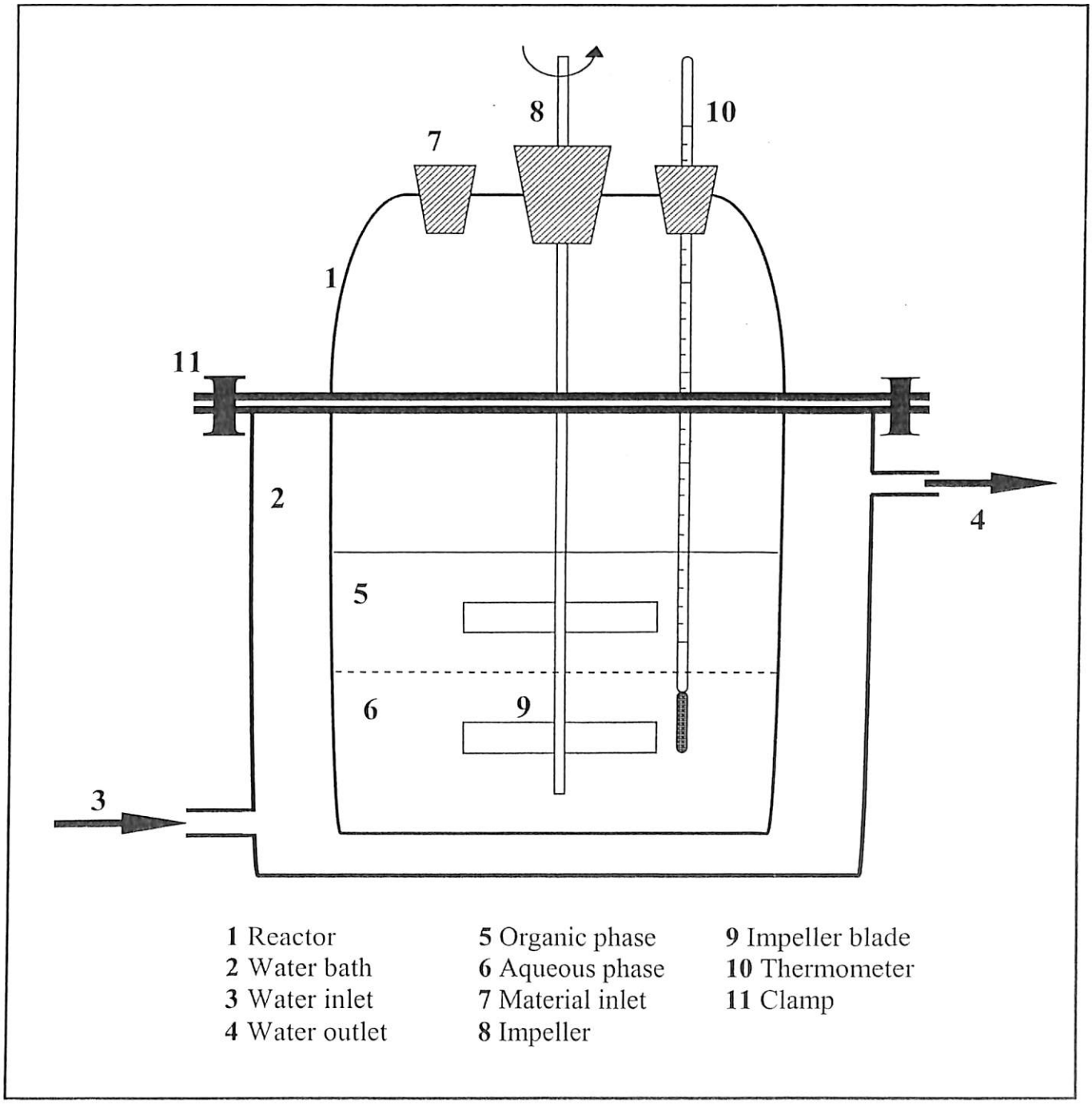


Figure 4.1 Schematic diagram of the reactor.

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capacity of 1000 cm^3 was used for this purpose. The internal diameter of the reactor was 10 cm. The glass reactor was placed in a water bath whose temperature was maintained by a thermostatic water circulator. The head of the reactor was fixed with clamps. The head was provided with three openings at the top. The glass stirrer was provided with two paddle-type impellers mounted on its shaft, such that the upper paddle stirred the organic phase, and the lower paddle stirred the aqueous phase. Both the paddle impellers had four vertical blades, which were fused to the agitator shaft at $\pi/2$ rad to each other. The length of the blades was 2.5 cm and their height was 1.5 cm. A thermometer was inserted from the top of the reactor to monitor the temperature of the medium.

The requisite amount of aqueous acid was first poured into the reactor. A known amount of nitrobenzene was then charged to the reactor very carefully on the top of the aqueous phase. Agitation was then started. The transfer of nitrobenzene into the aqueous phase was measured as a function of time. For determination of the amount of nitrobenzene in the aqueous phase, approximately one cm^3 of sample was collected at definite time intervals. The samples were dissolved in methanol. The amount of nitrobenzene present in the sample was determined by UV-Visible spectroscopy from its absorption at $\lambda_{max} = 260$ nm , as described in Section 3.2.2.1. The mass transfer coefficients were determined at 298 K and 313 K at sulfuric acid concentrations between 14.1 $kmol/m^3$ and 17.4 $kmol/m^3$ at the impeller speeds of 2π rad/s and 4π rad/s. All these measurements were repeated to check the reproducibility.

4.2.2.2 Determination of homogeneous reaction rate constants

Kinetic studies of nitration were carried out in the batch reactor under homogenized condition. Experiments for the determination of rate constants were carried out between 14.1 $kmol/m^3$ and 17.2 $kmol/m^3$ sulfuric acid concentrations at 298 K, 313 K and 323 K. Stock

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solutions of each sulfuric acid concentration were prepared for carrying out the reactions. Using the acid from the same stock solution, the nitration reactions were carried out at the three temperatures. The experimental procedure was as follows. A known volume of aqueous sulfuric acid of desired concentration was taken into the reactor placed in the water bath. The temperature of the bath was maintained at the desired level with a thermostatic water circulator. A known amount of nitrobenzene was dissolved in sulfuric acid and the mixture was stirred rapidly to attain homogeneity. The amount of nitrobenzene dissolved in sulfuric acid was 20 – 30% of its equilibrium solubility at the corresponding sulfuric acid concentration. After the dissolution of nitrobenzene was complete, nitric acid of required amount was added to the reactor and the reaction mixture was stirred at a specific impeller speed to obtain a homogeneous reaction mixture. About 0.2 cm^3 of sample was withdrawn from the reactor at certain time intervals. The samples were dissolved in 10 cm^3 of methanol and chilled to quench the reaction. The concentrations of the reactant (i.e., nitrobenzene) and product (i.e., 1,3-dinitrobenzene) were analyzed by reverse phase HPLC [column: Hibar-Purospher-STAR RP-18 (Merck), detector: UV, $\lambda = 254$ nm]. The mobile phase was constituted of acetonitrile and water in 3:2 volumetric ratio. Its flow rate was maintained at 16.67×10^{-3} cm^3/s. A typical absorbance versus time chromatogram of the separation of nitrobenzene and 1,3-dinitrobenzene (dissolved in methanol) in HPLC is shown in Figure 4.2. It is seen from the chromatogram that the resolution of separation was excellent, and it was achieved within a moderate retention time. The retention times for 1,3-dinitrobenzene and nitrobenzene were 335 s and 370 s, respectively.

Calibration was done by using solutions of known amounts of standard nitrobenzene and 1,3-dinitrobenzene in methanol using the method described above. The calibration plots for

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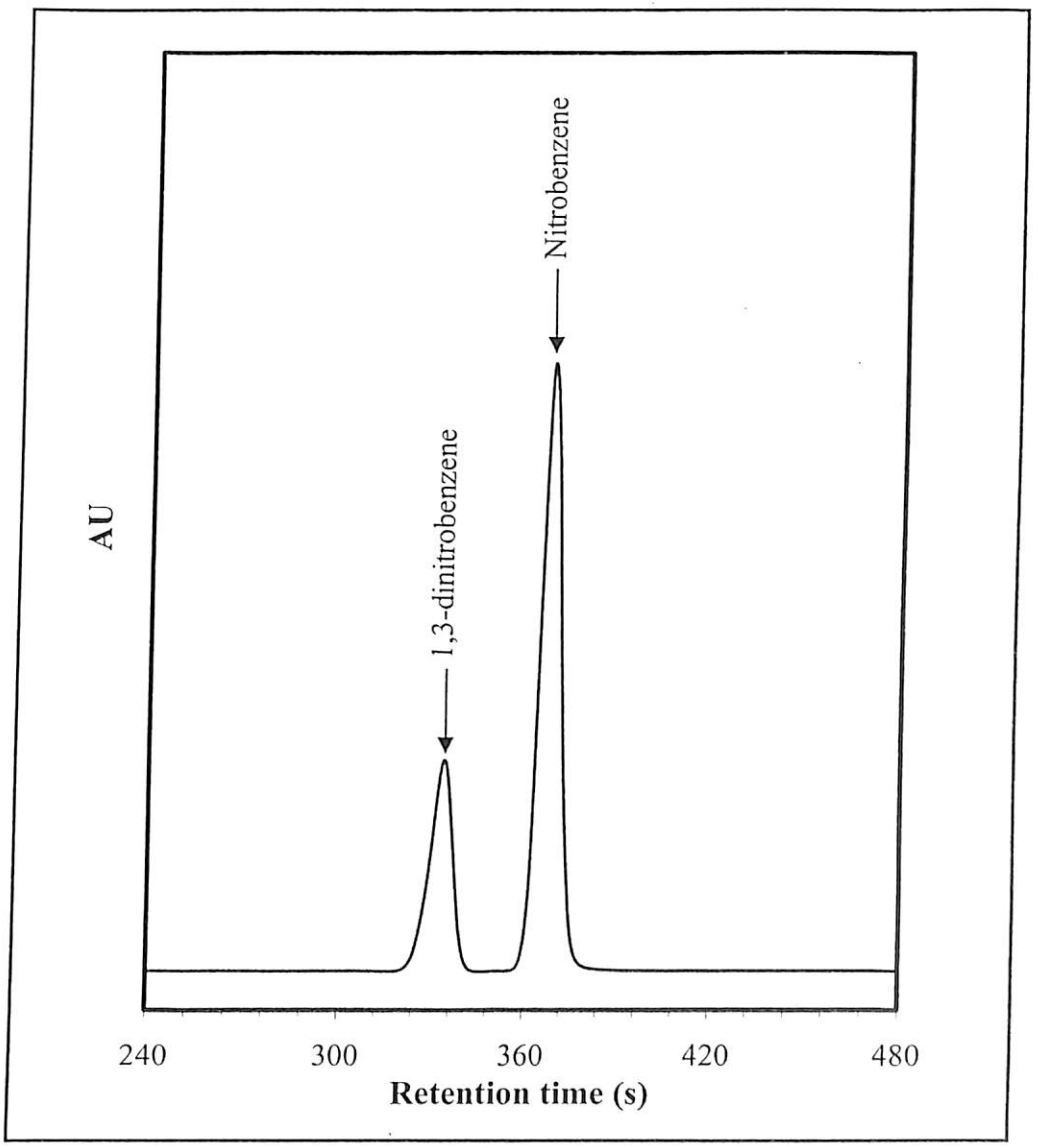


Figure 4.2 Chromatograms of nitrobenzene and 1,3-dinitrobenzene by reverse phase liquid chromatography.

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nitrobenzene and 1,3-dinitrobenzene are shown in Figure 4.3 and Figure 4.4, respectively. This method showed an excellent linearity for nitrobenzene in the concentration range of 0 to 175 mg/dm^3, and for 1,3-dinitobenzene in the concentration range of 0 to 150 mg/dm^3. The aforesaid method using HPLC was very proficient, and the average absolute deviation (AAD) in calculating the concentrations was within ±1% [see equation (3.1)]. The concentrations of nitrobenzene and 1,3-dinitrobenzene in the samples withdrawn from the reactor were determined by employing this method. The advantage of this experimental procedure was that the effect of water produced in the reaction was too small to dilute the sulfuric acid medium. Also, the analysis could be performed by HPLC rather than by UV-Visible spectrophotometry in which both nitrobenzene and the product (i.e., 1,3-dinitrobenzene) absorb at the same region of the spectrum. It was found that the maximum absorption wavelengths (λ_{max}) for nitrobenzene and 1,3-dinitrobenzene in methanol occur at 260 nm and 235 nm, respectively.

4.3 Results and discussion

4.3.1 Determination of mass transfer coefficient

The rate of change of concentration of nitrobenzene in the aqueous phase can be described by,

$$\frac{d}{dt}\left(V_a C^a_{NB}\right) = \left(\frac{k_L A}{V_a}\right)\left(V_\infty \bar{C}_{NB} - V_a C^a_{NB}\right) \qquad (4.1)$$

where C^a_{NB} is the concentration of nitrobenzene in the aqueous phase, $\bar{C}_{NB}$ is the equilibrium concentration of nitrobenzene in the aqueous phase, k_L is the mass transfer coefficient, A is the interfacial area ($=\pi d^2/4$, where d is the diameter of the reactor), V_∞ is

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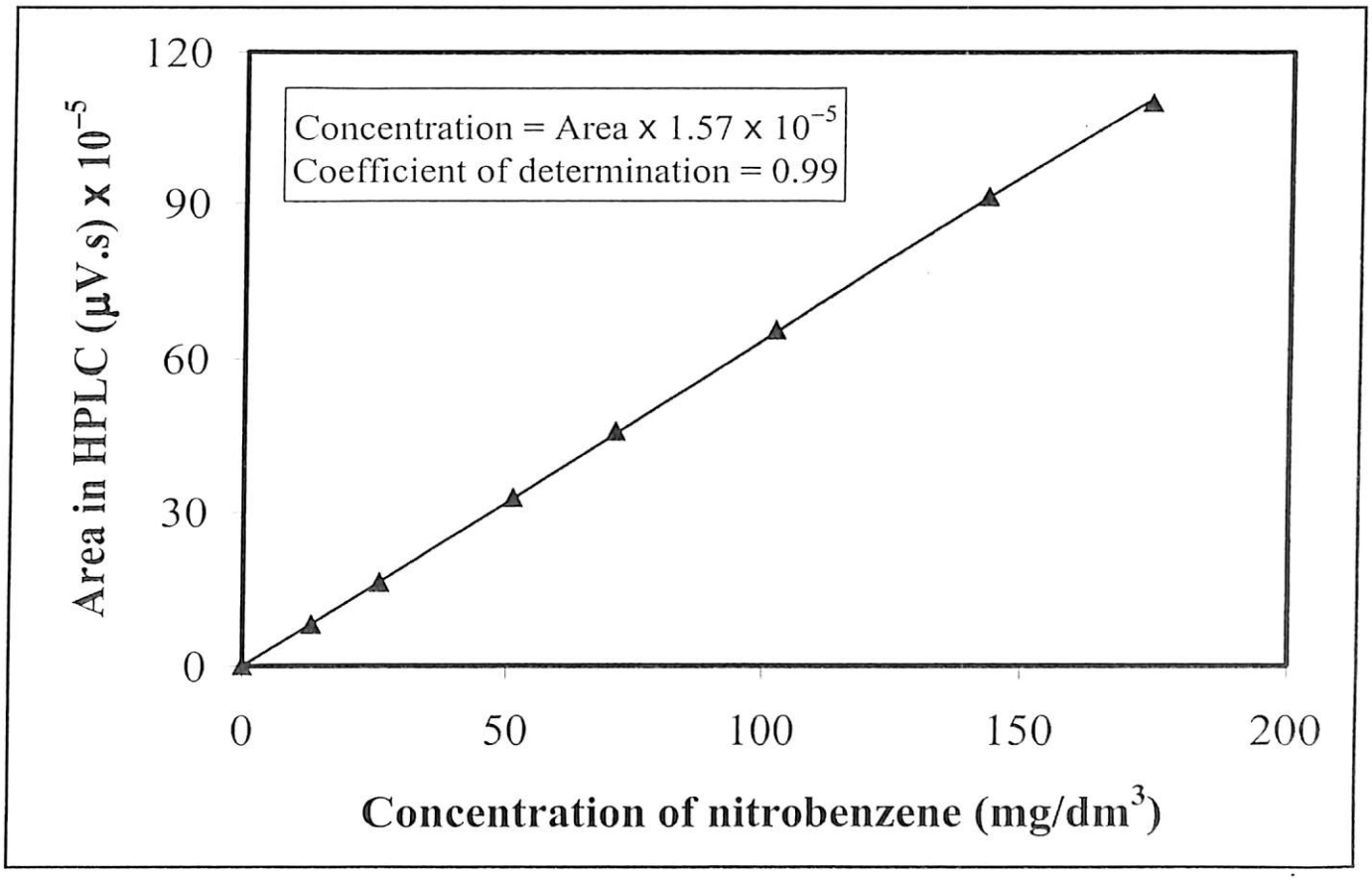


Figure 4.3 Calibration curve for nitrobenzene by reverse phase liquid chromatography.

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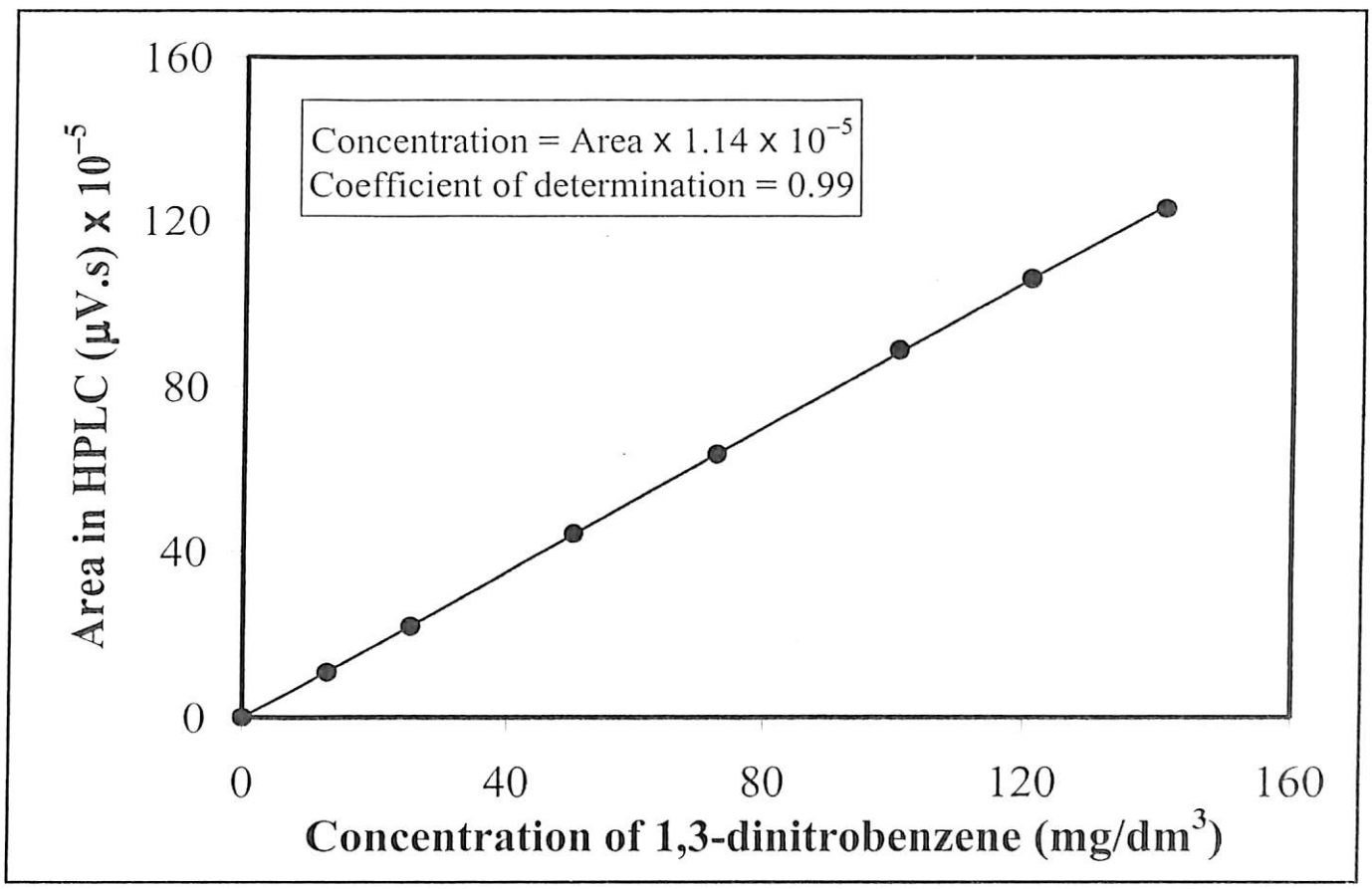


Figure 4.4 Calibration curve for 1,3-dinitrobenzene by reverse phase liquid chromatography.

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the volume of the equilibrated mixture of nitrobenzene and sulfuric acid, and V_a is the volume of the aqueous phase at time t. Equation (4.1) takes into account the changes in volume of the aqueous phase that occurs especially at the high concentrations of sulfuric acid. Equation (4.1) can be written as,

$$V_a \frac{dC^a_{NB}}{dt} + C^a_{NB} \frac{dV_a}{dt} = \left(\frac{k_L A}{V_a}\right)\left(V_\infty \bar{C}_{NB} - V_a C^a_{NB}\right) \tag{4.2}$$

Rearranging equation (4.2) we get,

$$\frac{dC^a_{NB}}{dt} + \frac{C^a_{NB}}{V_a}\frac{dV_a}{dt} = \left(\frac{k_L A}{V_a^2}\right)\left(V_\infty \bar{C}_{NB} - V_a C^a_{NB}\right) \tag{4.3}$$

From equation (4.3), it can be observed that the value of equilibrium concentration of nitrobenzene in the aqueous phase $\left(\bar{C}_{NB}\right)$ is required to determine the mass transfer coefficient. The data on equilibrium solubility of nitrobenzene in different concentrations of sulfuric acid and vice versa were depicted in Figure 3.3.

Assuming that the change in the volume of the aqueous phase occurs solely due to the transfer of nitrobenzene into the aqueous phase, and that the volume change of mixing is negligible, V_a can be expressed as,

$$V_a = V_0 + V_a C^a_{NB} M_{NB} / \rho_{NB} \tag{4.4}$$

where V_0 is the initial volume of the aqueous phase, M_{NB} is the molecular weight of nitrobenzene and ρ_{NB} is its density. By rearranging equation (4.4), V_a can be expressed as,

$$V_a = \frac{V_0}{\left(1 - C^a_{NB} M_{NB} / \rho_{NB}\right)} \tag{4.5}$$

Differentiating equation (4.5) with respect to t we get,

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$$\frac{dV_a}{dt} = \frac{V_a M_{NB}/\rho_{NB}}{\left(1 - C^a_{NB} M_{NB}/\rho_{NB}\right)} \frac{dC^a_{NB}}{dt} \tag{4.6}$$

Inserting the values of V_a and $\frac{dV_a}{dt}$ in equation (4.3) we get,

$$\frac{dC^a_{NB}}{dt} + \frac{C^a_{NB}}{V_a} \frac{V_a M_{NB}/\rho_{NB}}{\left(1 - C^a_{NB} M_{NB}/\rho_{NB}\right)} \frac{dC^a_{NB}}{dt} = \left\{ \frac{k_L A \left(1 - C^a_{NB} M_{NB}/\rho_{NB}\right)^2}{V_0^2} \right\} \left(V_\infty \bar{C}_{NB} - \frac{V_0}{\left(1 - C^a_{NB} M_{NB}/\rho_{NB}\right)} C^a_{NB} \right) \tag{4.7}$$

Rearranging equation (4.7) we get,

$$\frac{dC^a_{NB}}{dt} = \left(\frac{k_L A}{V_0^2} \right) \left(1 - C^a_{NB} M_{NB}/\rho_{NB}\right)^2 \left[V_\infty \bar{C}_{NB} - \left(V_\infty \bar{C}_{NB} M_{NB}/\rho_{NB} + V_0 \right) C^a_{NB} \right] \tag{4.8}$$

Equation (4.8) was numerically solved by the Runge-Kutta-Gill method using the initial condition: $C^a_{NB} = 0$ at $t = 0$. The mass transfer coefficient, k_L, was determined by fitting the concentration profile obtained by solving equation (4.8) to the experimental data obtained in this work. The computer program to solve equation (4.8) and computational output are given in the Section B.1 of Appendix B. The concentration profiles of nitrobenzene at different sulfuric acid concentrations at the impeller speeds of 2π and 4π rad/s at 298 K are shown in Figures 4.5 and 4.6, respectively. It can be observed from these figures that the data were fitted well by the profiles at all sulfuric acid concentrations. It can be seen from Figures 4.5 and 4.6 that the mass transfer rates were quite high even at such low speeds of agitation. For the impeller speed of 2π rad/s, about 22% of the equilibrium solubility was reached after 3 ks for 14.1 kmol/m^3 concentration of sulfuric acid whereas, 78% of the equilibrium solubility was reached after the same time for 17 kmol/m^3 concentration of sulfuric acid. In general, the

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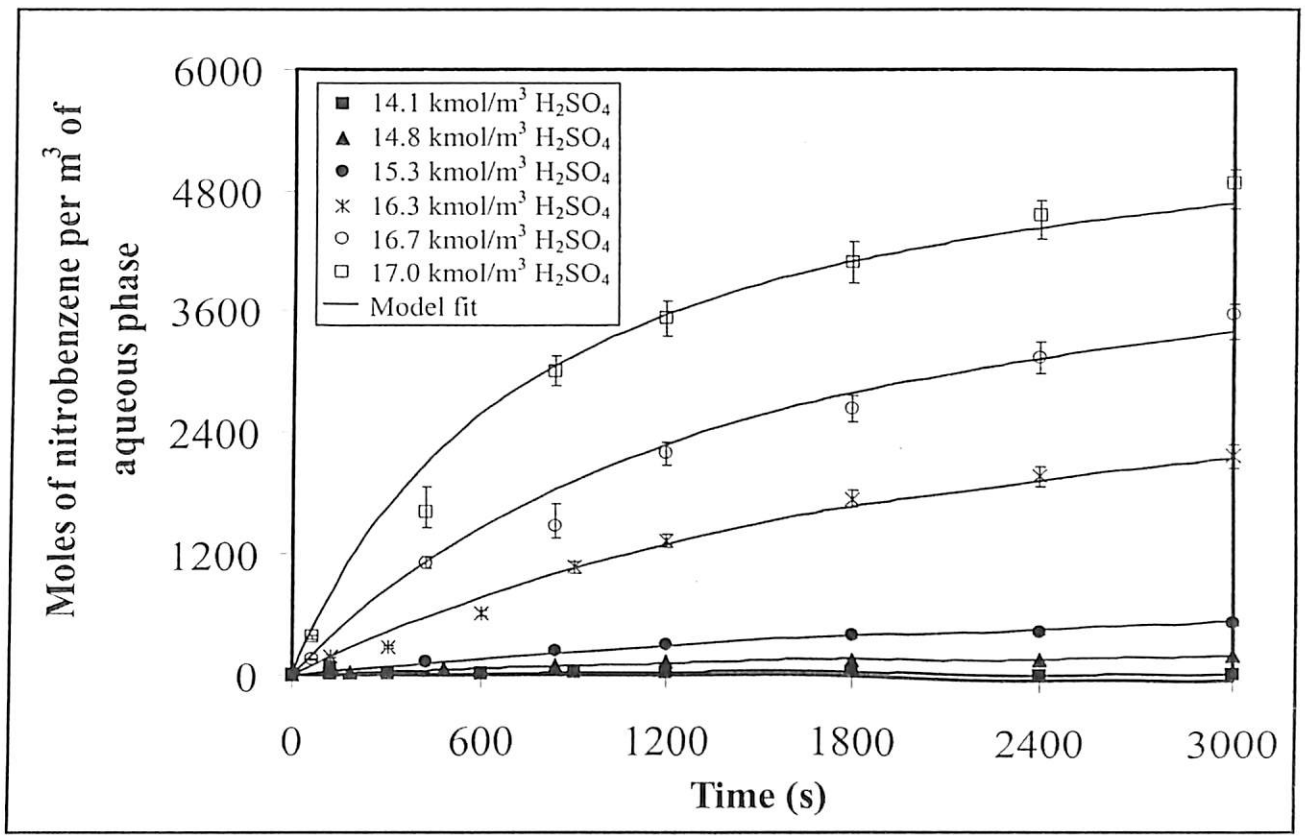


Figure 4.5 Determination of mass transfer coefficient of nitrobenzene at 298 K at different sulfuric acid concentrations at 2π rad/s impeller speed.

Concentration of sulfuric acid ($kmol/m^3$)	Mass transfer coefficient $(m/s) \times 10^5$
14.1	0.38
14.8	0.65
15.3	0.88
16.3	1.50
16.7	1.83
17.0	2.45

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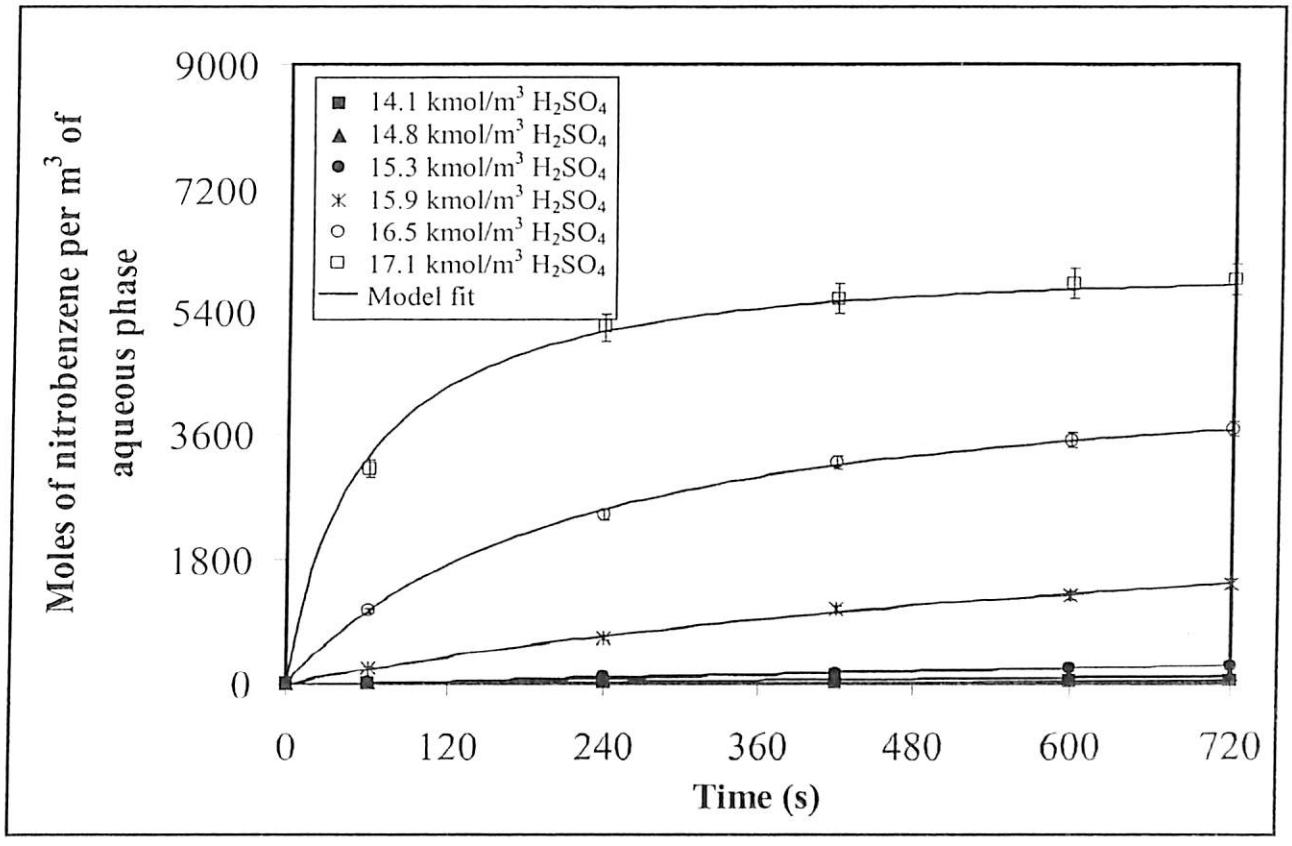


Figure 4.6 Determination of mass transfer coefficient of nitrobenzene at 298 K at different sulfuric acid concentrations at 4π rad/s impeller speed.

Concentration of sulfuric acid (kmol/m^3)	Mass transfer coefficient (m/s) × 10^5
14.1	0.83
14.8	1.12
15.3	1.28
15.9	5.37
16.5	15.20
17.1	34.00

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tendency to reach the equilibrium solubility increased as the concentration of sulfuric acid increased. The increase in k_L was spectacular beyond 16 kmol/m^3 concentration of sulfuric acid. The spontaneity observed in the dissolution of nitrobenzene in sulfuric acid is unique. It is likely that the stability achieved by the formation of microemulsion is the main driving force for the increase in mass transfer rate with the increase in sulfuric acid concentration. At 4π rad/s impeller speed, the rate of mass transfer was very fast, which can be observed from Figure 4.6. It was observed that 95% of the equilibrium solubility was attained in just 720 s for 17.1 kmol/m^3 concentration of sulfuric acid. The increase in k_L with the increase in the speed of stirring agrees qualitatively with the results reported in the literature on agitated liquid–liquid systems [1–3]. The mass transfer coefficient increased by one order of magnitude at the high-sulfuric acid concentrations when the agitation speed was doubled.

The concentration profiles of nitrobenzene at different sulfuric acid concentrations at 313 K using the impeller speeds of 2π and 4π rad/s are shown in Figures 4.7 and 4.8, respectively. It can be observed from these figures that the rate of mass transfer increased significantly with the increase in sulfuric acid concentration and impeller speed as observed in Figures 4.5 and 4.6. A comparison of k_L for 2π and 4π rad/s impeller speeds at 298 K and 313 K is presented in Figures 4.9 and 4.10, respectively. Apart from the increase in the value of k_L with increase in sulfuric acid concentration and speed of stirring (which has been discussed before), it is evident from this figure that k_L increased with the increase in temperature, which is also in qualitative agreement with the results reported in the literature [4]. The mass transfer experiments at temperatures higher than 313 K were not carried out due to the sulfonation of nitrobenzene. A comparison with the results reported by Modak and

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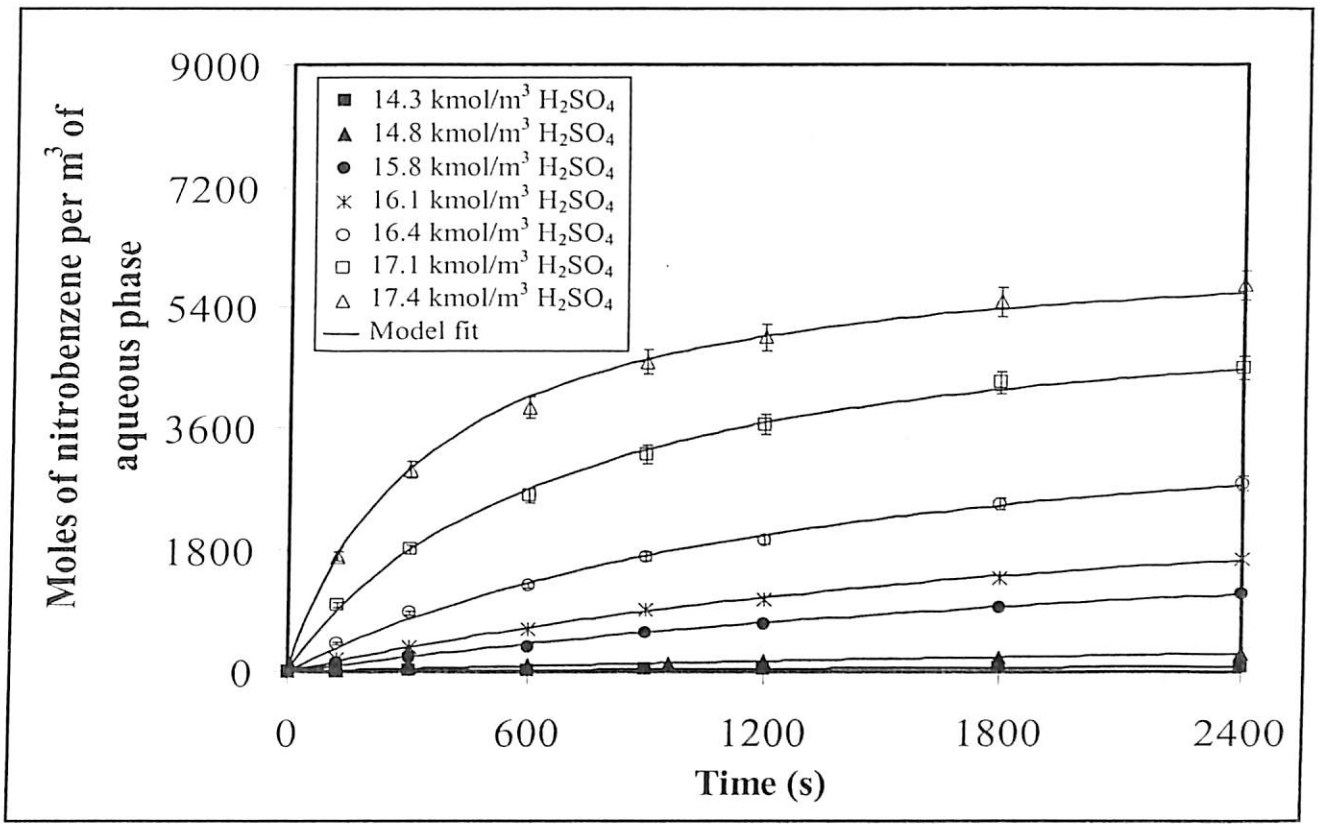


Figure 4.7 Determination of mass transfer coefficient of nitrobenzene at 313 K at different sulfuric acid concentrations at 2π rad/s impeller speed.

Concentration of sulfuric acid ($kmol/m^3$)	Mass transfer coefficient $(m/s) \times 10^5$
14.3	0.505
14.8	0.960
15.8	1.350
16.1	1.710
16.4	2.500
17.1	3.880
17.4	5.120

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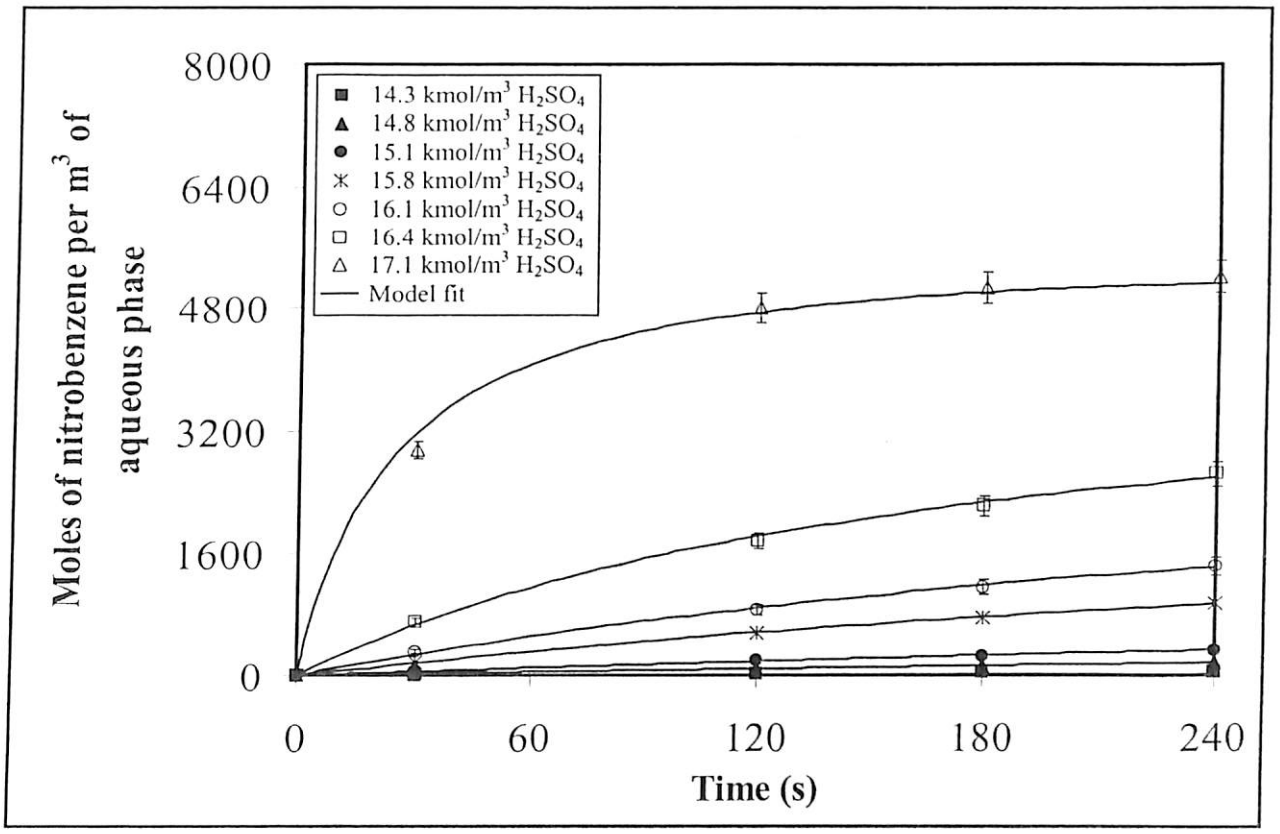


Figure 4.8 Determination of mass transfer coefficient of nitrobenzene at 313 K at different sulfuric acid concentrations at 4π rad/s impeller speed.

Concentration of sulfuric acid ($kmol/m^3$)	Mass transfer coefficient $(m/s) \times 10^5$
14.3	2.17
14.8	4.87
15.1	7.02
15.8	9.60
16.1	12.50
16.4	20.50
17.1	89.00

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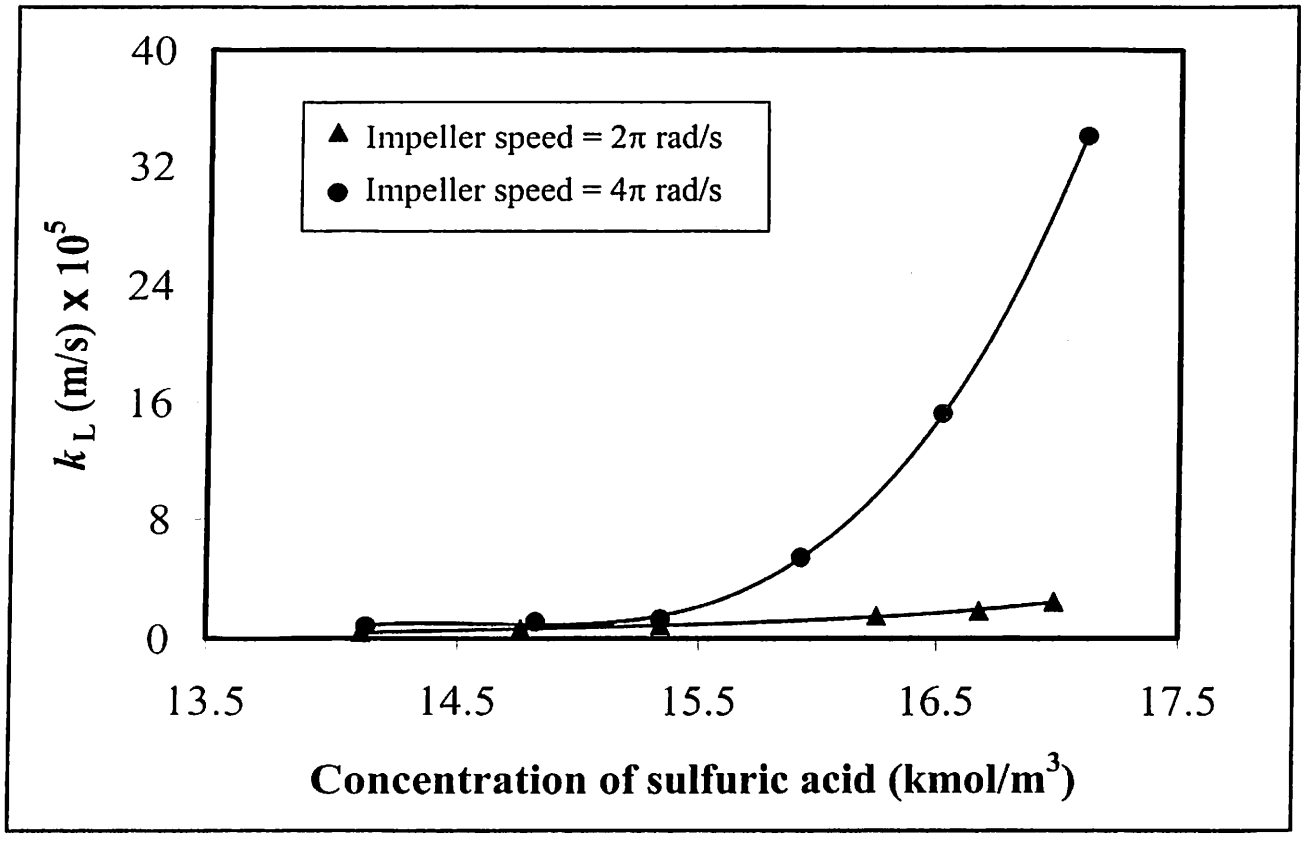


Figure 4.9 Comparison of the values of k_L obtained at different impeller speeds at 298 K.

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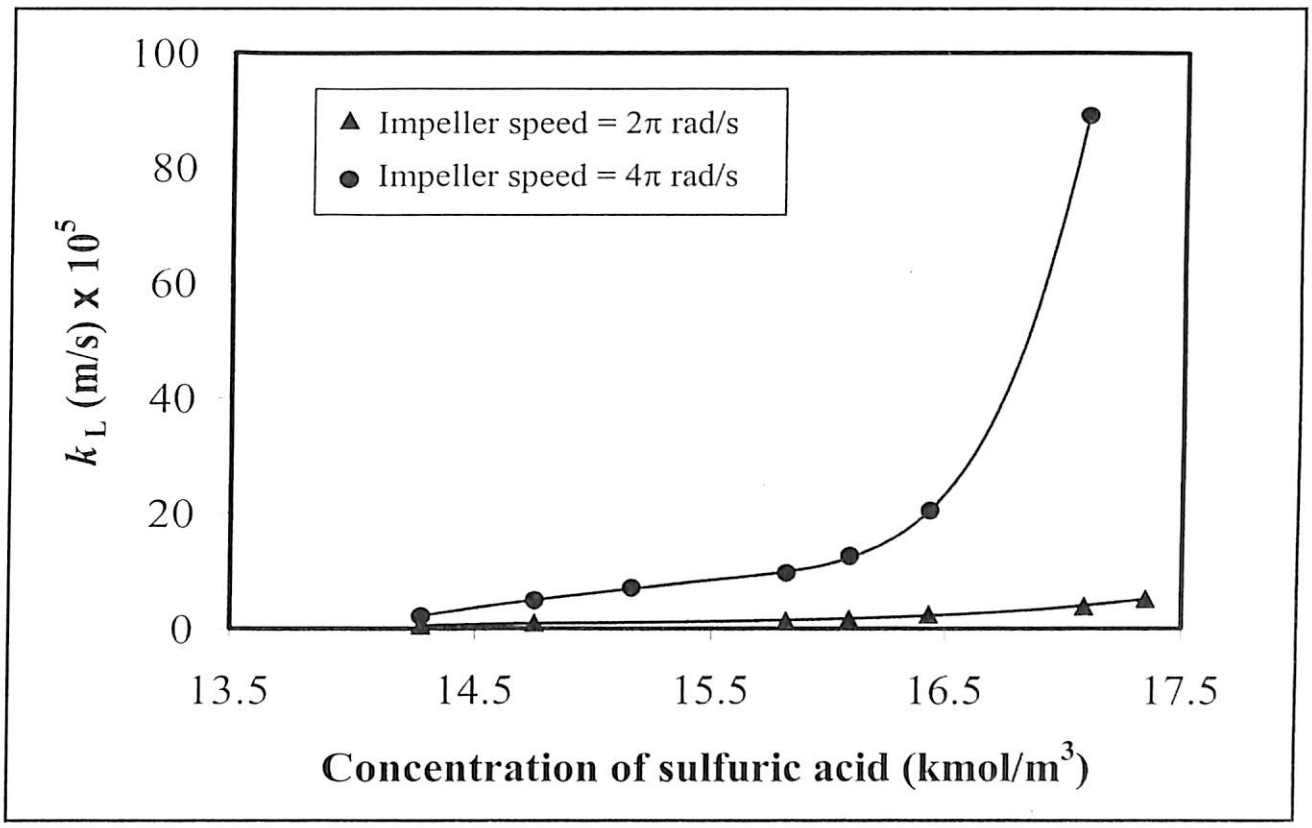


Figure 4.10 Comparison of the values of k_L obtained at different impeller speeds at 313 K.

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Juvekar [5] indicates that the values of mass transfer coefficient obtained in the present study are somewhat lower than that reported by them. It may be due to the fact the reactor used in the present study had larger diameter than the reactor used by them whereas, the diameter and height of the impellers were comparable. This probably caused lower values of the mass transfer coefficient in the present study.

4.3.2 Determination of reaction rate constants

The generation of nitronium ion in mixed acid and the mechanism by which nitrobenzene reacts with the nitronium ion is depicted in Figure 4.11. The rate of nitration can be expressed in terms of the concentrations of the reactants as [6,7],

$$\text{Rate} = -\frac{dC_{NB}}{dt} = k_{2,exp} C_{NB} C_{HNO_3} \tag{4.9}$$

where $k_{2,exp}$ is the observed (i.e., experimentally-determined) second-order rate constant, and C_{NB} and C_{HNO_3} are the concentrations of nitrobenzene and nitric acid in the aqueous phase, respectively. The observed rate constant $k_{2,exp}$ can be a strong function of sulfuric acid concentration. The rate expressed by equation (4.9) can change by several orders of magnitude if the concentration of sulfuric acid changes.

In the present study, the reactions were carried out in a single phase taking advantage of the high solubility of nitrobenzene in sulfuric acid. Therefore, the reaction mixture was homogeneous and the reaction was free from any mass transfer effect. The rate of homogeneous reaction in the constant-volume batch reactor can be described by the following rate equation.

$$C_{NB}^0 \frac{dX_{NB}}{dt} = k_{2,exp}\left(C_{NB}^0 - C_{NB}^0 X_{NB}\right)\left(C_{HNO_3}^0 - C_{NB}^0 X_{NB}\right) \tag{4.10}$$

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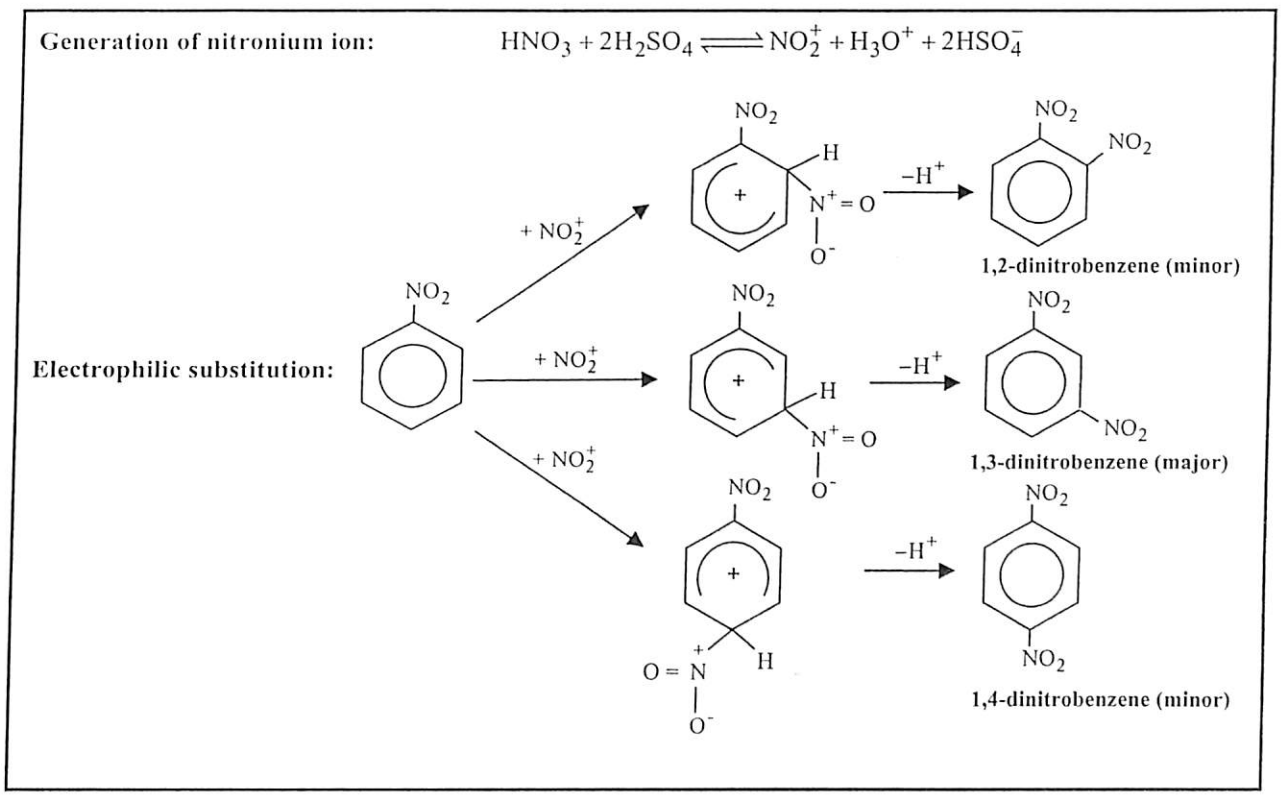


Figure 4.11 Reaction mechanism of nitration of nitrobenzene with mixed acid.

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where $C^0_{HNO_3}$ and C^0_{NB} are the initial concentrations of nitric acid and nitrobenzene, respectively, and X_{NB} is the conversion of nitrobenzene. Letting $M = C^0_{HNO_3} / C^0_{NB}$, the initial molar ratio of reactants, we obtain

$$C^0_{NB}\frac{dX_{NB}}{dt} = k_{2,exp}\left(C^0_{NB}\right)^2(1-X_{NB})(M-X_{NB}), \quad M \neq 1 \tag{4.11}$$

Integrating equation (4.11) we get,

$$\ln\left[\frac{M-X_{NB}}{M(1-X_{NB})}\right] = k_{2,exp}\left(C^0_{HNO_3} - C^0_{NB}\right)t \tag{4.12}$$

Therefore, a plot of $\ln\left[\frac{M-X_{NB}}{M(1-X_{NB})}\right]$ versus time should be linear passing through the origin with slope equal to $k_{2,exp}\left(C^0_{HNO_3} - C^0_{NB}\right)$. The observed rate constant, $k_{2,exp}$, can be calculated from the slope. To check the dependence of initial mole ratio of nitric acid and nitrobenzene (M) on the value of second-order rate constant, a series of reactions were carried out at 298 K with different values of M. The concentration profiles of nitrobenzene at 15.6 kmol/m^3 H_2SO_4 concentration are presented in Figure 4.12 (a) with different initial mole ratios of nitric acid and nitrobenzene. The corresponding plots of $\ln\left[\frac{M-X_{NB}}{M(1-X_{NB})}\right]$ versus time are shown in Figure 4.12 (b). The observed rate constants calculated from the slopes of the plots are presented in Table 4.1. It is seen from the table that the values of the second-order rate constants did not vary with M.

Experiments were carried out to determine the effect of stirring speed on the value of second-order rate constant using 15.9 kmol/m^3 concentration of sulfuric acid at 298 K. The concentration profiles of nitrobenzene and the corresponding linear plots are shown in Figure

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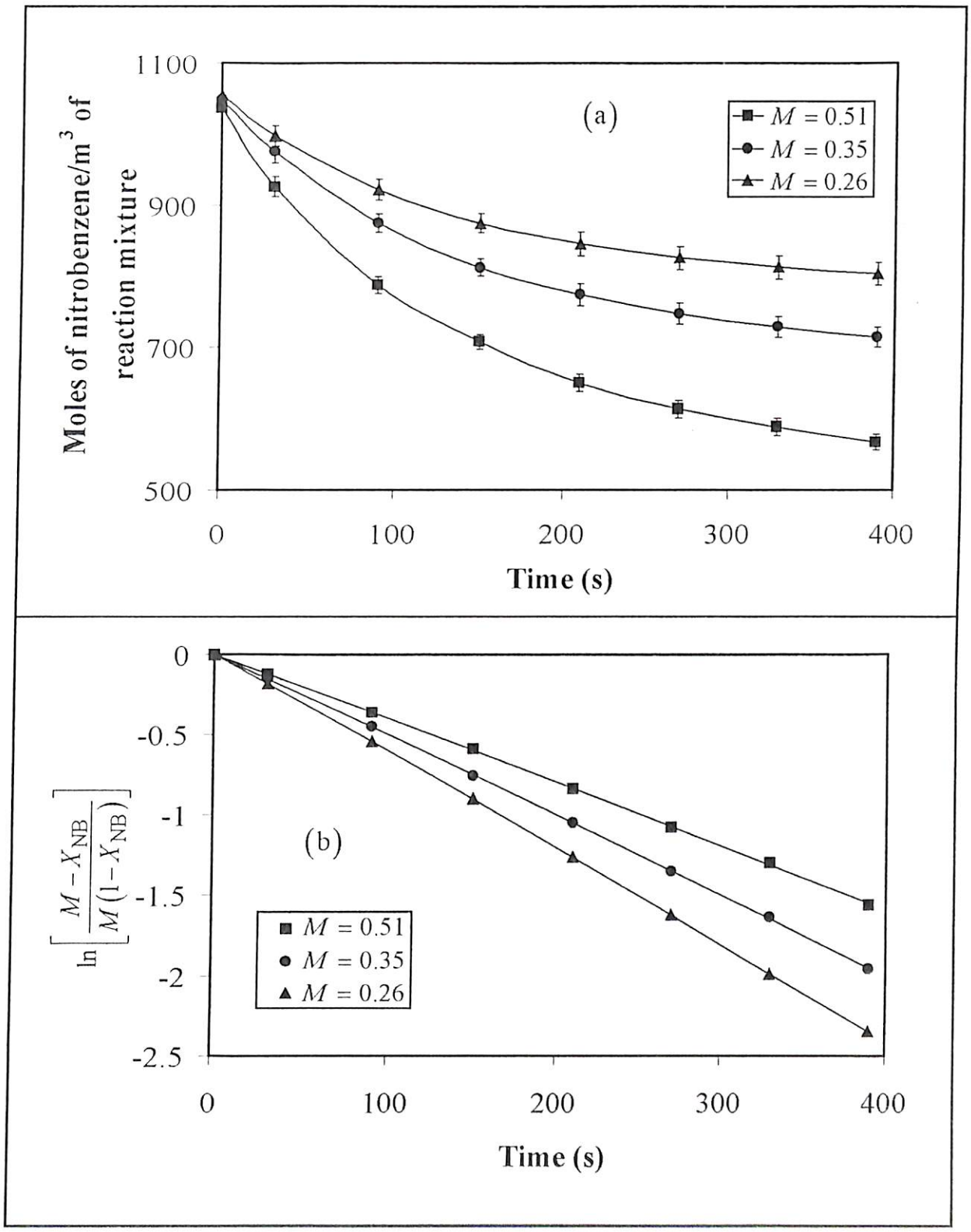


Figure 4.12 (a) Concentration profiles of nitrobenzene in the reaction mixture at three values of M, and (b) determination of second-order rate constants at these M at 298 K using 15.6 kmol/m^3 sulfuric acid.

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4.13. The observed rate constants determined from the slopes of the plots are presented in Table 4.2. It is observed from this table that the stirring speed had negligible effect on the second-order rate constant. The initial mole ratio of nitric acid and nitrobenzene (M) was taken as 0.48 for studying the second-order kinetics. The speed of agitation was maintained at 2π rad/s because it was apparent that this speed was sufficient to make the reaction mixture homogeneous. The homogeneous nitration of nitrobenzene for the determination of second-order rate constant was carried out at various sulfuric acid concentrations at three temperatures.

The concentration profiles of nitrobenzene at 14.4 kmol/m^3 H_2SO_4 concentration are presented in Figure 4.14 (a) at these three temperatures. The corresponding plots of $\ln\left[\frac{M - X_{NB}}{M(1 - X_{NB})}\right]$ versus time are shown in Figure 4.14 (b). It can be observed from Figure 4.14 (b) that the data were fitted well by the straight lines given by equation (4.12). Similarly, the concentration profiles of nitrobenzene and the corresponding linear plots are shown in Figures 4.15 – 4.20 for other sulfuric acid concentrations at 298 K, 313 K and 323 K. The observed rate constants calculated from the slopes of the plots are presented in Figure 4.21. It can be observed from this figure that the value of rate constant is maximum when the sulfuric acid concentration is ~16.7 kmol/m^3. The reason for this is explained in the subsequent section. The rate constants obtained in the present study are compared with the values reported in the literature at 298 K [8,9], 300 K [5] and 313 K [8] in Figure 4.21. It can be observed that the rate constants obtained in the present work compare well with the results reported in the literature.

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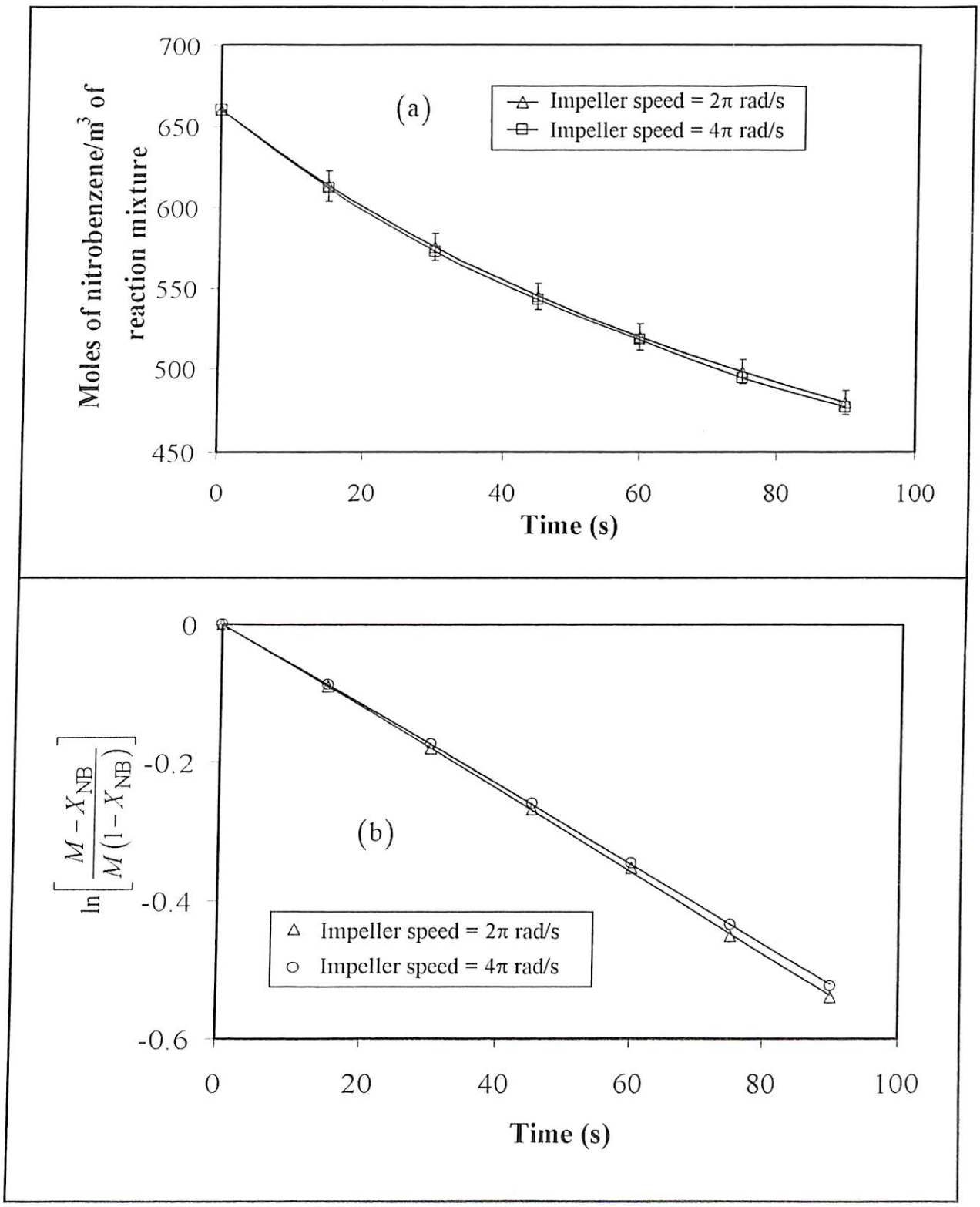


Figure 4.13 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of second-order rate constant with different stirring speeds at 298 K with 15.9 kmol/m^3 sulfuric acid (M = 0.48).

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Table 4.1 Variation of rate constant $\left(k_{2,\exp}\right)$ with M at 15.6 kmol/m^3 concentration of sulfuric acid at 298 K

M	$k_{2,\exp}\left(\mathrm{m^3 mol^{-1} s^{-1}}\right) \times 10^6$
0.51	7.86
0.35	7.36
0.20	7.65

Table 4.2 Variation of rate constant $\left(k_{2,\exp}\right)$ with stirring speed at 15.9 kmol/m^3 concentration of sulfuric acid at 298 K

Stirring speed (rad/s)	$k_{2,\exp}\left(\mathrm{m^3 mol^{-1} s^{-1}}\right) \times 10^6$
2π	16.8
4π	17.4

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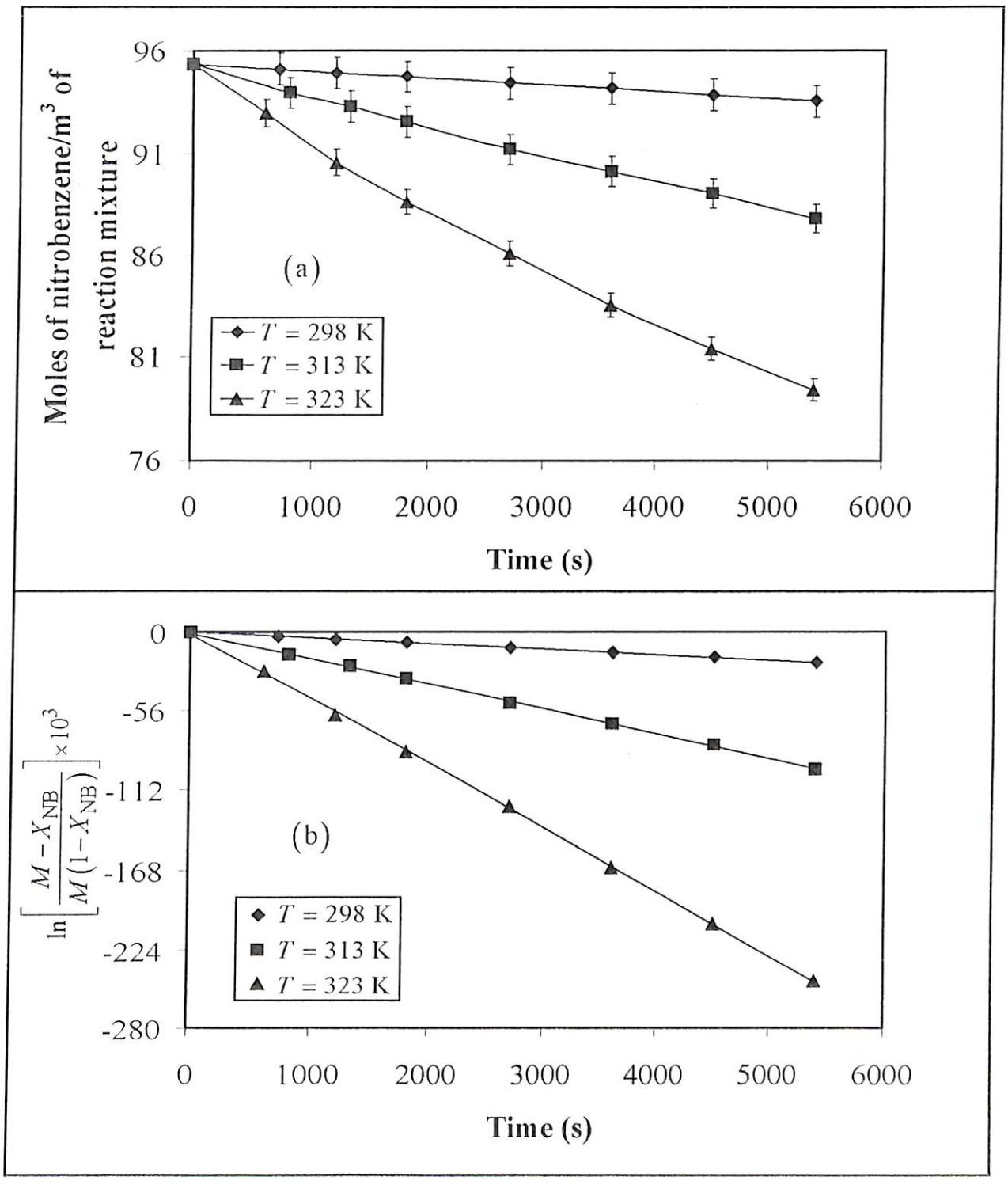


Figure 4.14 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of rate constants at 298 K, 313 K and 323 K at 14.4 kmol/m^3 concentration of sulfuric acid.

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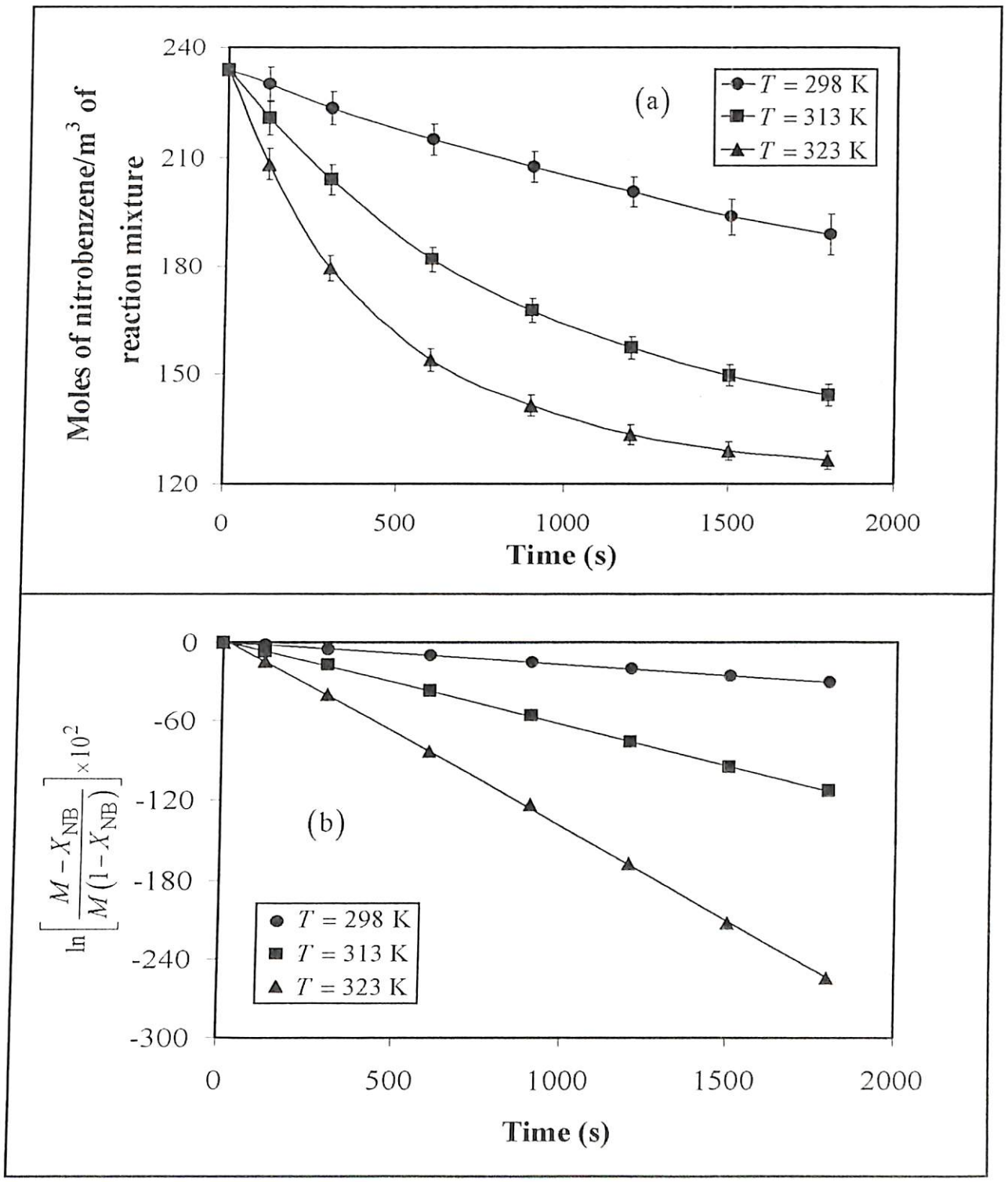


Figure 4.15 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of rate constants at 298 K, 313 K and 323 K at 15.0 kmol/m^3 concentration of sulfuric acid.

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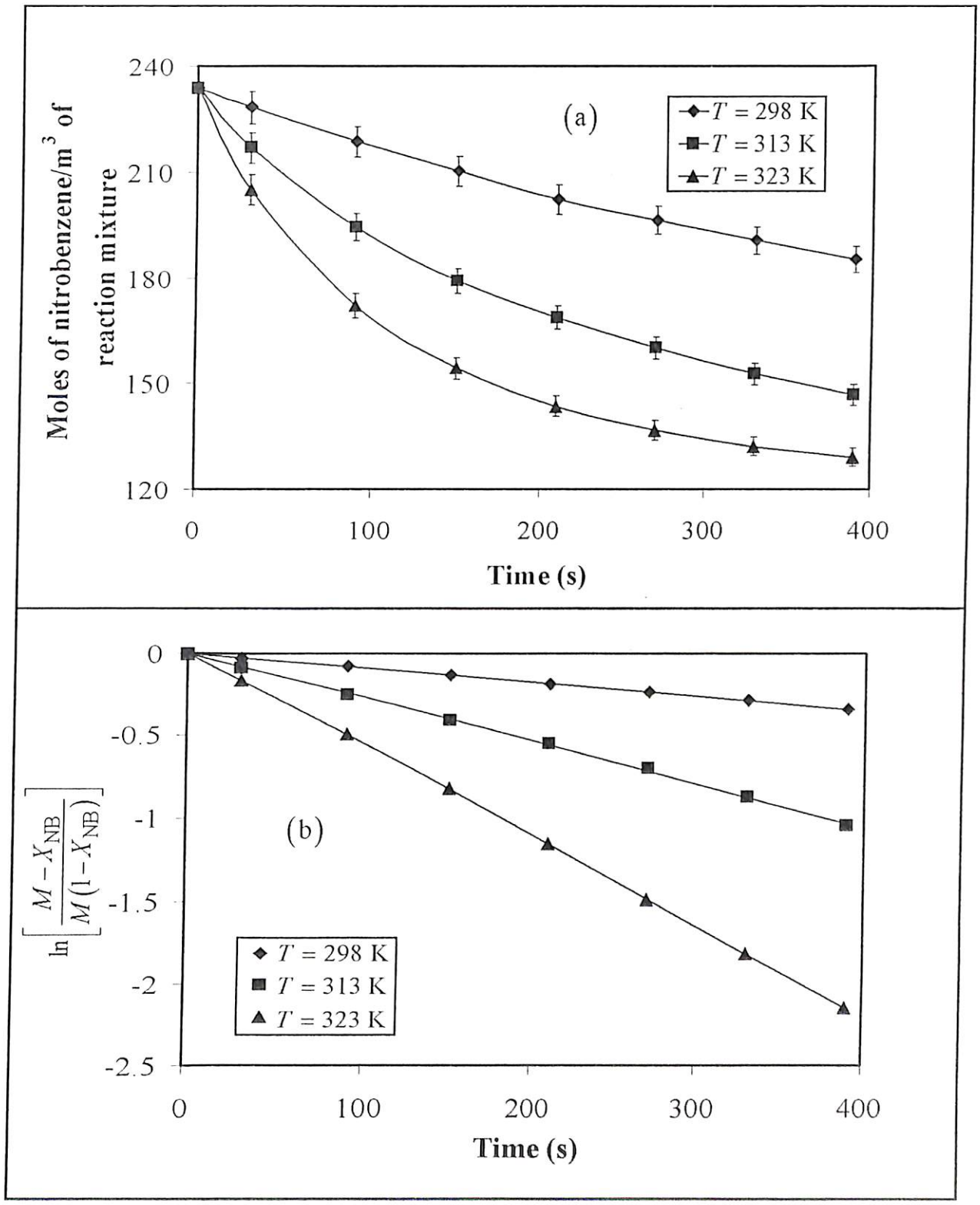


Figure 4.16 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of rate constants at 298 K, 313 K and 323 K at 15.6 kmol/m^3 concentration of sulfuric acid.

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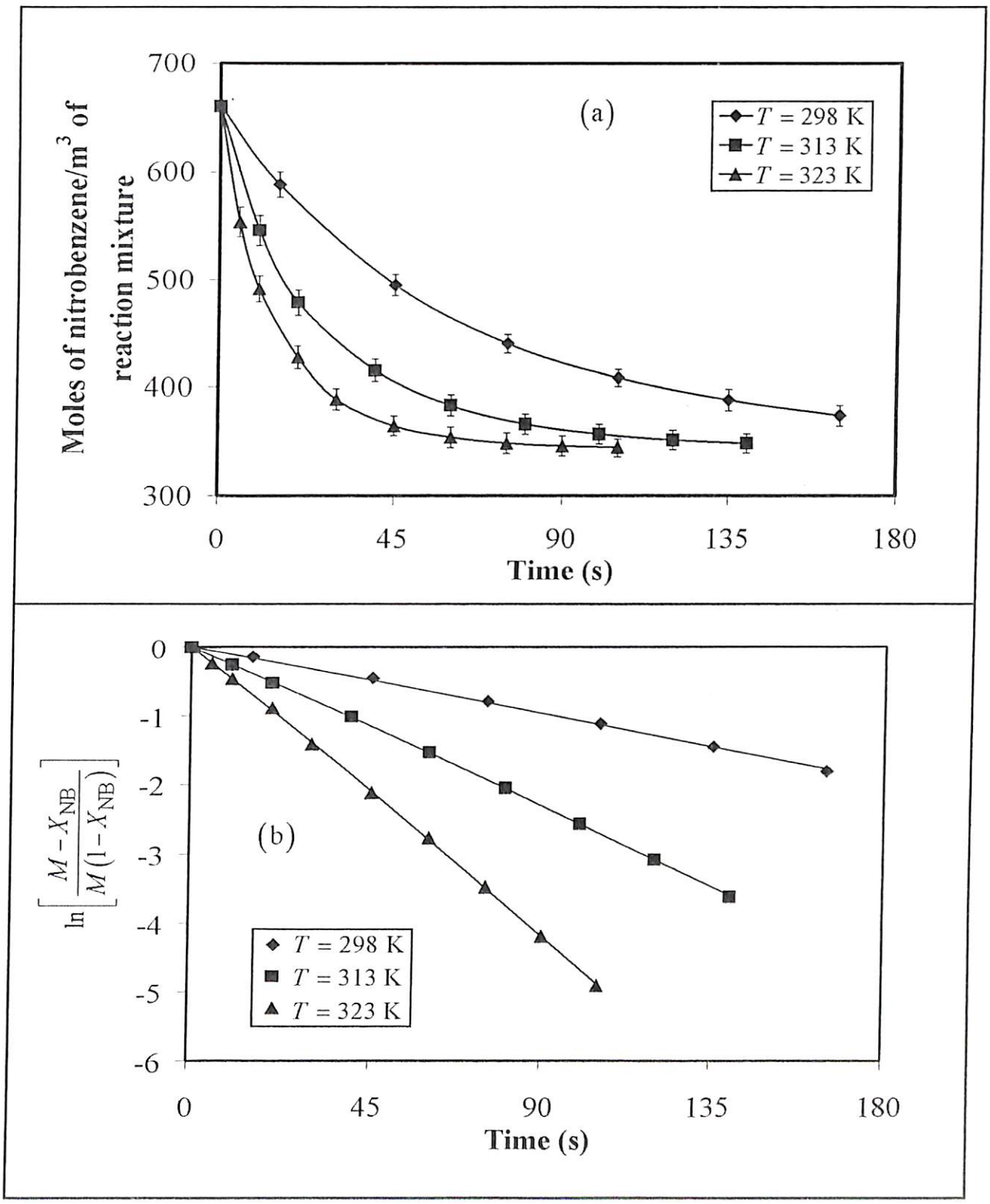


Figure 4.17 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of rate constants at 298 K, 313 K and 323 K at 16.2 kmol/m^3 concentration of sulfuric acid.

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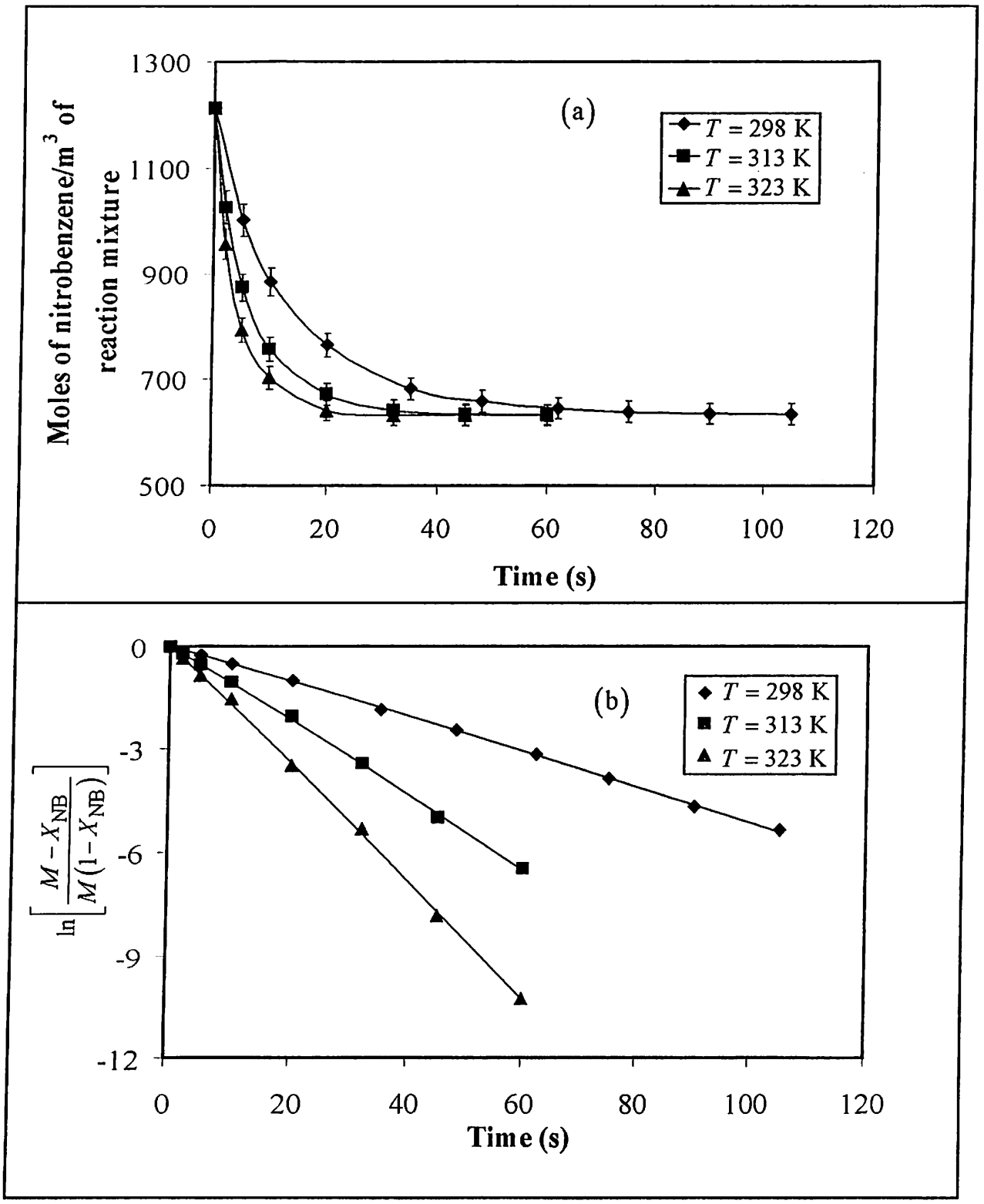


Figure 4.18 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of rate constants at 298 K, 313 K and 323 K at 16.6 kmol/m^3 concentration of sulfuric acid.

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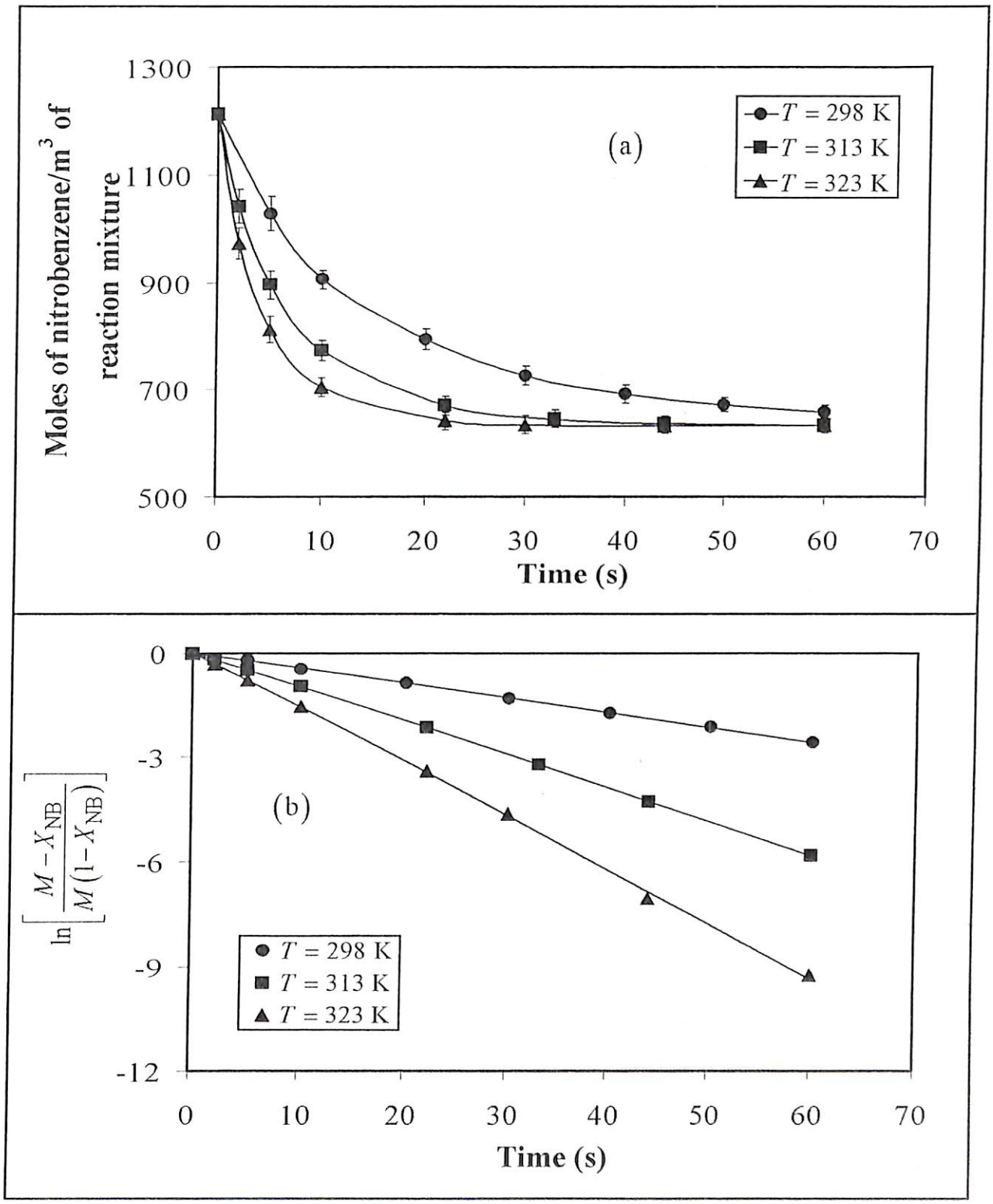


Figure 4.19 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of rate constants at 298 K, 313 K and 323 K at 16.9 kmol/m^3 concentration of sulfuric acid.

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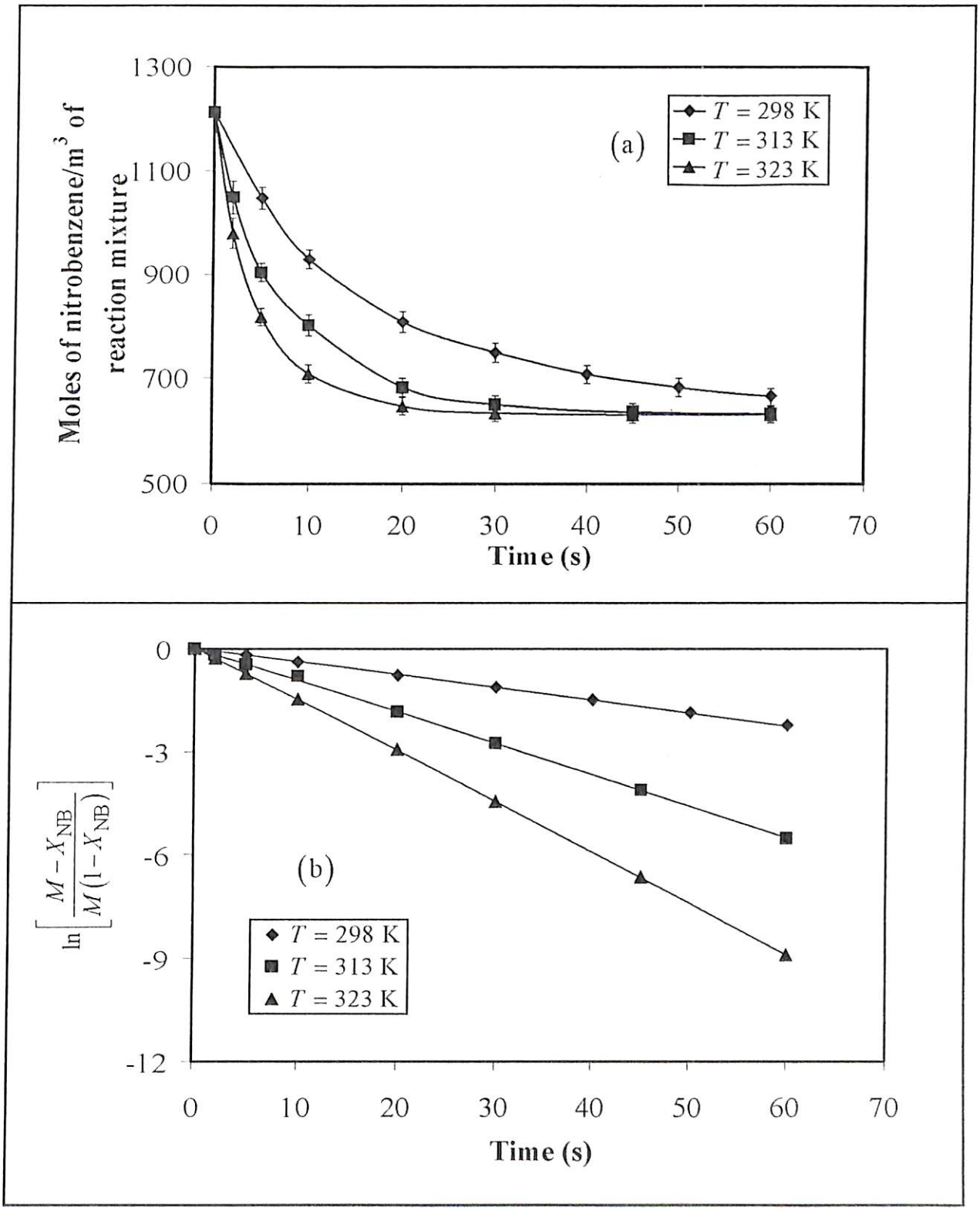


Figure 4.20 (a) Concentration profiles of nitrobenzene in the reaction mixture, and (b) determination of rate constants at 298 K, 313 K and 323 K at 17.1 kmol/m^3 concentration of sulfuric acid.

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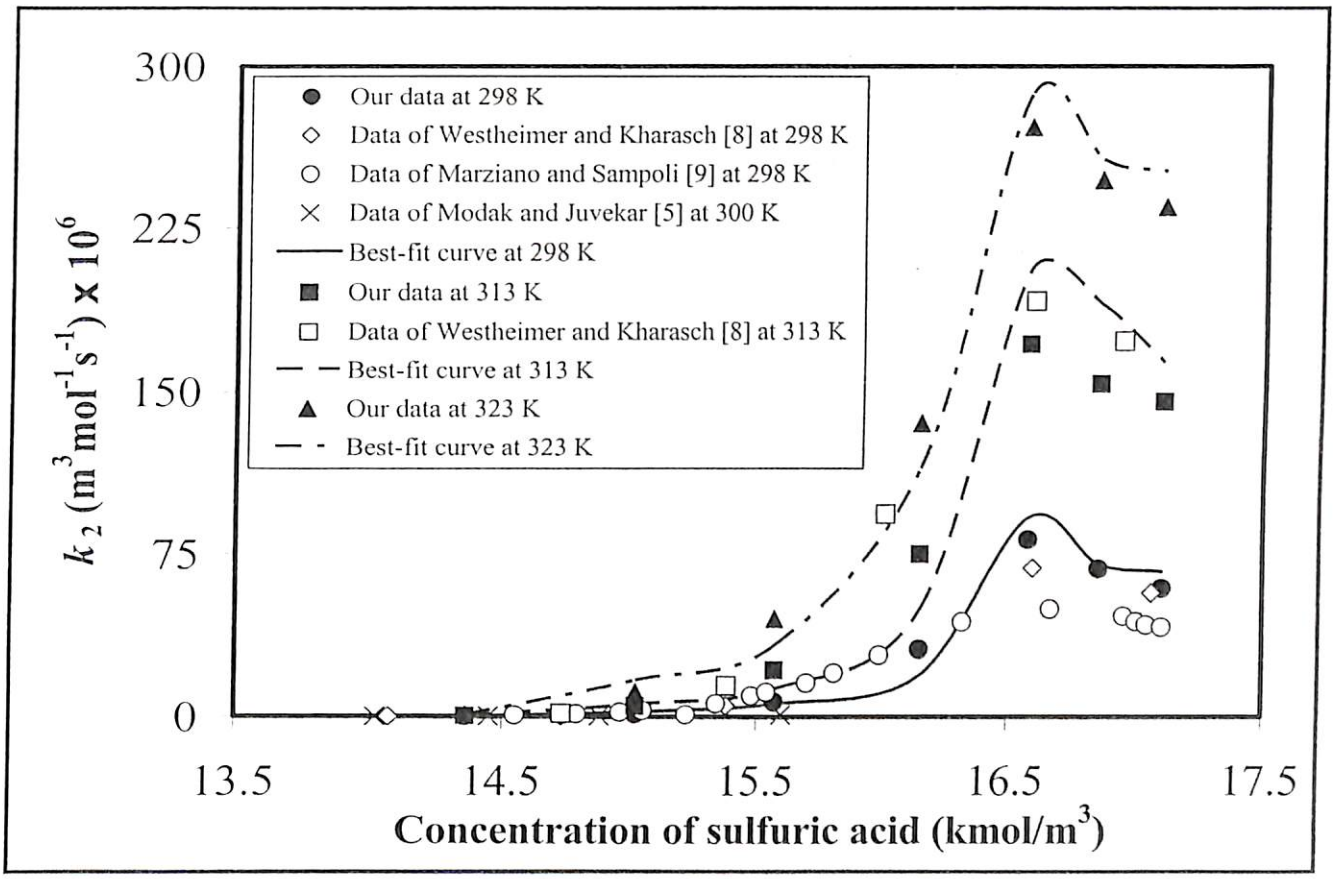


Figure 4.21 Variation of the second-order rate constant with the concentration of sulfuric acid at 298 K, 313 K and 323 K. Comparison with the experimental data reported in the literature is presented in the figure. The curves indicate the fit of the equation (4.17) described on page 119.

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4.3.3 Analysis of the kinetic results

The rate-determining step in homogeneous aromatic nitration in mixed acid is believed to be the attack of the nitronium ion $\left(NO_2^+\right)$ on the aromatic compound. The rate can be expressed in terms of the concentrations of nitrobenzene and nitronium ion as [6],

$$\text{Rate} = k^*_{2,\text{exp}} C_{\text{NB}} C_{NO_2^+} \tag{4.13}$$

where $k^*_{2,\text{exp}}$ is the observed rate constant and $C_{NO_2^+}$ is the concentration of the nitronium ion in the acid phase. In addition, the reaction-rate in the acid phase can be written using a Brønsted-Bjerrum rate law (transition-state theory) as [7],

$$\text{Rate} = k'_2 C_{\text{NB}} C_{NO_2^+} \frac{\gamma_{\text{NB}}\ \gamma_{NO_2^+}}{\gamma^{\#}} \tag{4.14}$$

where k'_2 is a thermodynamic parameter that depends on temperature, γ_{NB} and $\gamma_{NO_2^+}$ are the activity coefficients of nitrobenzene and nitronium ion, respectively, and $\gamma^{\#}$ is the activity coefficient of the transition-state intermediate. The parameter k'_2 is unique for each aromatic compound. Based on the rate expression given by equation (4.14), a rate equation has been proposed by Marziano and co-workers [9–11] employing the M_c function of sulfuric acid as,

$$\text{Rate} = k'_2 C_{\text{NB}} C_{NO_2^+} 10^{nM_c} \tag{4.15}$$

where n is another thermodynamic parameter which is unique for each aromatic compound. The M_c function for sulfuric acid represents a general scale that depicts its acidity. The value of M_c depends only on the concentration of the acid at a given temperature. The quantity 10^{nM_c} describes the change in the ratio of the activity coefficients in equation (4.14) with the change in sulfuric acid concentration, and takes into account the effective concentrations of

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the reactants.

From equations (4.9) and (4.13), the relation between $k^{*}_{2,\exp}$ and $k_{2,\exp}$ can be written as,

$$k^{*}_{2,\exp} = \frac{k_{2,\exp} C_{HNO_3}}{C_{NO_2^+}} \tag{4.16}$$

From equations (4.9) and (4.15), the relation between k'_2 and $k_{2,\exp}$ can be written as,

$$k'_2 = \frac{k_{2,\exp} C_{HNO_3}}{C_{NO_2^+}\ 10^{nM_c}} \tag{4.17}$$

From equation (4.17) we can write,

$$\log k_{2,\exp} - \log\left(C_{NO_2^+}/C_{HNO_3}\right) = \log k'_2 + nM_c \tag{4.18}$$

Therefore, a plot between $\left[\log k_{2,\exp} - \log\left(C_{NO_2^+}/C_{HNO_3}\right)\right]$ and M_c should produce a straight line with slope equal to n and intercept equal to $\log k'_2$. However, in order to determine the values of n and k'_2, it is necessary to know M_c and $\left(C_{NO_2^+}/C_{HNO_3}\right)$.

4.3.3.1 The M_c function

The M_c function at 298 K was developed in the form of a polynomial by using the data of Marziano et al. [11]. In the sulfuric acid concentration range between 14.0 and 17.2 kmol/m^3, the polynomial is given by,

$$-M_c = 6.47\times10^{-4} C^5_{H_2SO_4} - 39.8\times10^{-3} C^4_{H_2SO_4} + 91.8\times10^{-2} C^3_{H_2SO_4} - 9.39 C^2_{H_2SO_4} + 36.6 C_{H_2SO_4} \tag{4.19}$$

The fitted data using the polynomial is shown in Figure 4.22. The values of M_c at the higher temperatures were calculated by the following equation given by Marziano et al. [12],

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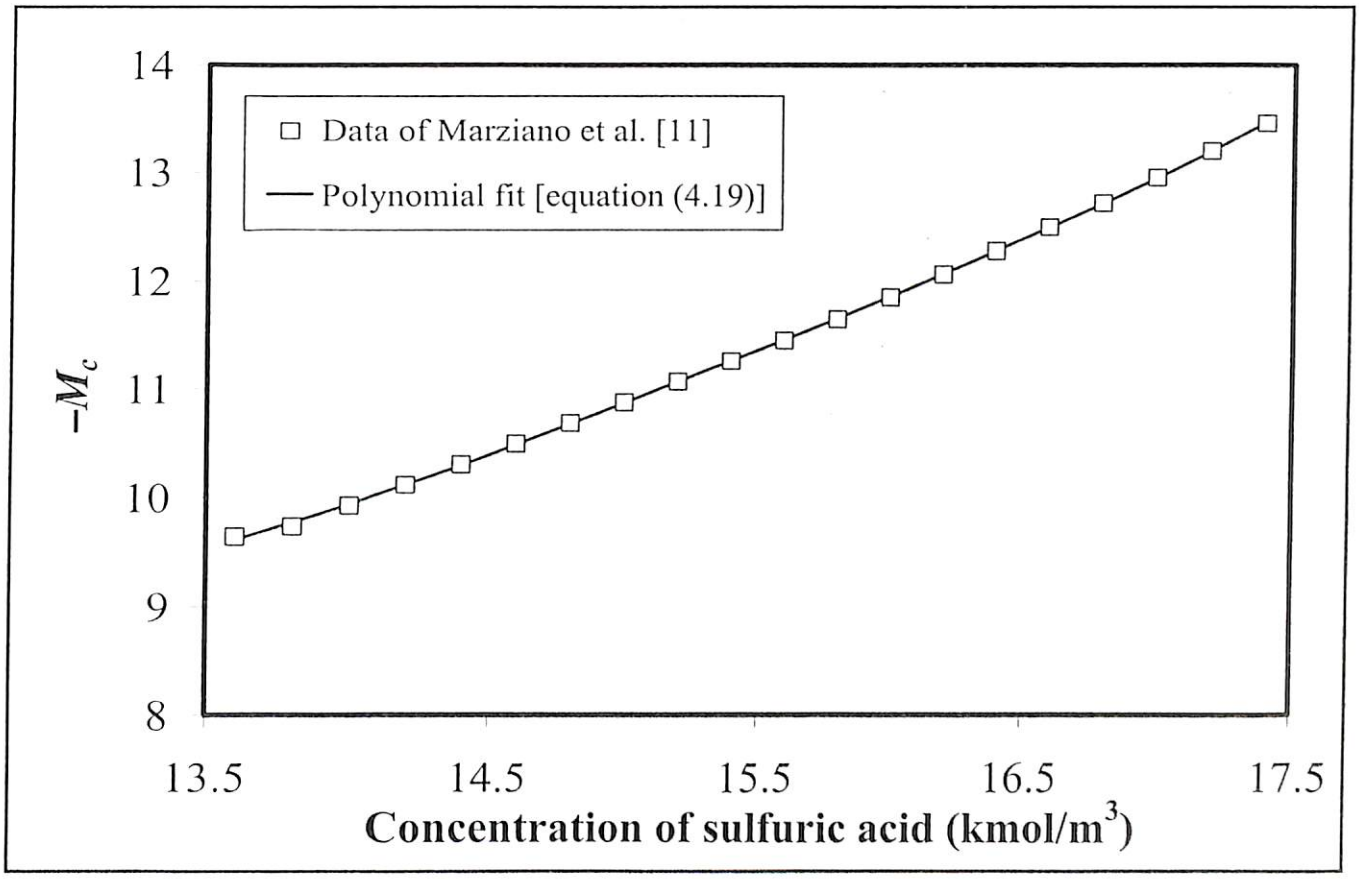


Figure 4.22 Variation of the M_c function with the concentration of sulfuric acid at 298 K.

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$$M_c(T) = M_c(298\ \text{K})\left[\frac{200}{T} + 0.3292\right] \tag{4.20}$$

4.3.3.2 The $\left(C_{NO_2^+}/C_{HNO_3}\right)$ ratio

The equilibria of nitric acid in aqueous sulfuric acid have been studied extensively at room temperature and at higher temperatures by different techniques such as Raman spectroscopy, UV spectroscopy and NMR spectroscopy. These works have identified the molecular and ionic species present in the solutions. The amounts of HNO_3 converted to NO_2^+ in different sulfuric acid solutions were shown in Figure 2.4. At the high-concentrations of sulfuric acid (>14.1 kmol/m^3), nitric acid is present as nitronium ion and molecular nitric acid (i.e., $C^0_{HNO_3} = C_{NO_2^+} + C_{HNO_3}$). The values of $\left(C_{NO_2^+}/C_{HNO_3}\right)$ at 298 K and 313 K were determined from the ionization ratio $\left(C_{NO_2^+}/C^0_{HNO_3}\right)$ presented in Figure 2.4. The values at 323 K were obtained by interpolation of the data between 313 K and 333 K.

Figure 4.23 shows the plots of $\left[\log k_{2,\text{exp}} - \log\left(C_{NO_2^+}/C_{HNO_3}\right)\right]$ versus M_c at different temperatures. It can be observed from this figure that the data were fitted well by straight lines in all cases. The values of n and $\log k_2'$ obtained at different temperatures are presented in Table 4.3. It is evident that the value of n was virtually constant over these temperatures whereas, the value of k_2' slightly increased with increase in temperature.

The best-fit curves corresponding to these values of n and k_2' were shown in Figure 4.21. It can be seen from the figure that the fit to the experimental values of the second-order rate constant was good, and the increase and decrease of the rate constant with increase in

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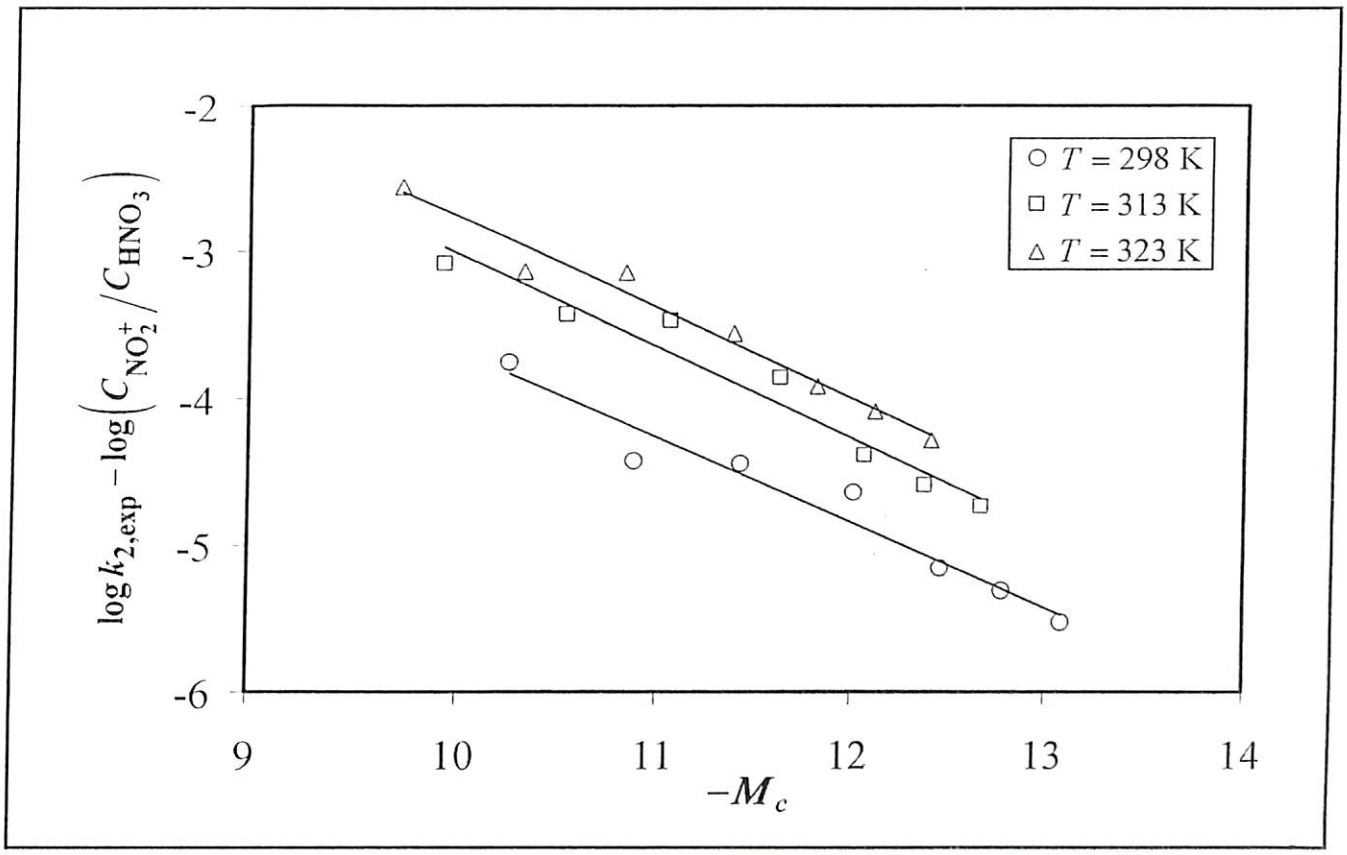


Figure 4.23 Determination of the thermodynamic parameters n and k_2'.

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Table 4.3 Values of n and $\log k_2'$ at three temperatures

Nitration temperature (K)	n	$\log k_2'$
298	0.586	2.185
313	0.626	3.239
323	0.616	3.390

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sulfuric acid concentration were explained well. The ratio $\left(C_{NO_2^+}/C_{HNO_3}\right)$ in equation (4.17) increases whereas the quantity 10^{nM_c} decreases with the increase in sulfuric acid concentration. The effect of the former quantity is stronger than the latter up to 16.7 kmol/m^3 sulfuric acid concentration. Beyond this concentration, the quantity 10^{nM_c} dominates over the $\left(C_{NO_2^+}/C_{HNO_3}\right)$ ratio. Therefore, a decrease in rate constant is observed beyond this sulfuric acid concentration.

Using the fitted values of n and k_2', we can calculate the value of k_2^* by using the following relationship.

$$k_{2,cal}^* = k_2' 10^{nM_C} \tag{4.21}$$

Figure 4.24 shows the comparison between the experimentally-observed and calculated values of k_2^* at different temperatures and at different concentrations of sulfuric acid. The calculated values compared well with values obtained from the experimental k_2^* values.

4.3.4 Determination of activation energies of nitration

From the values of $k_{2,cal}^*$ at three temperatures, the activation energy $\left(E_2^*\right)$ for the electrophilic attack of nitronium ion on the nitrobenzene molecule can be determined. The relationship between $k_{2,cal}^*$ and the reaction temperature (T) was described by the Arrhenius equation,

$$k_{2,cal}^* = k_{2,0}^* \exp\left(-\frac{E_2^*}{RT}\right) \tag{4.22}$$

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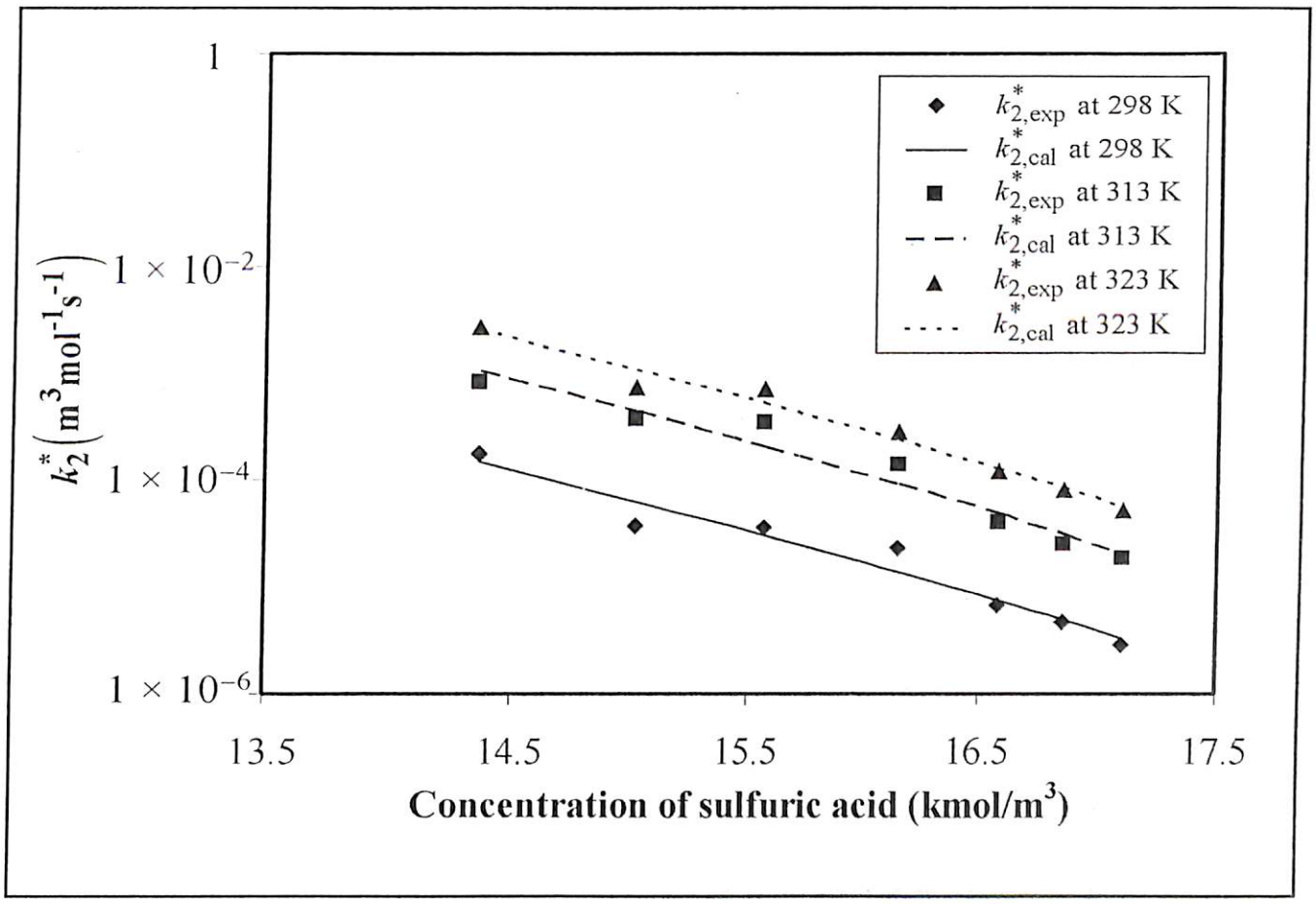


Figure 4.24 Variation of experimental and calculated values of k_2^* with sulfuric acid concentration at different temperatures.

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where $k^*_{2,0}$ is the frequency factor and R is the universal gas constant. The plots of $\ln k^*_{2,\text{cal}}$ versus $1/T$ are shown in Figure 4.25. The data were fitted well by the straight lines. The slopes of these straight lines give the values of the activation energy E^*_2 at each sulfuric acid concentration. It is observed from the figure that the linear plots are parallel to each other. The value of E^*_2 was found to be constant at 91.3 kJ/mol.

From the values of $k_{2,\text{exp}}$ at different temperatures, the activation energy (E_2) of the reaction between nitrobenzene and nitric acid was calculated at each sulfuric acid concentration by the Arrhenius equation,

$$k_{2,\text{exp}} = k_{2,0} \exp\left(-\frac{E_2}{RT}\right) \tag{4.23}$$

where $k_{2,0}$ is the frequency factor. The plots of $\ln k_{2,\text{exp}}$ versus $1/T$ are shown in Figure 4.26. The data were fitted well by the straight lines. The values of the activation energy E_2 were calculated from the slopes of these straight lines. It was found that the values of E_2 varied with the concentration of sulfuric acid. The relation between E_2 and E^*_2 is shown schematically in Figure 4.27. From the figure it can be seen that the activation energies E_2 and E^*_2 can be correlated as,

$$E_2 = E^*_2 + \Delta H \tag{4.24}$$

where ΔH is the enthalpy change for the reaction: $HNO_3 + H^+ \rightarrow NO_2^+ + H_2O$. The value of ΔH at each sulfuric acid concentration was determined and these are presented in Figure 4.28. It is observed from the figure that the exothermicity of the reaction increased with the increase in sulfuric acid concentration. This agrees with the prediction of Cox and Strachan

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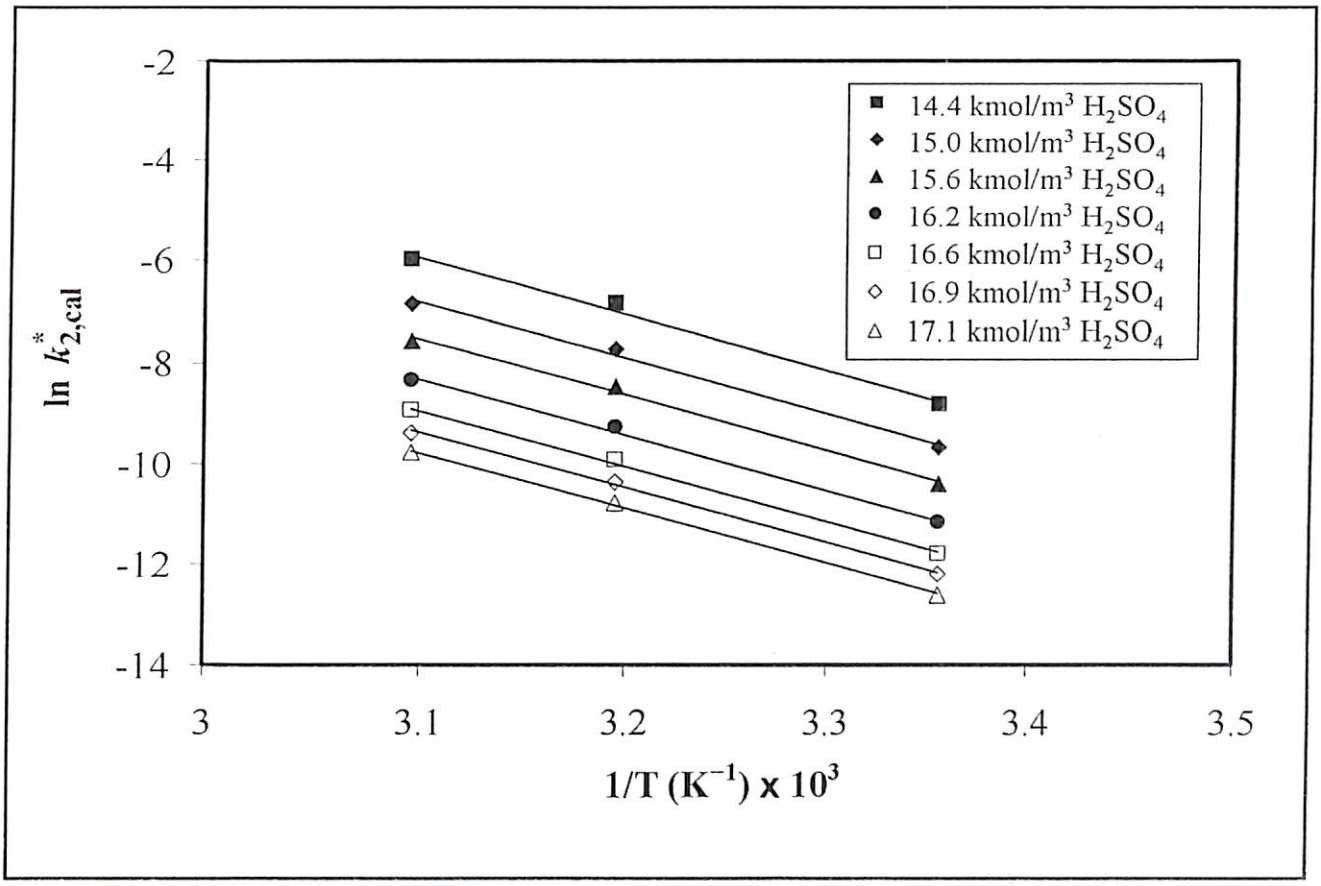


Figure 4.25 Arrhenius plots at different concentrations of sulfuric acid.

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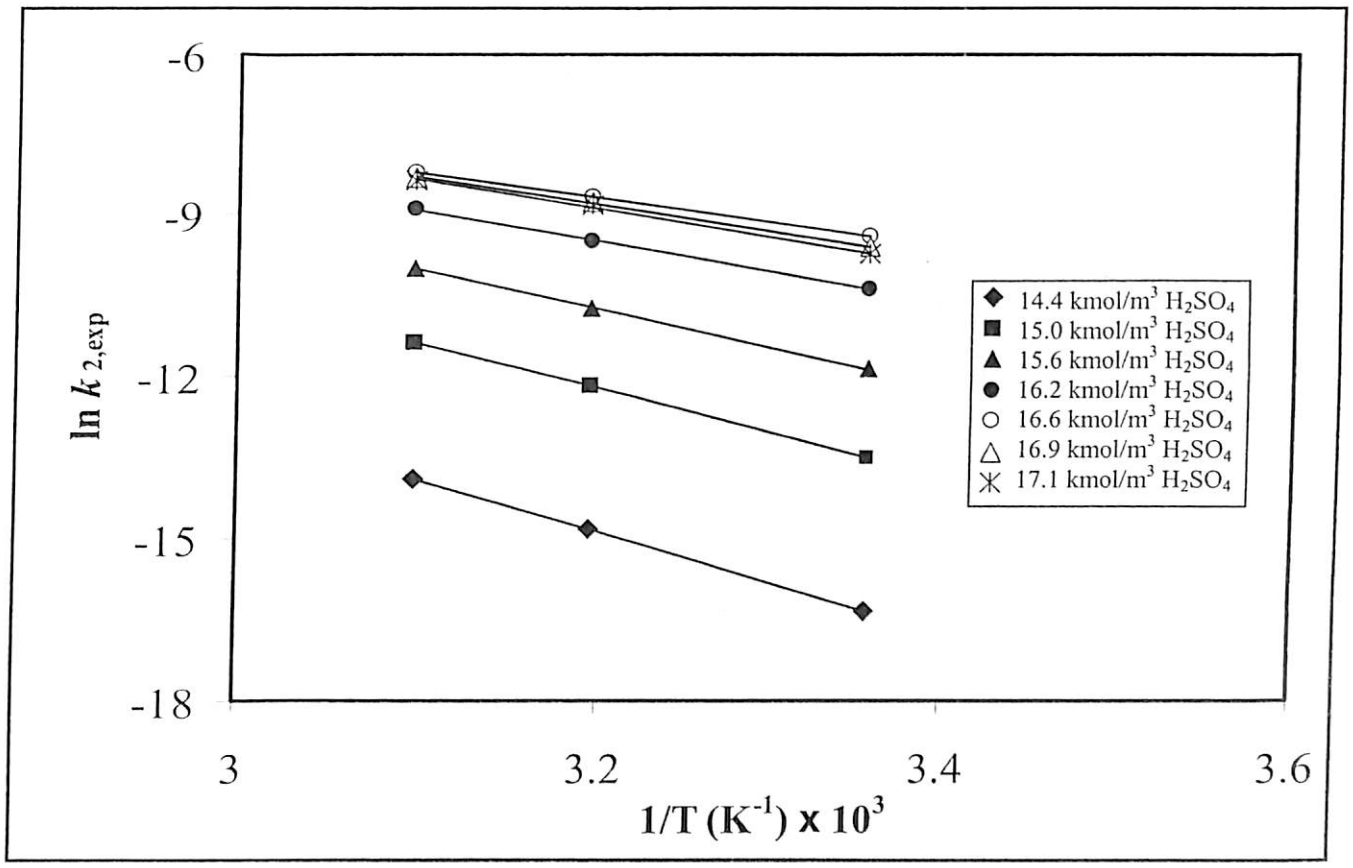


Figure 4.26 Arrhenius plots at different concentrations of sulfuric acid.

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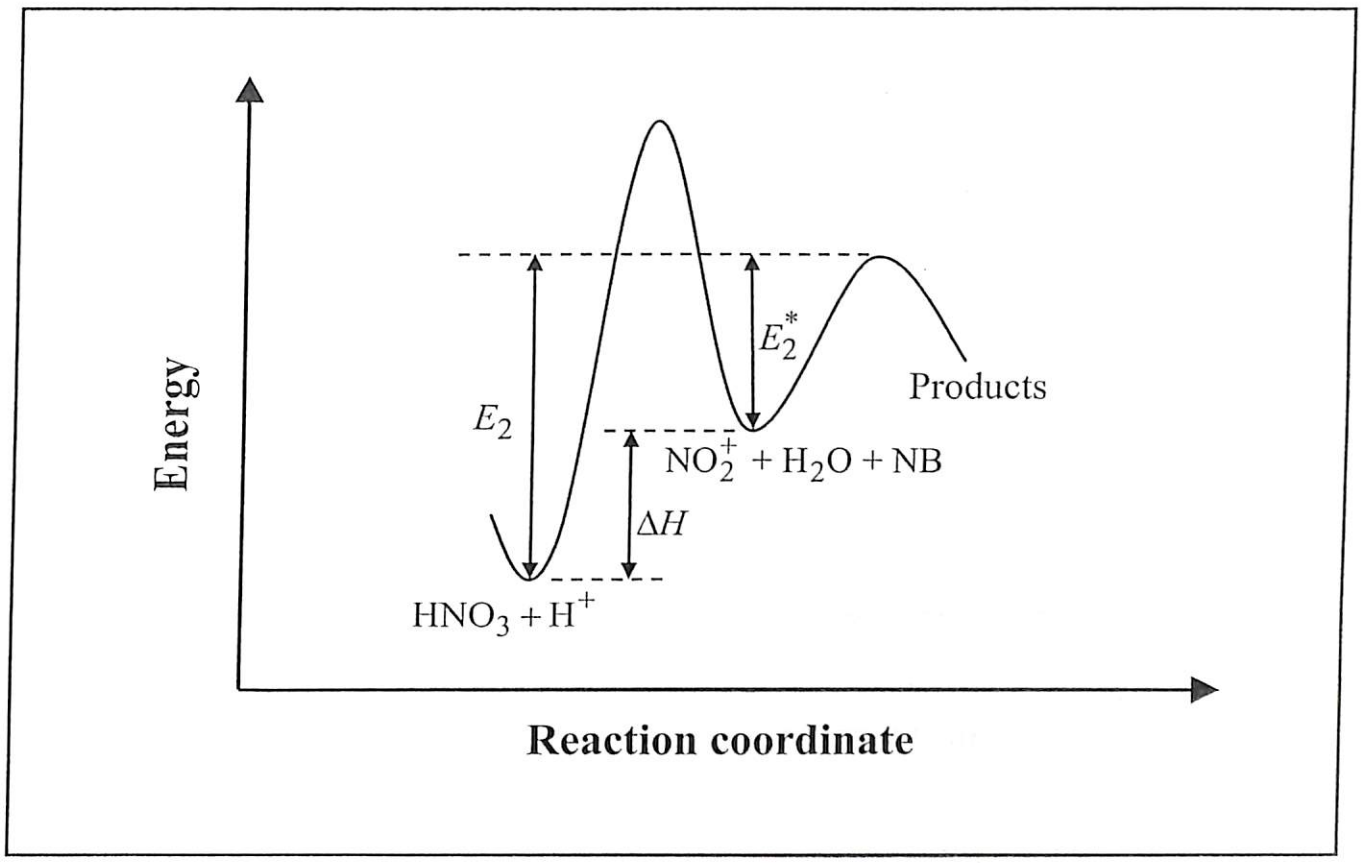


Figure 4.27 Relation between E_2 and E_2^*.

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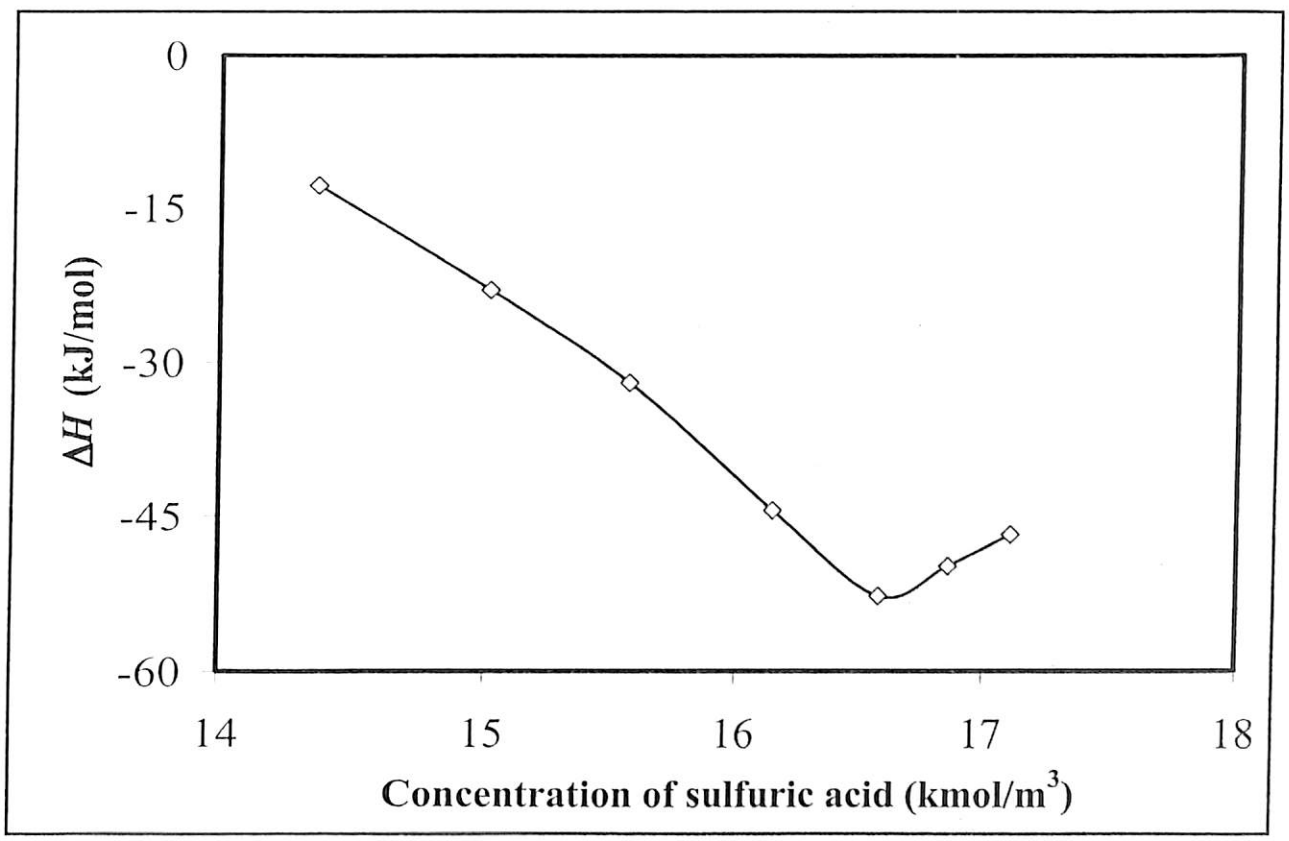


Figure 4.28 Variation of the enthalpy change for the reaction: $HNO_3 + H^+ \rightarrow NO_2^+ + H_2O$ with sulfuric acid concentration.

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[13,14]. The value of ΔH passed through a minimum and then increased at the high-concentrations of sulfuric acid. The values of ΔH agree well with the values reported in the literature [15].

4.3.5 Determination of reaction regime

The diffusivity of nitrobenzene (D_{NB}) in sulfuric acid was calculated by using the modified Wilke-Chang equation proposed by Perkins and Geankoplis [16].

$$D_{NB} = \frac{7.4\times10^{-15} T\left(\bar{\phi}\bar{M}\right)^{1/2}}{\mu v_m^{0.6}} \tag{4.25}$$

where μ is the viscosity of aqueous sulfuric acid, v_m is the molar volume of nitrobenzene at normal boiling point and T is the temperature. The quantity $\bar{\phi}\bar{M}$ is defined as [13],

$$\bar{\phi}\bar{M} = x_w\phi_w M_w + x_s\phi_s M_s \tag{4.26}$$

where x_w and x_s are the mole fractions, ϕ_w and ϕ_s are the association factors, and M_w and M_s are the molecular weights of water and sulfuric acid, respectively. The diffusivity of nitrobenzene at different sulfuric acid concentrations at 298 K and 313 K are presented in Table 4.4. A typical calculation involved in the determination of diffusivity of nitrobenzene in sulfuric acid is presented in the Section A.2.1 of Appendix A. It can be observed from Table 4.4 that the diffusivity decreased with increase in sulfuric acid concentration, passed through a minimum and then increased at the high-sulfuric acid concentrations. This happened because $\bar{\phi}\bar{M}$ increased with increase in sulfuric acid concentration whereas, the viscosity increased with sulfuric acid concentration up to 15.9 kmol/m^3, and then decreased.

The Hatta number was calculated by the following expression [17], using the values of k_L and $k_{2,exp}$ reported in the Sections 4.3.1 and 4.3.2, respectively.

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Table 4.4 Diffusivities of nitrobenzene in sulfuric acid and Hatta numbers

Reaction temperature (K)	Sulfuric acid concentration (kmol/m^3)	$D_{NB} \times 10^{10}$ (m^2/s)	Ha $\times 10^2$
298	14.1	0.82	0.24
	14.8	0.72	1.19
	15.3	0.70	1.99
	16.3	0.74	6.68
	16.7	0.78	11.25
	17.0	0.81	7.51
313	14.3	1.32	0.85
	14.8	1.24	2.01
	15.8	1.20	5.41
	16.1	1.22	9.81
	16.4	1.26	13.87
	17.1	1.37	9.38
	17.4	1.40	7.05

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$$\mathrm{Ha} = \frac{\sqrt{D_{\mathrm{NB}} k_{2,\mathrm{exp}} C^{0}_{\mathrm{HNO_3}}}}{k_L} \tag{4.27}$$

The Hatta number at different sulfuric acid concentrations at 298 K and 313 K are presented in Table 4.4. A typical calculation of Hatta number is shown in the Section A.2.2 of Appendix A. The values of Hatta number indicate that the reactions took place in the slow regime [17]. The Hatta number increased with the increase in sulfuric acid concentration, passed though a maximum and then decreased at the high-sulfuric acid concentrations. This can be explained as follows. The mass transfer coefficient (k_L) increased with increase in sulfuric acid concentration. The rate constant $(k_{2,\mathrm{exp}})$ increased with sulfuric acid concentration up to 16.7 kmol/m^3, and then decreased. The diffusivity decreased with increase in sulfuric acid concentration, passed through a minimum and then increased at the high sulfuric acid concentrations. However, the variation of diffusivity with sulfuric acid concentration was much less as compared to the variation of $k_{2,\mathrm{exp}}$ with sulfuric acid concentration. Therefore, the resulting effect was an increase in Hatta number followed by a decrease, as mentioned before. Hatta number was found to increase with the increase in temperature. The increase in Hatta number with increase in temperature can be attributed to the large increase in the reaction rate constant with temperature.

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Notation

A	interfacial area (m^2)
C_{HNO_3}	concentration of nitric acid in the aqueous phase (mol/m^3)
$C_{H_2SO_4}$	concentration of sulfuric acid ($kmol/m^3$)
C_{NB}	concentration of nitrobenzene in the aqueous phase in presence of reaction (mol/m^3)
$\overline{C}_{NB}$	equilibrium concentration of nitrobenzene in the aqueous phase (mol/m^3)
$C_{NO_2^+}$	concentration of the nitronium ion in the aqueous phase (mol/m^3)
C_{NB}^0	initial concentration of nitrobenzene in the aqueous phase (mol/m^3)
$C_{HNO_3}^0$	initial concentration of nitric acid in the aqueous phase (mol/m^3)
C_{NB}^a	concentration of nitrobenzene in the aqueous phase in absence of reaction (mol/m^3)
d	diameter of the reactor (m)
D_{NB}	diffusivity of nitrobenzene (m^2/s)
E_2	activation energy of nitration of nitrobenzene (J/mol)
E_2^*	activation energy for the attack of NO_2^+ on the nitrobenzene molecule (J/mol)
Ha	Hatta number
k_L	mass transfer coefficient (m/s)
$k_{2,exp}$	observed second-order rate constant ($m^3\,mol^{-1}\,s^{-1}$)
k_2'	thermodynamic parameter defined in equation (4.14)
$k_{2,0}$	frequency factor ($m^3\,mol^{-1}\,s^{-1}$)
$k_{2,0}^*$	frequency factor ($m^3\,mol^{-1}\,s^{-1}$)
$k_{2,cal}^*$	calculated second-order rate constant with respect to the actual concentration of the nitrating agent, NO_2^+ ($m^3\,mol^{-1}\,s^{-1}$)
$k_{2,exp}^*$	observed second-order rate constant with respect to actual concentration of the

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	nitrating agent, NO_2^+ ($m^3\ mol^{-1}\ s^{-1}$)
M	initial molar ratio of nitric acid and nitrobenzene
$\bar{M}$	molecular weight of aqueous sulfuric acid (kg/mol)
M_c	activity coefficient function
M_{NB}	molecular weight of nitrobenzene (kg/mol)
M_s	molecular weight of sulfuric acid (kg/mol)
M_w	molecular weight of water (kg/mol)
n	thermodynamic parameter defined in equation (4.15)
Rate	rate of reaction (mol $m^{-3}\ s^{-1}$)
R	universal gas constant (J $mol^{-1}\ K^{-1}$)
t	time (s)
T	temperature (K)
v_m	molar volume of nitrobenzene at its normal boiling point (cm^3/mol)
V_0	initial volume of aqueous phase (m^3)
V_∞	volume of the aqueous phase constituted of nitrobenzene and sulfuric acid under equilibrium conditions (m^3)
V_a	volume of aqueous phase (m^3)
x_s	mole fraction of sulfuric acid
x_w	mole fraction of water
X_{NB}	conversion of nitrobenzene

Greek letters

γ_{NB}	activity coefficient of nitrobenzene
$\gamma_{NO_2^+}$	activity coefficient of nitronium ion
$\gamma^{\#}$	activity coefficient of the transition-state intermediate
ΔH	enthalpy change (J/mol)
λ	wavelength of detection in HPLC (nm)

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λ_{max}	wavelength at which the maximum absorption occurs (nm)
μ	viscosity of aqueous sulfuric acid (Pa s)
ρ_{NB}	density of nitrobenzene (kg/m^3)
$\overline{\phi}$	association factor of aqueous sulfuric acid
ϕ_s	association factor of sulfuric acid
ϕ_w	association factor of water

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CHAPTER 5

MASS TRANSFER WITH CHEMICAL REACTION IN NITRATION OF NITROBENZENE

This chapter presents various features of heterogeneous nitration of nitrobenzene in concentrated sulfuric acid media. Heterogeneous two-phase nitration of nitrobenzene in mixed acid was carried out. A model was developed for simultaneous mass transfer with chemical reaction to predict the concentration profiles of the reactants and products in the reactor. The yields of the products were determined at various sulfuric acid concentrations at room temperature and moderately higher temperatures. The percentage of the three isomers of dinitrobenzene in the product was also determined at these sulfuric acid concentrations at these temperatures.

5.1 Introduction

As mentioned in earlier chapters, the nitration reaction takes place in the aqueous phase where the mixed acid produces nitronium ion. The nitrobenzene molecule diffuses into the aqueous phase and thereafter the electrophilic substitution takes place in that phase. In industrial practice, nitration of nitrobenzene is carried out under heterogeneous conditions employing high temperature and high stirring speed. It has been discussed in Chapter 4 that the rate of nitration of nitrobenzene is very sensitive to the concentration of sulfuric acid, and a high rate can be achieved at a low stirring speed using a high-concentration of sulfuric acid. In this chapter, a model has been developed incorporating the mass transfer of nitrobenzene from the organic phase to the aqueous phase, and simultaneous chemical reaction occurring in

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the aqueous phase. The concentration profiles of the reactants and the products as well as the conversion profiles of the reactants in the aqueous phase during nitration can be predicted from this model. The yields of the product have been determined at different sulfuric acid concentrations at three temperatures. The variation of isomer distribution with sulfuric acid concentration and temperature was analyzed. It has been found that more than 90% conversion of nitrobenzene is possible at high-sulfuric acid concentrations resulting in high yield of the product even at moderate temperatures and at low-speeds of stirring.

5.2 Experimental

5.2.1 Materials

Nitrobenzene (99% purity), sulfuric acid (18.3 kmol/m^3) and nitric acid (15.5 kmol/m^3) were procured from Merck (India). Standard organic samples, 1,2-dinitrobenzene (99% purity), 1,3-dinitrobenzene (97% purity) and 1,4-dinitrobenzene (98% purity) were procured from Alfa Aesar (India). HPLC-grade methanol, water, acetonitrile, pentane, dichloromethane and 2-propanol were procured from Merck (India). Sulfuric acid solutions of lower concentrations were prepared by diluting the concentrated acid (18.3 kmol/m^3) with water. The desired concentrations of aqueous sulfuric acid were prepared by acid-base titration using aqueous NaOH that was standardized with oxalic acid. The water used in this study was purified from a Millipore® water purification system.

5.2.2 Apparatus and procedure

5.2.2.1 Heterogeneous nitration of nitrobenzene

Heterogeneous liquid–liquid nitration of nitrobenzene was carried out in batch mode using a glass reactor placed in a water bath. The temperature of the bath was maintained by a

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thermostatic water circulator. The glass reactor was described in Section 4.2.2.1. A known volume of mixed acid was prepared by mixing nitric acid, sulfuric acid and water in the required proportion. First the mixed acid was charged into the reactor. Thereafter a known amount of pure nitrobenzene was poured carefully on top of the aqueous phase. Nitric acid and nitrobenzene were charged to the reactor in 1 : 3 mole ratio. This ensured that the formation of solid dinitrobenzene isomers in the aqueous phase was small. Agitation of the two phases was then started and maintained at 2π rad/s under flat-interface condition. The reactions were carried out for 30 minutes. The samples from the aqueous as well as the organic phases were collected at definite time intervals. The reaction was quenched by diluting the collected sample into a large volume of methanol followed by rapid chilling. The concentrations of the reactant (i.e., nitrobenzene) in the aqueous phase, and the product (i.e., the dinitrobenzene isomers) in both phases were analyzed by HPLC as described in Section 4.2.2.2. Reactions were carried out at two temperatures, viz. 298 K and 313 K (because the values of k_L are available at these two temperatures). The range of the sulfuric acid concentration employed was 14.2 kmol/m^3 to 15.7 kmol/m^3.

5.2.2.2 Determination of the yield of product

The total yields of the dinitrobenzene isomers were determined in the glass reactor. The molar ratio of sulfuric acid : nitrobenzene : nitric acid was kept constant at 4:1:1. The aqueous phase was prepared by mixing nitric acid, sulfuric acid and water in the required proportion. Pure nitrobenzene was charged into the reactor on top of the aqueous phase. The two phases were stirred at 2π rad/s. The reactions were carried out for one hour. The solid product and the unreacted reactants were removed immediately from the reactor, diluted with water and chilled with ice to quench any further reaction. The solid product was filtered out and

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repeatedly washed with water to remove the trace amounts of the reactants. Then, it was dried *in vacuo* and the amount of product was determined gravimetrically. The yields of the dinitrobenzene isomers were determined at different sulfuric acid concentrations in the range from 14.1 kmol/m^3 to 17.1 kmol/m^3 at 298 K, 313 K and 323 K.

5.2.2.3 Determination of distribution of isomers of dinitrobenzene

The amounts of the three isomers of dinitrobenzene were determined at different sulfuric acid concentrations at the three temperatures, viz. 298 K, 313 K and 323 K. The solid product was thoroughly triturated in a mortar and the triturated mixture was ground in a ball mill to obtain a uniform mixture of the isomers. The isomer distribution was analyzed by HPLC by adapting the method given in literature [1]. The procedure was as follows. A small amount of the reaction product (after triturating and grinding) was dissolved in 2-propanol and diluted with dichloromethane. The solution was then analyzed by normal-phase HPLC (column: Brownlee Analytical Silica 5 μm (Perkin-Elmer), detector: UV, $\lambda = 254$ nm). The mobile phase was constituted of a mixture of pentane (99.5 %) and 2-propanol (0.5 %), and dichloromethane in 4:1 volumetric ratio. Its flow rate was maintained at 11.67×10^{-3} cm^3/s. A typical absorbance versus time chromatogram of the separation of nitrobenzene, 1,2-dinitrobenzene, 1,3-dinitrobenzene and 1,4-dinitrobenzene by HPLC is shown in Figure 5.1. It is observed from the chromatogram that the separation was good with moderate retention times. The retention times for nitrobenzene, 1,4-dinitrobenzene, 1,3-dinitrobenzene and 1,2-dinitrobenzene were 305 s, 350 s, 406 s and 475 s, respectively.

Standard solutions of nitrobenzene and dinitrobenzene isomers at different concentrations were prepared in 2-propanol and diluted with dichloromethane. Their chromatograms were taken in HPLC employing the method described above. The calibration

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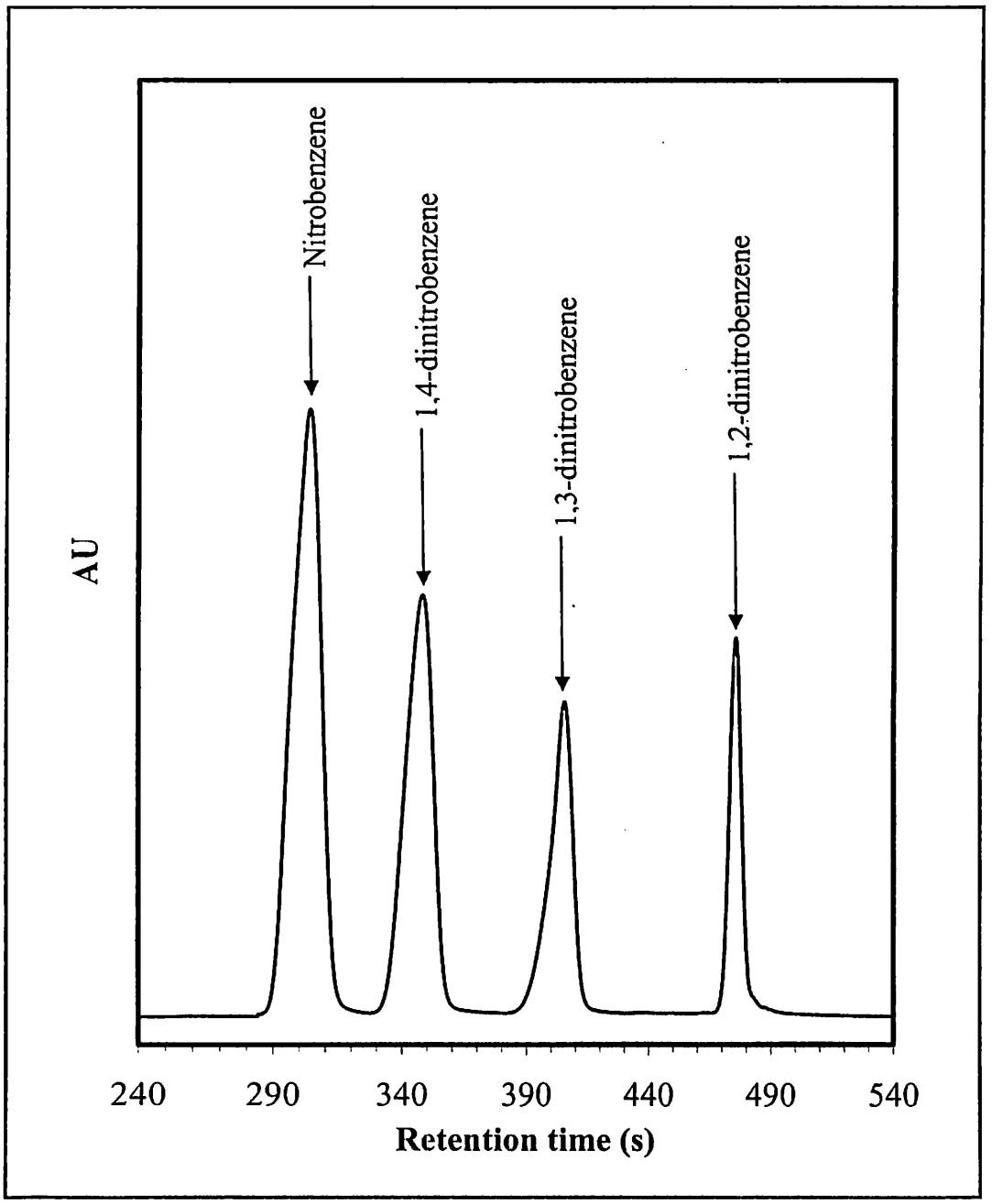


Figure 5.1 Chromatograms of nitrobenzene and dinitrobenzene isomers by normal phase liquid chromatography.

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plots for nitrobenzene, 1,2-dinitrobenzene, 1,3-dinitrobenzene and 1,4-dinitrobenzene are shown in Figures 5.2 – 5.5, respectively. The plots of area versus concentration were linear for a wide range of concentrations of nitrobenzene and the dinitrobenzene isomers. This liquid chromatographic method was very proficient and the precision of the determination of concentrations was ±1% [see equation (3.1)]. All these experiments were repeated at least three times to check their reproducibility. The results were found to be highly reproducible. A typical calculation of determination of distribution of isomers of dinitrobenzene in the product is presented in the Section A.3 of Appendix A.

5.3 Results and discussion

5.3.1 Modeling of mass transfer with chemical reaction

A model has been developed for the nitration process employing mass balance in the aqueous phase by taking into account the amount of nitrobenzene transferred through the interface, the amount of nitrobenzene reacted, and its accumulation. This model will be useful to predict the concentration profiles of the reactants and the products as well as the conversion profiles of the reactants in the aqueous phase during nitration. It was confirmed from the values of the Hatta number that the reaction takes place in the slow regime. This enables us to use the mass transfer coefficients obtained in absence of chemical reaction without a significant loss in accuracy. The model presented here is based on a few assumptions. The aqueous phase is assumed to be homogeneous. The mass transfer is assumed to occur from the organic phase to the aqueous phase, and the reverse is not significant. The change in volume of the aqueous phase occurs solely due to the transfer of nitrobenzene into the aqueous phase. The solid product present in the aqueous phase is assumed to have negligible effect on the volume change. The change in volume due to the formation of water and the

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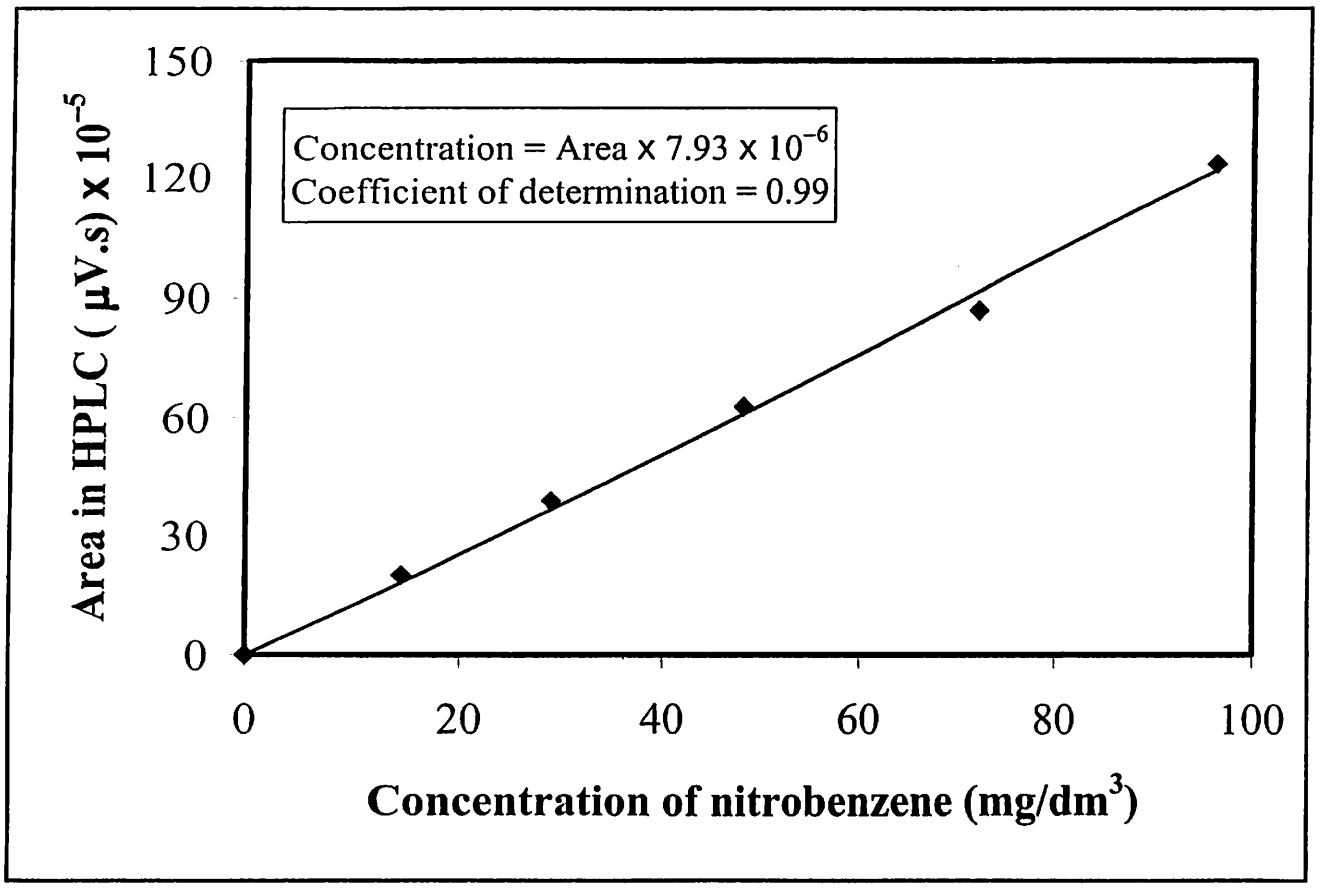


Figure 5.2 Calibration curve for nitrobenzene by normal phase liquid chromatography.

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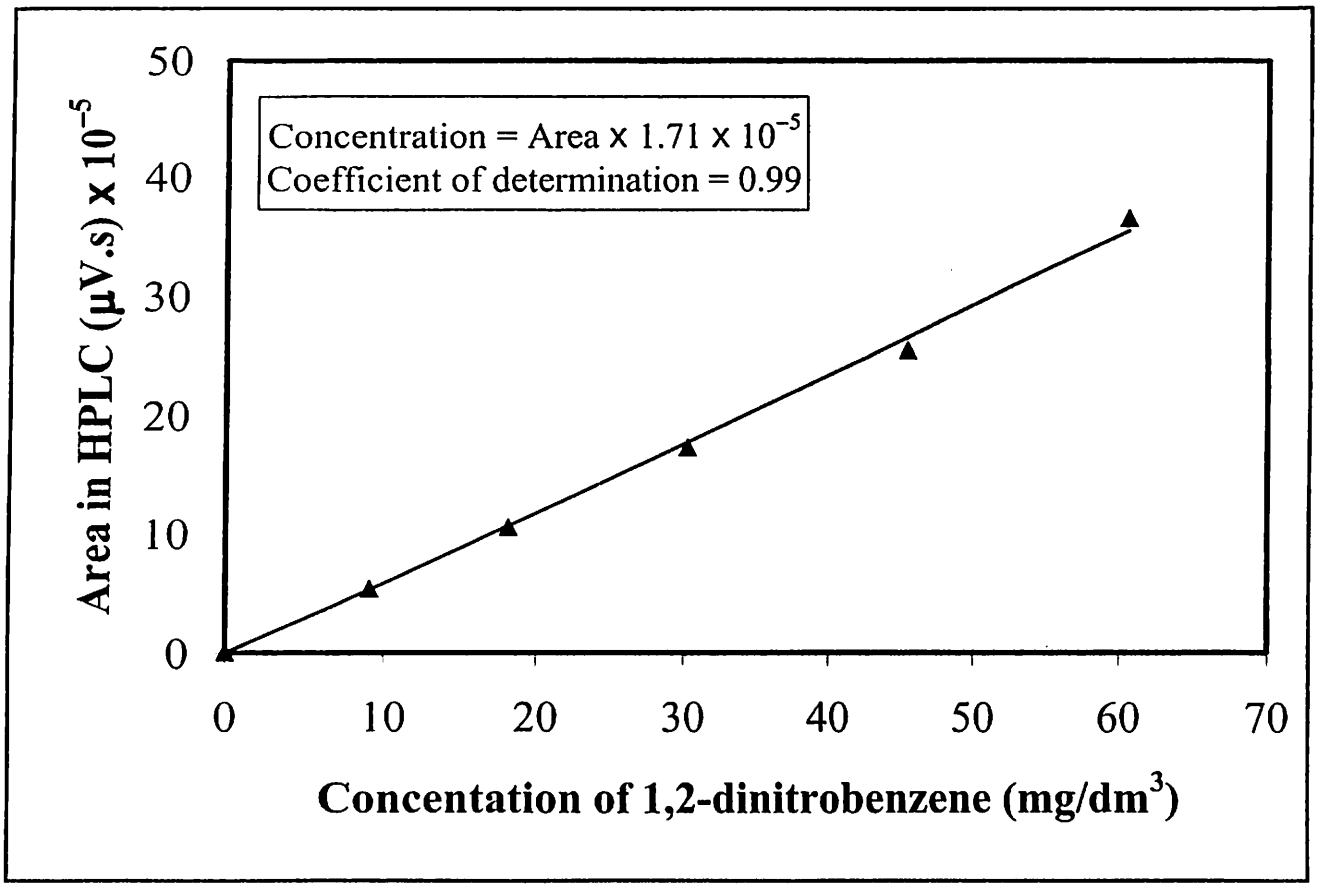


Figure 5.3 Calibration curve for 1,2-dinitrobenzene by normal phase liquid chromatography.

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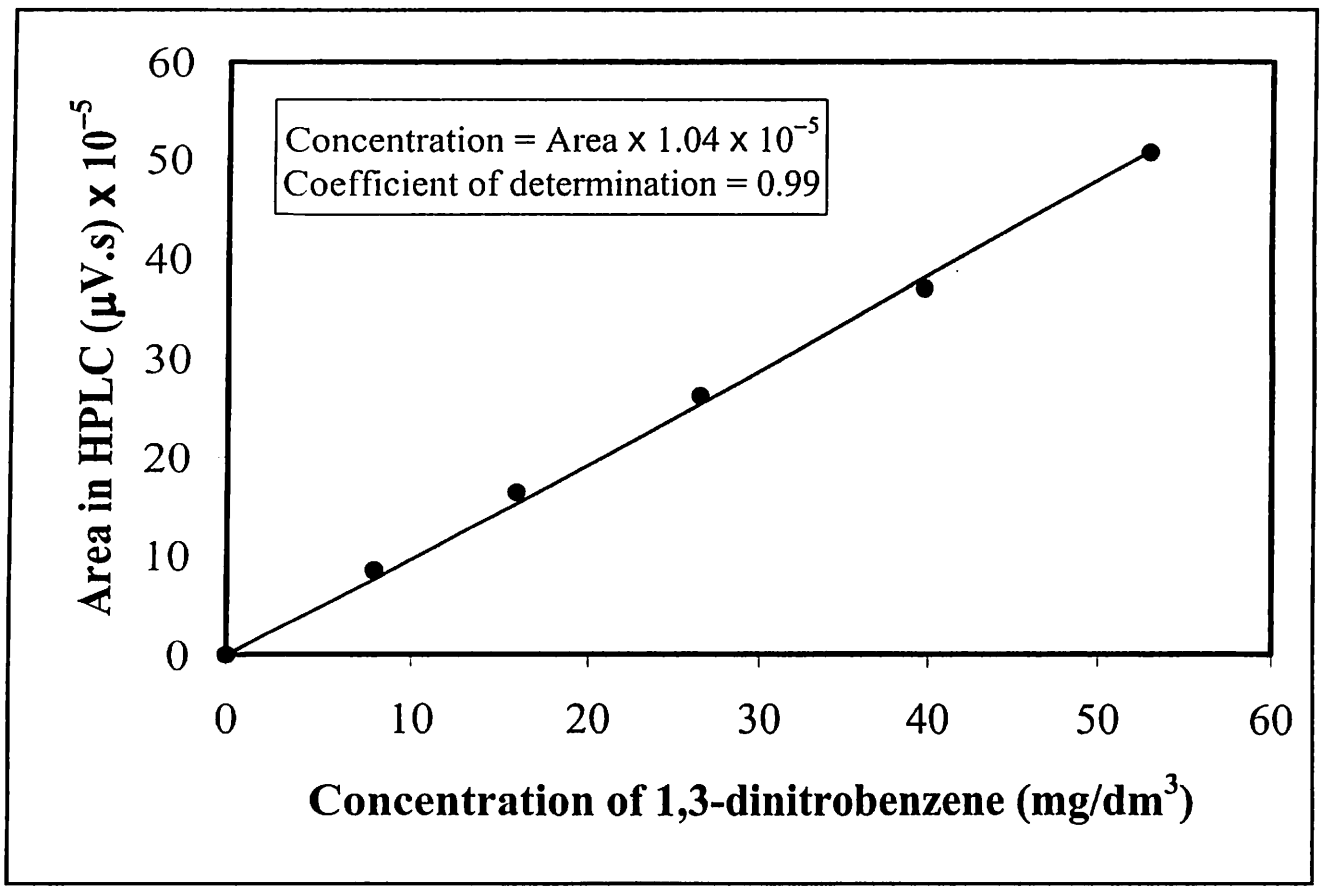


Figure 5.4 Calibration curve for 1,3-dinitrobenzene by normal phase liquid chromatography.

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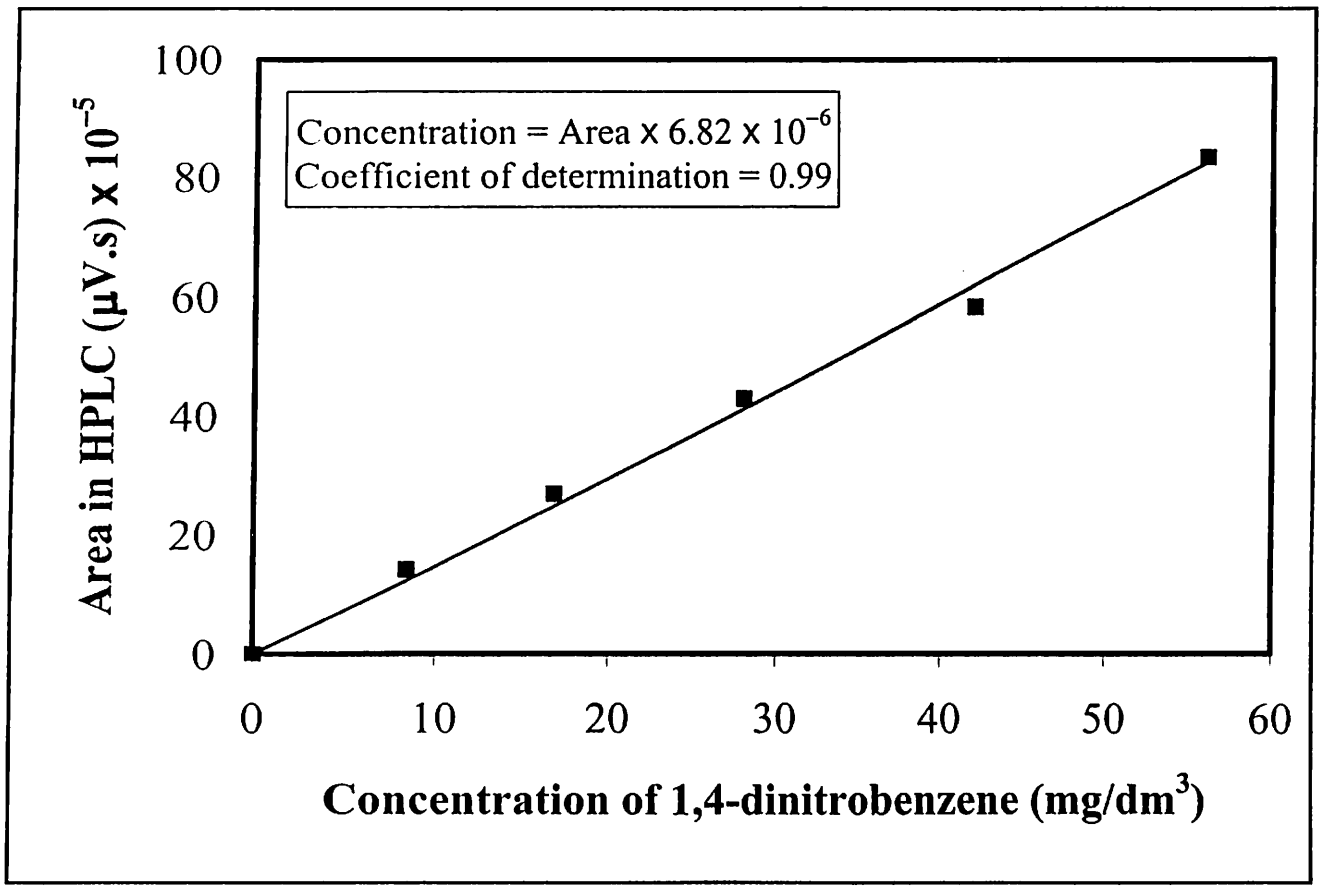


Figure 5.5 Calibration curve for 1,4-dinitrobenzene by normal phase liquid chromatography.

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consumption of nitric acid is assumed to be negligible. It is further assumed that the volume change of mixing is negligible. The equilibrium concentration of nitrobenzene in the aqueous phase in absence of chemical reaction is assumed to remain the same in the reaction mixture. Therefore, it is apparent that this model can be expected to be sound up to moderately-high sulfuric acid concentrations.

The material balance for nitrobenzene in the aqueous phase is given by,

$$\frac{d}{dt}\left(V_R C_{NB}\right) = \frac{k_L A}{V_R}\left(V_\infty \bar{C}_{NB} - V_R C_{NB}\right) - k_{2,exp} C_{HNO_3} C_{NB} V_R \qquad (5.1)$$

where V_R is the volume of the aqueous phase, V_∞ is the volume of the equilibrated mixture of nitrobenzene and sulfuric acid, k_L is the mass transfer coefficient, A is the interfacial area ($=\pi d^2/4$, where d is the diameter of the reactor), $\bar{C}_{NB}$ is the equilibrium concentration of nitrobenzene in the aqueous phase, C_{NB} is the concentration nitrobenzene in the aqueous phase, C_{HNO_3} is the concentration nitric acid in the aqueous phase, and $k_{2,exp}$ is the observed second-order rate constant. Equation (5.1) can be rearranged as,

$$V_R \frac{dC_{NB}}{dt} + C_{NB} \frac{dV_R}{dt} = \frac{k_L A}{V_R}\left(V_\infty \bar{C}_{NB} - V_R C_{NB}\right) - k_{2,exp} C_{HNO_3} C_{NB} V_R \qquad (5.2)$$

Rearranging and simplifying equation (5.2) we get,

$$\frac{dC_{NB}}{dt} = k_L A \bar{C}_{NB}\left(\frac{V_\infty}{V_R^2}\right) - \left(\frac{k_L A}{V_R} + k_{2,exp} C_{HNO_3}\right) C_{NB} - \frac{C_{NB}}{V_R}\frac{dV_R}{dt} \qquad (5.3)$$

As the change in the volume of the aqueous phase occurs only due to the transfer of nitrobenzene into the aqueous phase, V_R can be expressed as,

$$V_R = V_0 + V_R C_{NB} M_{NB}/\rho_{NB} \qquad (5.4)$$

where V_0 is the initial volume of the aqueous phase, M_{NB} is the molecular weight of

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nitrobenzene and ρ_{NB} is its density. By rearranging equation (5.4), V_R can be expressed as

$$V_R = \frac{V_0}{(1 - C_{NB} M_{NB}/\rho_{NB})} \tag{5.5}$$

Differentiating V_R with respect to t we get,

$$\frac{dV_R}{dt} = \frac{V_R M_{NB}/\rho_{NB}}{(1 - C_{NB} M_{NB}/\rho_{NB})} \frac{dC_{NB}}{dt} \tag{5.6}$$

Inserting the values of V_R and $\frac{dV_R}{dt}$ in equation (5.3) we get,

$$\frac{dC_{NB}}{dt} = k_L A \bar{C}_{NB} \left(\frac{V_\infty}{V_0^2}\right)(1 - C_{NB} M_{NB}/\rho_{NB})^2 - \left[\frac{k_L A (1 - C_{NB} M_{NB}/\rho_{NB})}{V_0} + k_{2,exp} C_{HNO_3}\right] C_{NB} - \frac{C_{NB} M_{NB}/\rho_{NB}}{(1 - C_{NB} M_{NB}/\rho_{NB})} \frac{dC_{NB}}{dt} \tag{5.7}$$

Rearranging and simplifying equation (5.7) we get,

$$\frac{dC_{NB}}{dt} = k_L A \bar{C}_{NB} \left(\frac{V_\infty}{V_0^2}\right)(1 - C_{NB} M_{NB}/\rho_{NB})^3 - \left[\frac{k_L A (1 - C_{NB} M_{NB}/\rho_{NB})}{V_0} + k_{2,exp} C_{HNO_3}\right](1 - C_{NB} M_{NB}/\rho_B) C_{NB} \tag{5.8}$$

The material balance for nitric acid in the aqueous phase is given by,

$$\frac{d}{dt}(V_R C_{HNO_3}) = -k_{2,exp} C_{HNO_3} C_{NB} V_R \tag{5.9}$$

Equation (5.9) can be written as,

$$V_R \frac{dC_{HNO_3}}{dt} + C_{HNO_3} \frac{dV_R}{dt} = -k_{2,exp} C_{HNO_3} C_{NB} V_R \tag{5.10}$$

Rearranging equation (5.10) we get,

$$\frac{dC_{HNO_3}}{dt} = -k_{2,exp} C_{HNO_3} C_{NB} - \frac{C_{HNO_3}}{V_R} \frac{dV_R}{dt} \tag{5.11}$$

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Substituting the values of V_R and $\frac{dV_R}{dt}$ from equations (5.5) and (5.6) in equation (5.11) we get,

$$\frac{dC_{HNO_3}}{dt} = -k_{2,exp} C_{HNO_3} C_{NB} - \frac{C_{HNO_3} M_{NB}/\rho_{NB}}{(1 - C_{NB} M_{NB}/\rho_{NB})} \frac{dC_{NB}}{dt} \tag{5.12}$$

The material balance for dinitrobenzene isomers in the aqueous phase is given by,

$$\frac{d}{dt}(V_R C_{DNB}) = k_{2,exp} C_{HNO_3} C_{NB} V_R \tag{5.13}$$

where C_{DNB} is the concentration of the dinitrobenzene isomers in the reactor. Upon rearrangement of equation (5.13) we get,

$$\frac{dC_{DNB}}{dt} = k_{2,exp} C_{HNO_3} C_{NB} - \frac{C_{DNB}}{V_R} \frac{dV_R}{dt} \tag{5.14}$$

Inserting the values of V_R and $\frac{dV_R}{dt}$ in equation (5.14) we get,

$$\frac{dC_{DNB}}{dt} = k_{2,exp} C_{HNO_3} C_{NB} - \frac{C_{DNB} M_{NB}/\rho_{NB}}{(1 - C_{NB} M_{NB}/\rho_{NB})} \frac{dC_{NB}}{dt} \tag{5.15}$$

Equations (5.8), (5.12) and (5.15) were simultaneously solved by the Runge-Kutta-Gill method using the initial conditions: $C_{NB} = 0$, $C_{DNB} = 0$ and $C_{HNO_3} = C^0_{HNO_3}$ at $t = 0$. The computer program to solve these equations and the computational output are given in the Section B.2 of Appendix B. The values of $\overline{C}_{NB}$, $k_{2,exp}$ and k_L reported in the Chapters 3 and 4 were used. The fractional conversion of nitric acid $\left(X_{HNO_3}\right)$ was calculated by the following equation.

$$X_{HNO_3} = 1 - \frac{V_R C_{HNO_3}}{V_0 C^0_{HNO_3}} \tag{5.16}$$

where $C^0_{HNO_3}$ is the initial concentration of nitric acid.

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5.3.2 Studies on heterogeneous nitration of nitrobenzene

The concentration profiles of nitrobenzene in the aqueous phase at 298 K are shown in Figure 5.6. The concentration of nitrobenzene in the aqueous phase increased with time. Transfer of nitrobenzene from the organic to the aqueous phase, and its reaction with nitric acid took place simultaneously. At low concentrations of sulfuric acid, the reaction rate was slow. Therefore the concentration of nitrobenzene increased steadily with time. However, the concentration of nitrobenzene in the aqueous phase decreased after some time at 15.7 kmol/m^3 sulfuric acid due to the high reaction rate. The concentration profiles of nitric acid in the aqueous phase at 298 K are shown in Figure 5.7. It is evident from this figure that the reaction rate was high at the 15.7 kmol/m^3 concentration of sulfuric acid. The concentration profiles of the product (i.e., dinitrobenzene isomers) are depicted in Figure 5.8. The conversion of nitric acid during the reaction is shown in Figure 5.9. The conversion of nitric acid was calculated from the amount of the main product (i.e., 1,3-dinitrobenzene) formed, and its percentage in the mixture of the three isomers (see Section 5.3.4). From Figure 5.9, it is evident that the conversion increased with the increase in concentration of sulfuric acid. This is due to the increase in the concentration of nitrobenzene in the aqueous phase. In this reaction, the ratio of nitric acid and nitrobenzene charged to the reactor was 1:3. However, the concentrations of nitric acid and nitrobenzene in the aqueous phase (where the reaction took place) were comparable, especially in the low range of acid concentrations. Therefore, the rate of reaction depended on the concentrations of both nitric acid and nitrobenzene.

Figures 5.6 – 5.9 also show the comparison between the experimental and the theoretical concentration profiles of the reactants and the product isomers at different sulfuric acid concentrations at 298 K. The theoretical concentration profiles were obtained from the model described in Section 5.3.1. It is seen from these figures that the theoretical concentration and

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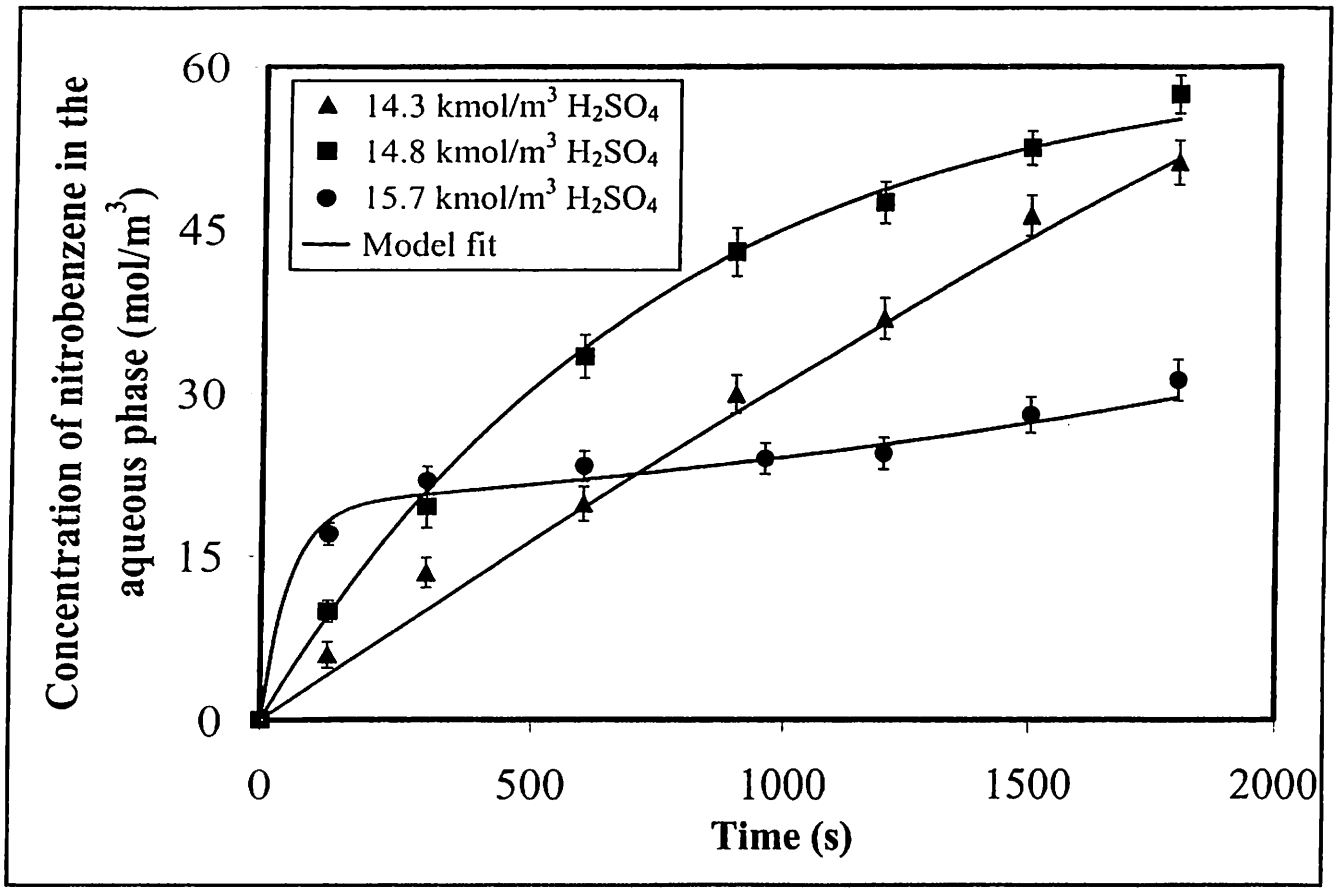


Figure 5.6 Concentration profiles of nitrobenzene in the aqueous phase at different sulfuric acid concentrations at 298 K.

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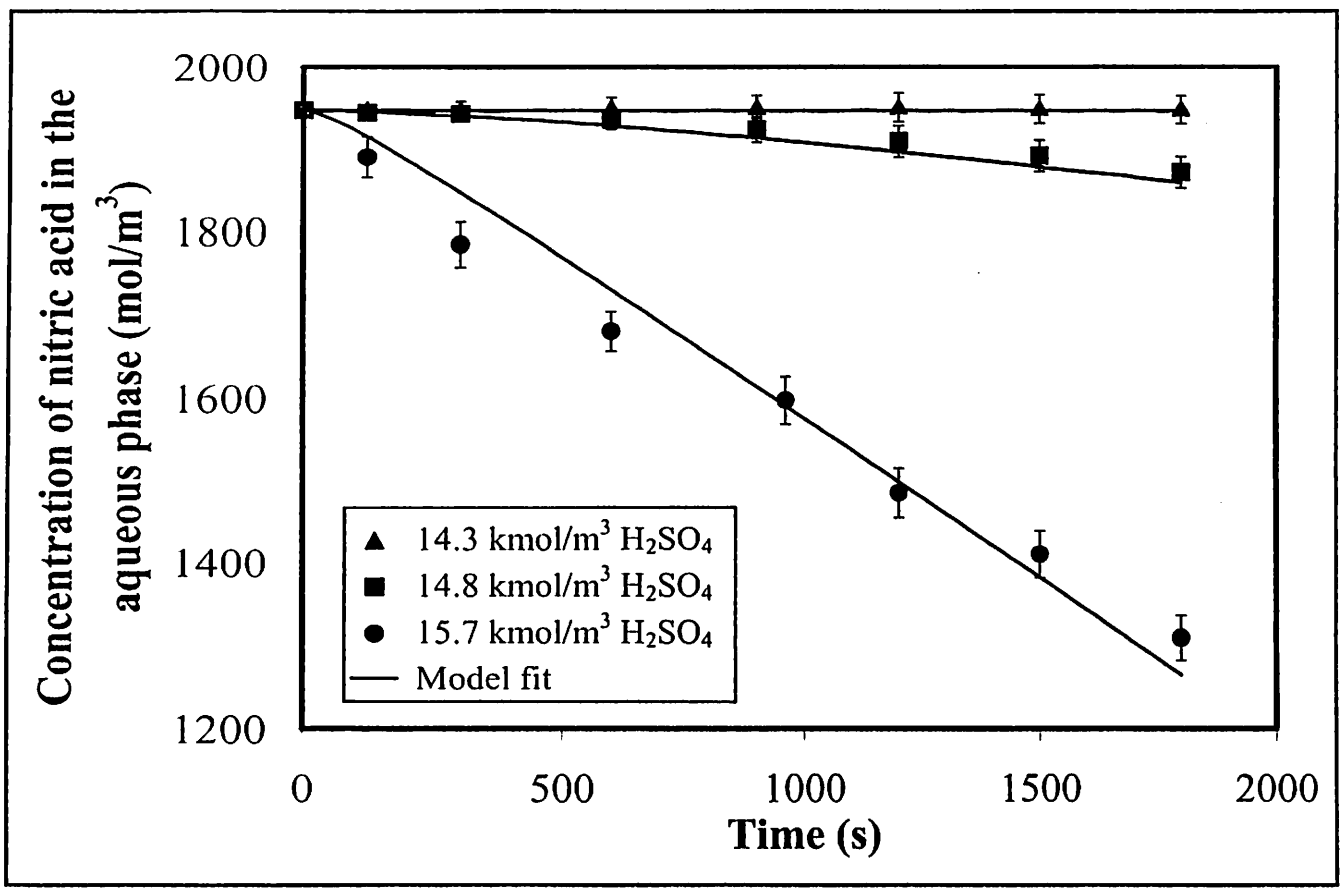


Figure 5.7 Concentration profiles of nitric acid in the aqueous phase at different sulfuric acid concentrations at 298 K.

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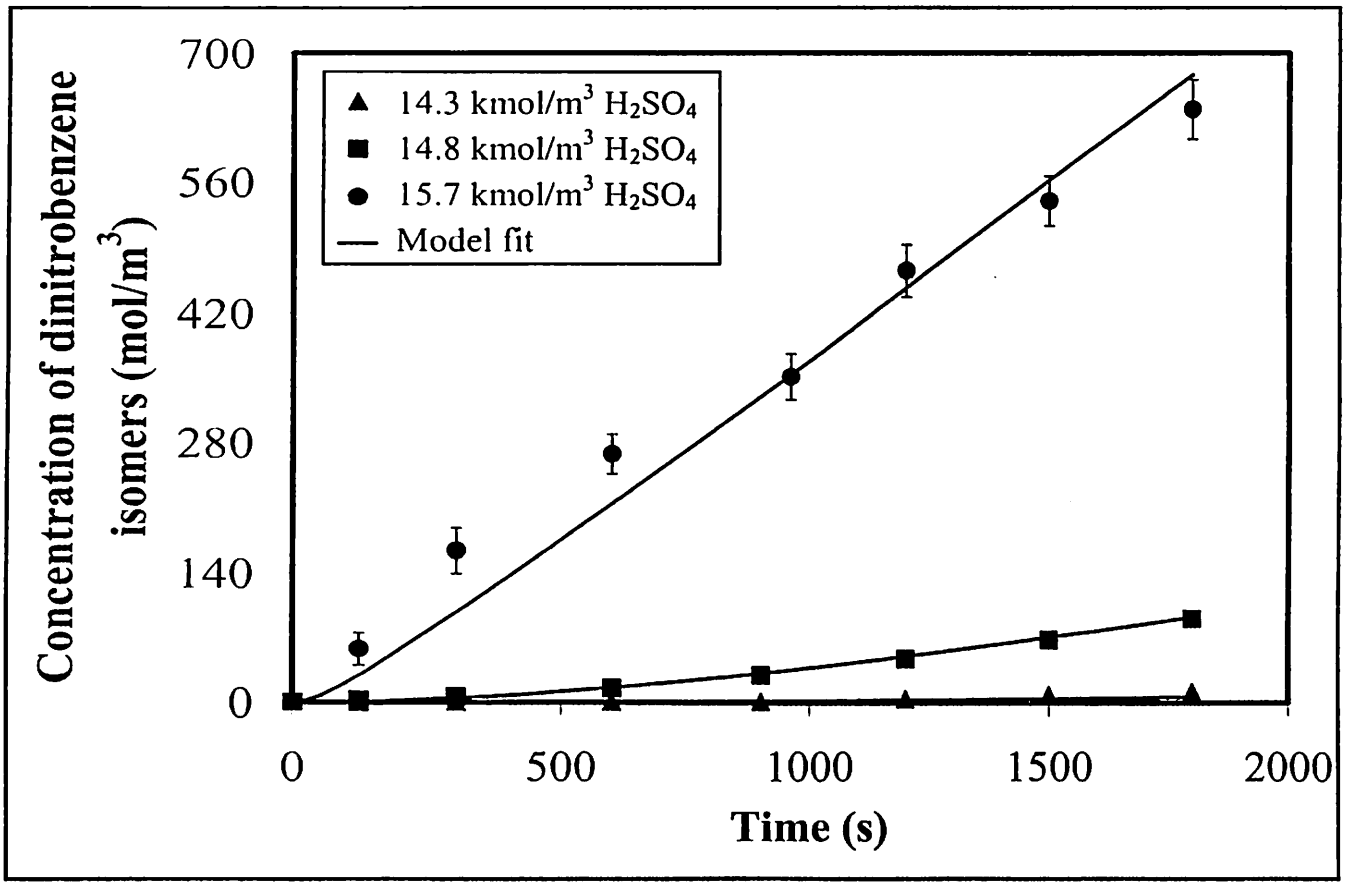


Figure 5.8 Concentration profiles of the dinitrobenzene isomers at different sulfuric acid concentrations at 298 K.

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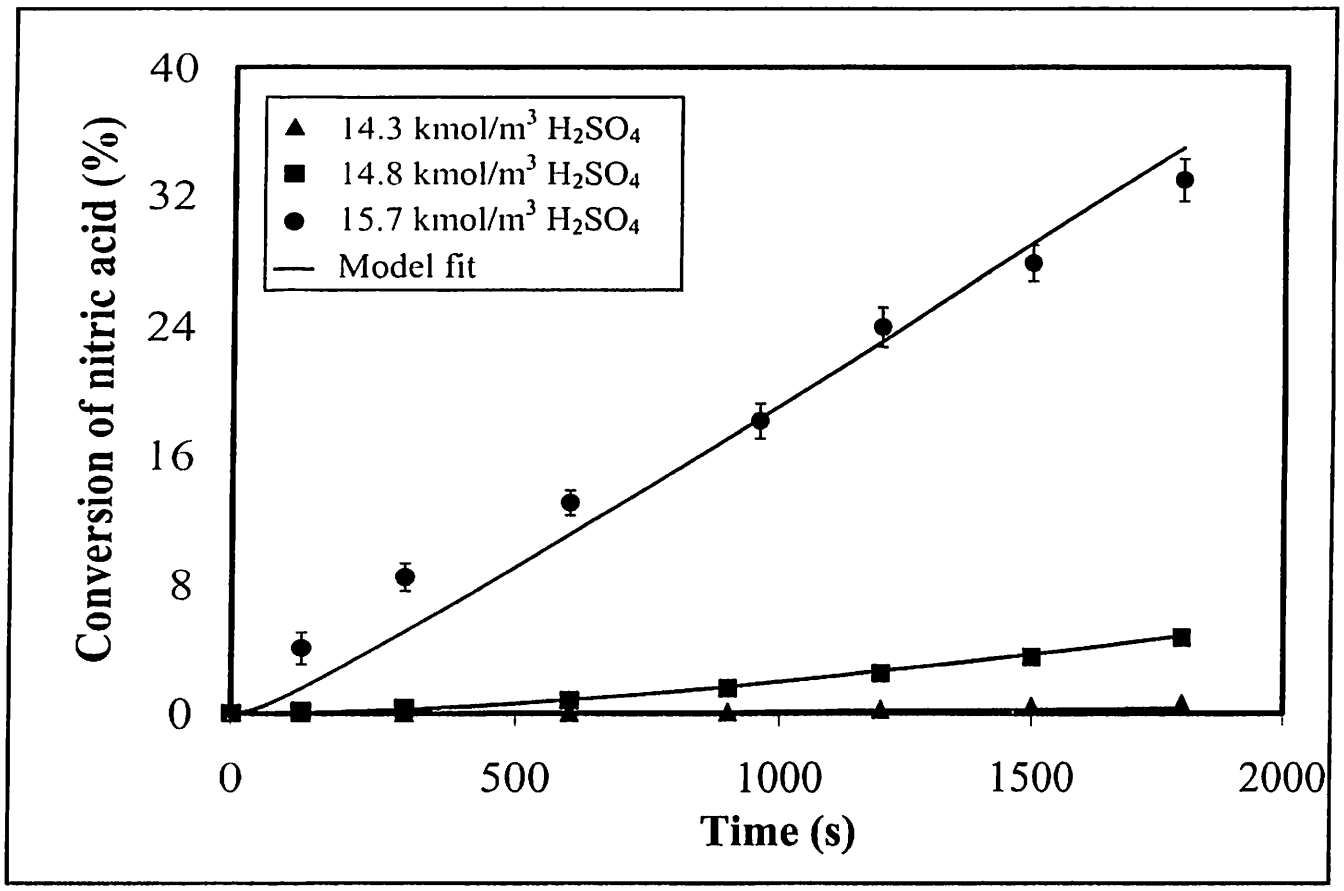


Figure 5.9 Conversion profiles of nitric acid at different sulfuric acid concentrations at 298 K.

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conversion profiles were in good agreement with the experimental data. The deviation of the experimental data from the profiles in the initial period is likely due to the turbulence created in the aqueous phase when the agitation was started.

The concentration profiles of nitrobenzene in the aqueous phase at 313 K are depicted in Figure 5.10. The concentration profiles of nitric acid and the dinitrobenzene isomers are shown in Figures 5.11 and 5.12, respectively. It is evident from these figures that at the high temperature, the rate of reaction was high and amount of product formed increased after the same reaction time. The conversion of nitric acid during the reaction at 313 K is shown in Figure 5.13. It is observed from the figure that the conversion increased with the increase in sulfuric acid concentration, and also with the temperature. The high-concentration of nitrobenzene in the aqueous phase and the high-concentration of the NO_2^+ ion in the same phase are believed to be the main factors behind this significant increase in the conversion of the nitric acid.

Figures 5.10 – 5.13 also depict the comparison between the experimental and the theoretical concentration profiles of the reactants and the product at different sulfuric acid concentrations at 313 K. It is seen from these figures that the experimental concentration and conversion profiles matched well with the prediction of the model.

5.3.3 Determination of yield

The net yields of the three isomers of dinitrobenzene at various concentrations of sulfuric acid at different temperatures are presented in Figure 5.14. The yields were determined after one hour of reaction. It can be observed from the figure that the amount of product formed at 14.1 kmol/m^3 and 14.9 kmol/m^3 sulfuric acid concentrations was very small. However, the yield increased with the increase in concentration of sulfuric acid. The

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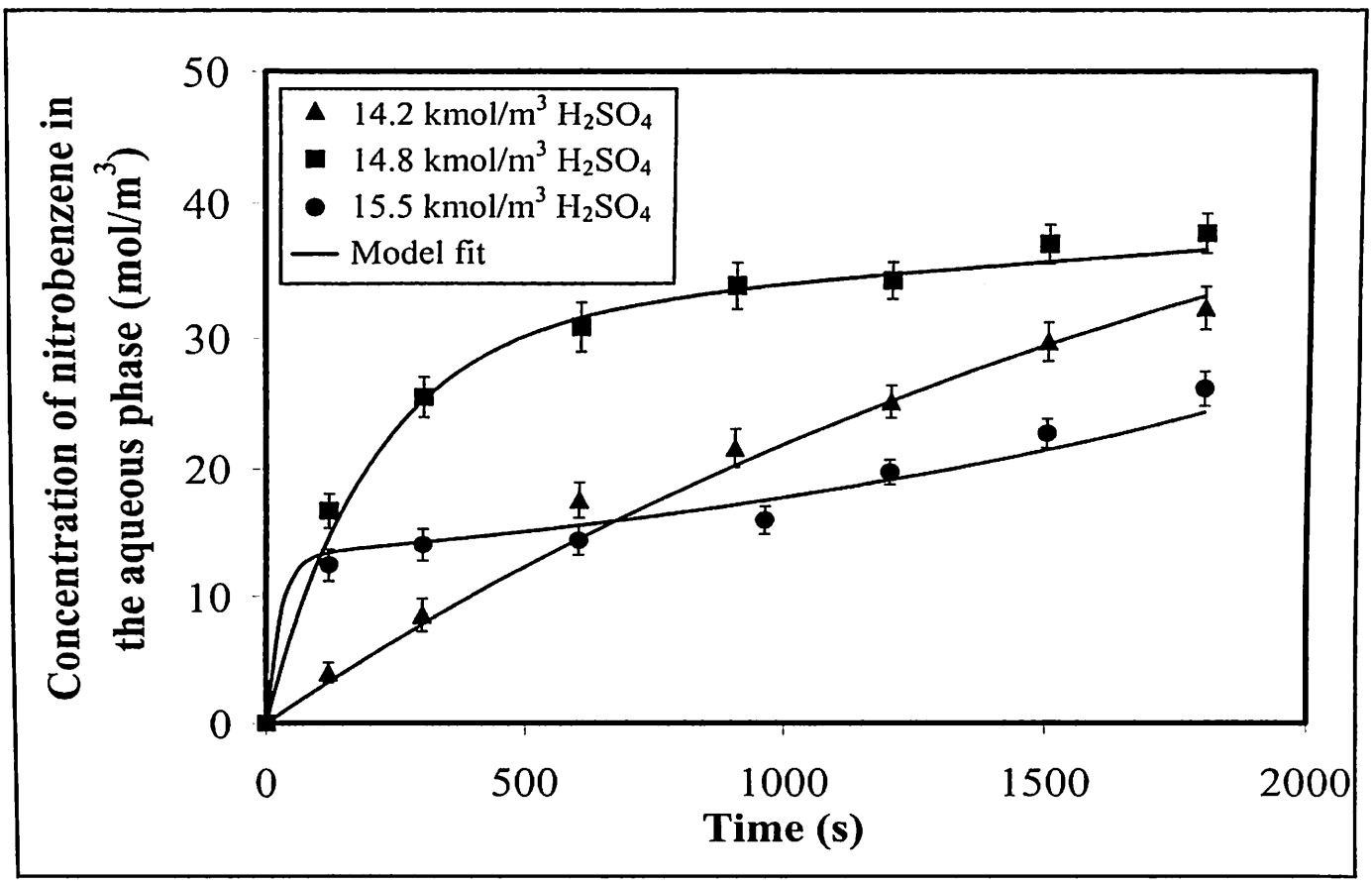


Figure 5.10 Concentration profiles of nitrobenzene in the aqueous phase at different sulfuric acid concentrations at 313 K.

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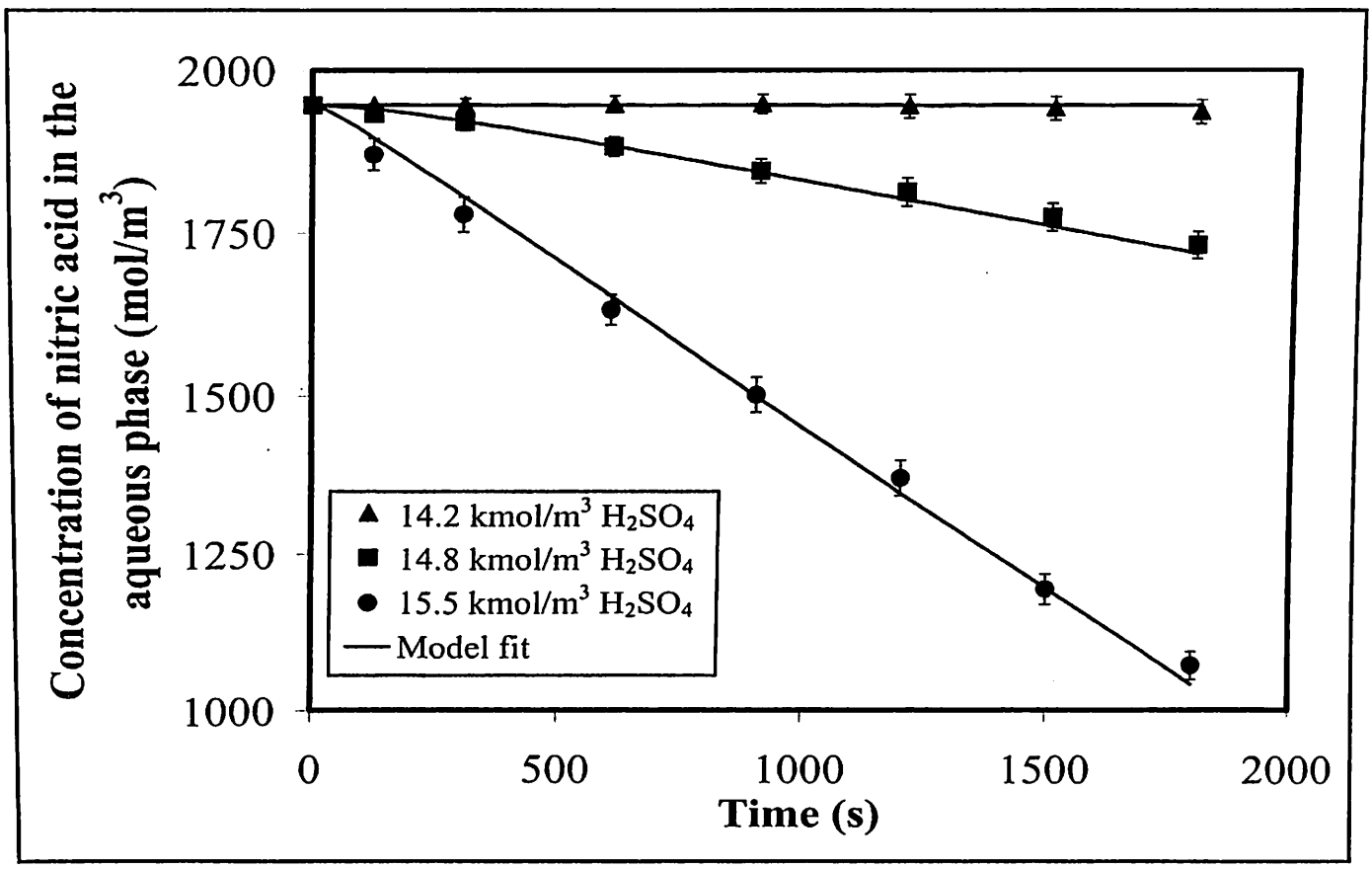


Figure 5.11 Concentration profiles of nitric acid in the aqueous phase at different sulfuric acid concentrations at 313 K.

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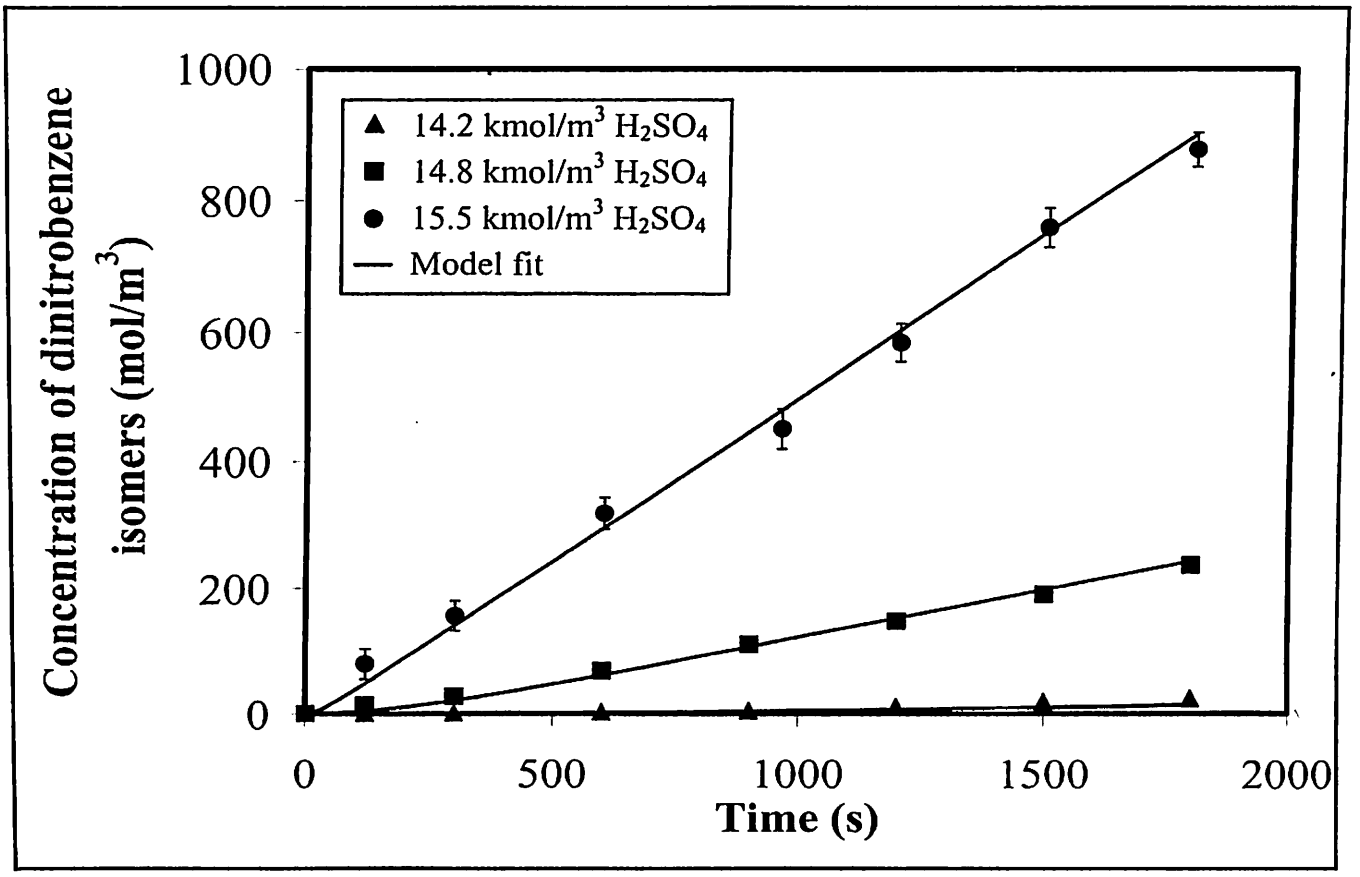


Figure 5.12 Concentration profiles of the dinitrobenzene isomers at different sulfuric acid concentrations at 313 K.

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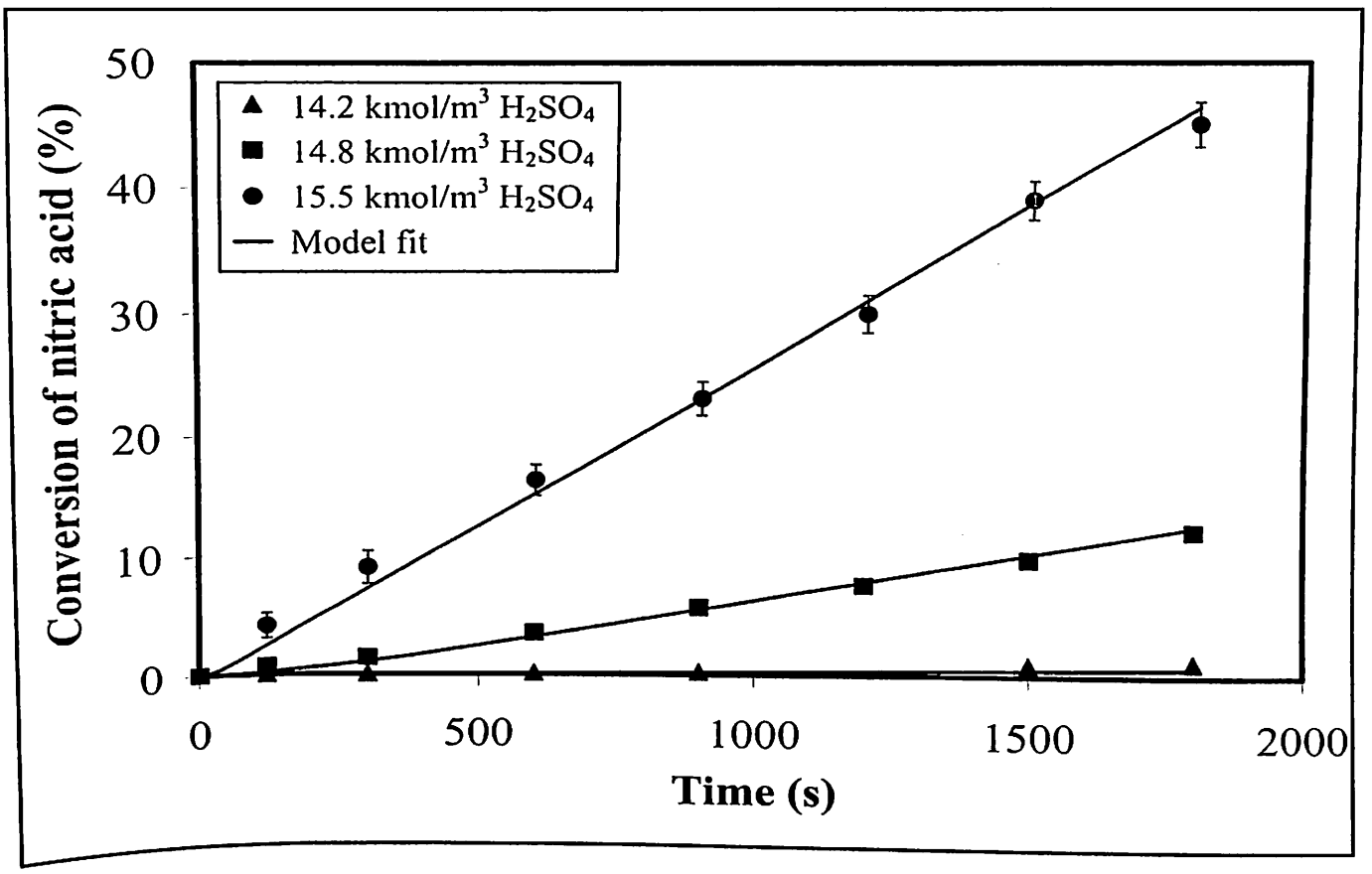


Figure 5.13 Conversion profiles of nitric acid at different sulfuric acid concentrations at 313 K.

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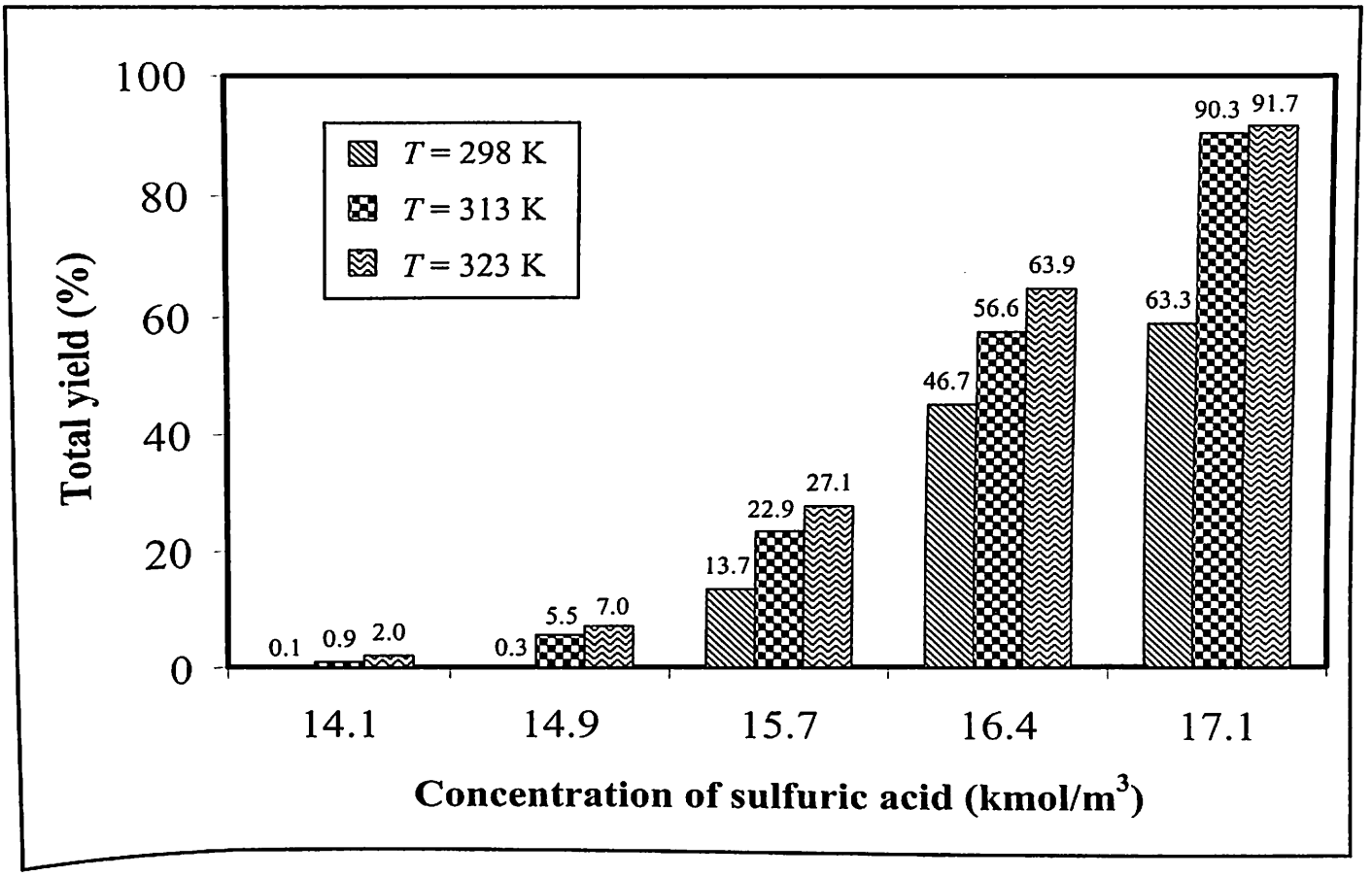


Figure 5.14 Variation of overall yields of the dinitrobenzene isomers with the concentration of sulfuric acid at three temperatures after one hour of reaction. The reactants were charged to the reactor in the molar ratio, HNO_3 : Nitrobenzene : H_2SO_4 = 1:1:4.

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yield also increased with the increase in temperature. The highest yields obtained at 298 K, 313 K and 323 K were 63.3%, 90.3% and 91.7%, respectively, at 17.1 kmol/m^3 concentration of sulfuric acid. Although the rate constant decreased beyond 16.7 kmol/m^3 concentration of sulfuric acid, the high-concentration of nitrobenzene in the aqueous phase is believed to be the main factor behind this significant increase in the yield of the product, apart from the high-concentration of the nitronium ion in the concentrated sulfuric acid. At the high conversions of nitrobenzene, a major portion of the product turned into a hard porous solid mass inside the reactor. A significant amount of nitrobenzene was trapped inside the pores. The mixing was not sufficient in this three-phase system. This factor, along with the water produced in the nitration reaction probably did not allow the reaction to proceed further and hence, did not allow the yield to be even higher. Also, the yield did not increase further at the higher-concentrations of sulfuric acid. In this work, nitric acid and nitrobenzene were charged to the reactor in 1:1 molar ratio to determine the yield of the reaction. The usual industrial practice is to use excess nitric acid during nitration. Therefore it is expected that even higher yields may be obtained by charging excess amount of nitric acid to the reactor.

5.3.4 Distribution of isomers of dinitrobenzene

The percentages of the dinitrobenzene (DNB) isomers (i.e., 1,2-dinitrobenzene, 1,3-dinitrobenzene and 1,4-dinitrobenzene) in the product are presented in Table 5.1. It is observed from the table that the percentage of 1,3-dinitrobenzene in the product decreased with the increase in concentration of sulfuric acid whereas, the amounts of other isomers, especially 1,2-dinitrobenzene, steadily increased. Also, the yield of 1,2-dinitrobenzene was higher than the yield of 1,4-dinitrobenzene. This is probably due to the stabilization of the transition state for the *ortho*-substitution by dipolar interaction between nitrobenzene and the

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Table 5.1 Distribution of isomers of dinitrobenzene in the product

Concentration of sulfuric acid ($kmol/m^3$)	Isomers of DNB in the product (mol %)								
	298 K			313 K			323 K		
	1,3-DNB	1,2-DNB	1,4-DNB	1,3-DNB	1,2-DNB	1,4-DNB	1,3-DNB	1,2-DNB	1,4-DNB
14.1	99.98	0.01	0.01	99.94	0.02	0.04	98.95	0.96	0.09
14.9	99.98	0.02	0.00	99.02	0.94	0.04	98.98	0.96	0.06
15.7	95.55	4.21	0.24	98.13	1.86	0.01	96.76	2.97	0.27
16.4	95.08	4.61	0.31	94.17	5.82	0.01	96.10	3.64	0.26
17.1	91.64	7.35	1.01	91.48	8.33	0.19	91.07	8.00	0.93

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electrophile NO_2^+ [2]. The reason behind the stabilization is due to the existence of $-I$ and $-R$ effects in the nitrobenzene molecule [3], which results in non-uniform distribution of positive charge at the *ortho* and *para* positions in the resonating structures. The higher concentration of positive charge in the *para* position than that in the *ortho* position causes greater stabilization for the *ortho* substitution. Therefore, a higher amount of the *ortho* isomer is produced. It has been reported in the literature that a solvent of high dielectric constant facilitates the electrophilic substitution at the *ortho* position [4,5]. With increase in sulfuric acid concentration, the dielectric constant of sulfuric acid increases (e.g., the dielectric constant of water is 78.5 whereas, the dielectric constant of 18.6 kmol/m^3 sulfuric acid is 101 [6]). Therefore, the high dielectric constant of concentrated sulfuric acid favors the *ortho* product.

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Notation

A	interfacial area (m^2)
C_{DNB}	concentration of dinitrobenzene isomers in the reactor (mol/m^3)
C_{HNO_3}	concentration of nitric acid in the aqueous phase (mol/m^3)
C_{NB}	concentration of nitrobenzene in the aqueous phase in presence of reaction (mol/m^3)
$\overline{C}_{NB}$	equilibrium concentration of nitrobenzene in the aqueous phase (mol/m^3)
$C^0_{HNO_3}$	initial concentration of nitric acid in the aqueous phase (mol/m^3)
d	diameter of the reactor (m)
k_L	mass transfer coefficient (m/s)
$k_{2,exp}$	observed second-order rate constant ($m^3\ mol^{-1}\ s^{-1}$)
M_{NB}	molecular weight of nitrobenzene (kg/mol)
t	time (s)
V_0	initial volume of aqueous phase (m^3)
V_∞	volume of the aqueous phase constituted of nitrobenzene and sulfuric acid under equilibrium conditions (m^3)
V_R	volume of aqueous phase during reaction (m^3)
X_{HNO_3}	conversion of nitric acid

Greek letters

λ	wavelength of detection in HPLC (nm)
ρ_{NB}	density of nitrobenzene (kg/m^3)

Abbreviations

DNB	dinitrobenzene
NB	nitrobenzene

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CHAPTER 6

CONCLUSIONS AND SCOPE FOR FUTURE RESEARCH

This chapter summarizes the inferences drawn from the present work and provides recommendation toward the future directions.

6.1 Conclusions

In this work, the nitration of nitrobenzene in sulfuric acid at high-concentrations has been studied. Several important physicochemical phenomena associated with the process are presented. Some important kinetic and mass transfer aspects of nitration in a batch reactor have been studied at room temperature and at moderately higher temperatures. The salient accomplishments and major conclusions are briefly presented below.

- A very rare spontaneous microemulsification phenomenon was observed when nitrobenzene was dissolved in concentrated sulfuric acid. This phenomenon resulted in the dispersion of fine droplets of nitrobenzene in the aqueous acid phase. This is believed to be responsible for the high solubility of nitrobenzene in the acid phase. It also generated a large amount of interfacial area. The nitrobenzene molecules were not involved in any reaction with sulfuric acid, and they were chemically free to participate in the nitration reaction.
- The rate of transport of nitrobenzene from the organic phase to the aqueous phase was

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found to increase with the increase in sulfuric acid concentration, stirring speed and temperature. The main reason for the increase in the mass transfer coefficient with the increase in sulfuric acid concentration is the stability attained by the formation of microemulsion.

- The rate constants of the homogeneous nitration of nitrobenzene at 298 K, 313 K and 323 K at different sulfuric acid concentrations were determined. The rate constant increased with increase in sulfuric acid concentration. The rate constant was highest at 16.7 kmol/m^3 sulfuric acid concentration at all three temperatures. The rate constant decreased beyond this concentration due to the changes in the activity coefficients of the reactants. These variations of the rate constant with the concentration of sulfuric acid were explained by the M_c function. The activation energy for the elctrophilic attack of nitronium ion on the nitrobenzene molecule was determined. The value was found to be 91.3 kJ/mol. The activation energy of reaction between nitrobenzene and nitric acid was found to vary with the concentration of sulfuric acid.
- To determine the regime of reaction, Hatta numbers were calculated using the values of mass transfer coefficient and the rate constant. The slow regime prevailed at all conditions. The Hatta number increased with the increase in sulfuric acid concentration, passed through a maximum and then decreased at the high-sulfuric acid concentrations. The Hatta number was found to increase with the increase in temperature. The increase in Hatta number with temperature was due to the huge increase in the reaction rate constant with temperature.
- Net yields of the dinitrobenzene isomers increased with increase in sulfuric acid concentration, and temperature as well. Although the rate constant decreased at the

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high-sulfuric acid concentrations (>16.7 kmol/m^3), the yield of the products increased at these concentrations due to the high-concentration of nitrobenzene and nitronium ion present in the aqueous phase. The increase in yield with temperature was due to the tremendous increase in rate constant with temperature. In this work, nitric acid and nitrobenzene were charged to the reactor in 1:1 molar ratio to determine the yield of reaction. The usual industrial practice is to use excess nitric acid. Therefore it is expected that even higher yields may be obtained by charging excess amount of nitric acid to the reactor.

- The proportion of the dinitrobenzene isomers in the product varied with sulfuric acid concentration as well as temperature. The percentage of 1,2-dinitrobenzene increased whereas the percentage of 1,3-dinitrobenzene decreased with increase in sulfuric acid concentration.
- A model was developed for simultaneous mass transfer with chemical reaction for heterogeneous nitration of nitrobenzene. The experimental concentration and conversion profiles matched well with the prediction of the model.

6.2 Recommendations for future work

- In this work, the nitration of nitrobenzene using mixed acid at high-concentrations of sulfuric acid is presented. This work should be extended to the other aromatic compounds such as benzene, toluene and chlorobenzene.
- Nitration by mixed acid employs large quantities of concentrated sulfuric acid. This method leads to excessive acid in the waste stream and corrosion of equipment. Most of the problem can be overcome by using a solid acid catalyst in the nitration process.

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A few solid acid catalysts have been reported in the literature. However, the cost of preparation of the solid catalyst makes them less attractive for implementation in the industrial scale. Further study can be done to make a cost-effective solid acid catalyst.

- The use of superacids and derivatives of nitric acid such as alkyl or acyl nitrates, and nitryl halides can be used as the nitration reagents. They allow nitration to be carried out under anhydrous conditions with recyclable acid systems.
- The stable nitronium salts are the most suitable and effective nitrating agents (although more expensive than mixed acid). Nitration can be carried out using the nitronium salts in organic solvents under completely acid-free conditions. This eliminates the use of corrosive acids and their disposal problems.

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APPENDIX A

SAMPLE CALCULATIONS

A.1 Measurement of solubility of nitrobenzene in sulfuric acid (and vice versa)

A.1.1 Measurement of equilibrium solubility of nitrobenzene in sulfuric acid

The solubility of nitrobenzene in the sulfuric acid phase was determined by UV-Visible spectroscopy as described in Section 3.2.2.1. A sample calculation for the determination of solubility of nitrobenzene in the sulfuric acid is presented here at 15.3 kmol/m^3 sulfuric acid concentration at 298 K.

Sample taken from the aqueous phase = 1.2161 g

Methanol taken to dissolve the sample = 50 cm^3

Dilution factor for measurement of absorbance of the sample = 100

The absorbance at 260 nm = 1.6724

From the calibration curve of nitrobenzene (Figure 3.2), concentration of sample taken in the cuvette = (1.6728 × 15.528) mg/dm^3 = 25.98 mg/dm^3 = 25.98 × 10^{-6} g/cm^3

Concentration of nitrobenzene present in the original sample dissolved in methanol

= (25.98 × 10^{-6} × 100) g/cm^3 = 25.98 × 10^{-4} g/cm^3

Amount of nitrobenzene present in the original sample = (25.98 × 10^{-4} × 50) g

$$= (129.9 \times 10^{-3})\ \text{g}$$

$$= \frac{129.9 \times 10^{-3}}{123}\ \text{mol}$$

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$$= 1.056 \times 10^{-3} \text{ mol}$$

Solubility of nitrobenzene in the sulfuric acid = $\frac{1.056 \times 10^{-3}}{1.2161}$ mol/g of aqueous phase

$$= 0.8683 \text{ mol/kg of aqueous phase}$$

Density of 15.3 kmol/m^3 sulfuric acid equilibrated with nitrobenzene (Figure 3.7) = 1635.56 kg/m^3

Solubility of nitrobenzene in the sulfuric acid = (0.8683 × 1635.56) mol/m^3 of aqueous phase

$$= 1420.16 \text{ mol/m}^3 \text{ of aqueous phase}$$

The above procedure of determination of solubility of nitrobenzene in the sulfuric acid phase was repeated three times, and the mean value was taken. Similarly, the equilibrium solubility of nitrobenzene at various sulfuric acid concentrations was determined at 298 K and 313 K. The values are presented in Figure 3.3.

A.1.2 Measurement of equilibrium solubility of sulfuric acid in nitrobenzene

The solubility of sulfuric acid in organic phase was determined by acid–base titration using NaOH standardized with standard oxalic acid. About 1 cm^3 of sample was withdrawn from the organic phase and dissolved in water. A sample calculation for the determination of solubility of sulfuric acid in the organic phase is shown below at 15.6 kmol/m^3 sulfuric acid concentration at 298 K.

Sample taken from the organic phase = 1.0 cm^3

Strength of the aqueous NaOH (standardized with oxalic acid) = 0.00963 mol/dm^3

Amount of NaOH taken to neutralize the sample = 46.6 cm^3

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Moles of H_2SO_4 present per dm^3 the sample = $\frac{46.6 \times 0.00963}{2 \times 1} = 0.22438$

Moles of H_2SO_4 present per m^3 the sample = 224.38

The aforesaid procedure for the measurement of solubility of sulfuric acid in the organic phase was repeated three times and the average value was taken. Similarly, the solubility of sulfuric acid in the organic phase at other sulfuric acid concentrations was determined at 298 K and 313 K. The values are presented in Figure 3.3.

A.2 Determination of reaction regime

A.2.1 Determination of diffusivity of nitrobenzene (D_{NB}) in sulfuric acid

The diffusivity of nitrobenzene (D_{NB}) in sulfuric acid was calculated by the following relation.

$$D_{NB} = \frac{7.4 \times 10^{-15} T (\bar{\phi}\bar{M})^{1/2}}{\mu v_m^{0.6}} \qquad \text{(A.1)}$$

The quantity $\bar{\phi}\bar{M}$ is determined from the following relation.

$$\bar{\phi}\bar{M} = x_w \phi_w M_w + x_s \phi_s M_s \qquad \text{(A.2)}$$

A sample calculation is shown for the determination of diffusivity of nitrobenzene in 16.3 $kmol/m^3$ sulfuric acid at 298 K.

The values of association factors are as follows [1].

Association factor of sulfuric acid, $\phi_s = 2$

Association factor of water, $\phi_w = 2.6$

At 16.3 $kmol/m^3$ sulfuric acid,

Mole fraction of sulfuric acid, $x_s = 0.59$

Mole fraction of water, $x_w = 0.41$

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From equation (A.2), we get

$$\bar{\phi}\bar{M} = \left[(0.41\times 2.6\times 18)+(0.59\times 2\times 98)\right] = \left[19.19+115.64\right] = 134.83$$

Values of the other physical parameters are as follows.

Viscosity of aqueous sulfuric acid [2], $\mu = 21.5 \times 10^{-3}$ Pa s

Molar volume of nitrobenzene at its normal boiling point [3], $v_m = 102.7$ cm^3/mol

From equation (A.1), the diffusivity of nitrobenzene in 16.3 kmol/m^3 sulfuric acid at 298 K is given by,

$$D_{NB} = \frac{7.4 \times 10^{-15} \times 298 \times (134.83)^{1/2}}{21.5 \times 10^{-3} \times (102.7)^{0.6}} \text{ m}^2/\text{s}$$

$$= 0.74 \times 10^{-10} \text{ m}^2/\text{s}$$

A.2.2 Determination of Hatta number

The Hatta number was calculated by the following expression.

$$\text{Ha} = \frac{\sqrt{D_{NB} k_{2,exp} C^0_{HNO_3}}}{k_L} \qquad \text{(A.3)}$$

A sample calculation is shown for the determination of Hatta number in 16.3 kmol/m^3 sulfuric acid at 298 K.

The value of k_L is taken from Chapter 4 (Section 4.3.1). The value of diffusivity of nitrobenzene (D_{NB}) is taken from Table 4.4. The values of $k_{2,exp}$ and $C^0_{HNO_3}$ are taken from Chapter 4 (Section 4.3.2). These values are presented below.

$k_L = 1.5 \times 10^{-5}$ m/s

$k_{2,exp} = 40.0 \times 10^{-6}$ m^3 mol^{-1} s^{-1}

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$C^0_{HNO_3}$ = 339.8 mol/m^3

From the equation (A.3), the value of Hatta number is given by,

$$Ha = \frac{\sqrt{0.74\times10^{-10}\times40.0\times10^{-6}\times339.8}}{1.5\times10^{-5}} = 0.0668$$

A.3 Determination of distribution of isomers of dinitrobenzene

The concentrations of the isomers of dinitrobenzene (DNB) were determined from the solid product. The analysis was carried out by normal phase HPLC as described in Section 5.2.2.3. A small amount of the solid product was dissolved in 2-propanol and diluted with dichloromethane. A sample calculation for the determination of the amount of dinitrobenzene isomers present in the product is shown below. The product was obtained from the reaction at 298 K using 17.1 kmol/m^3 sulfuric acid.

Sample taken from the product = 16.1 mg

Solution of 2-propanol and dichloromethane taken to dilute the sample = 30 cm^3

Dilution factor for measurement of area in HPLC = 10

Area obtained for the respective compounds in normal phase HPLC are as follow.

Nitrobenzene = 508.97 μV.s

1,4-dinitrobenzene = 76392.77 μV.s

1,3-dinitrobenzene = 4446785.69 μV.s

1,2-dinitrobenzene = 216657.48 μV.s

Using the calibration curves for nitrobenzene and dinitrobenzene isomers (see Figures 5.2 – 5.5), the amounts of the compounds present in the sample are as follow.

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$$\text{Nitrobenzene} = \frac{508.97 \times 7.93 \times 10^{-6} \times 10 \times 30}{1000} \text{ mg} = 1.21 \times 10^{-3} \text{ mg}$$

$$\text{1,4-dinitrobenzene} = \frac{76392.77 \times 6.82 \times 10^{-6} \times 10 \times 30}{1000} \text{ mg} = 0.156 \text{ mg}$$

$$\text{1,3-dinitrobenzene} = \frac{4446785.69 \times 1.04 \times 10^{-5} \times 10 \times 30}{1000} \text{ mg} = 13.87 \text{ mg}$$

$$\text{1,2-dinitrobenzene} = \frac{216657.48 \times 1.71 \times 10^{-5} \times 10 \times 30}{1000} \text{ mg} = 1.11 \text{ mg}$$

It can be observed from these results that the amount of nitrobenzene present in the product was very small. Therefore, we can neglect it. Neglecting the amount of nitrobenzene, the moles of the dinitrobenzene isomers present in the product are as follows.

$$\text{1,4-dinitrobenzene} = \frac{0.156 \times 10^{-3}}{168} = 9.29 \times 10^{-7} \text{ mol}$$

$$\text{1,3-dinitrobenzene} = \frac{13.87 \times 10^{-3}}{168} = 8.26 \times 10^{-5} \text{ mol}$$

$$\text{1,2-dinitrobenzene} = \frac{1.11 \times 10^{-3}}{168} = 6.61 \times 10^{-6} \text{ mol}$$

Therefore, the distribution of isomers in the product in % (mol) is as follows:

$$\text{1,4-dinitrobenzene} = \left[\frac{9.29 \times 10^{-7}}{\left(9.29 \times 10^{-7} + 8.26 \times 10^{-5} + 6.61 \times 10^{-6}\right)} \right] \times 100 = 1.03 \%$$

$$\text{1,3-dinitrobenzene} = \left[\frac{8.26 \times 10^{-5}}{\left(9.29 \times 10^{-7} + 8.26 \times 10^{-5} + 6.61 \times 10^{-6}\right)} \right] \times 100 = 91.64 \%$$

$$\text{1,2-dinitrobenzene} = \left[\frac{6.61 \times 10^{-6}}{\left(9.29 \times 10^{-7} + 8.26 \times 10^{-5} + 6.61 \times 10^{-6}\right)} \right] \times 100 = 7.33 \%$$

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The above procedure of determination of distribution of isomers was repeated thrice at each sulfuric acid concentration at each temperature.

Literature cited

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3. Charlton, A. K., Daniels, C. R., Wold, R. M., Pustejovsky, E., Acree, Jr. W. E. and Abraham, M. H., "Solubility of crystalline nonelectrolyte solutes in organic solvents: Mathematical correlation of 3-nitrobenzoic acid solubilities with the Abraham general solvation model," *J. Mol. Liq.*, **116**, 19 – 28 (2005).

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APPENDIX B

COMPUTER PROGRAM AND TYPICAL PROGRAM OUTPUT

B.1 Determination of mass transfer coefficient (supplementary information of Chapter 4)

The mass transfer coefficient of nitrobenzene in the sulfuric acid was determined from the best fit of equation (4.8) to the experimental data. A computer code has been developed to solve equation (4.8). For determination of mass transfer coefficient at 16.7 kmol/m^3 sulfuric acid at 298 K with stirring speed 2π rad/s, a typical C++ program and computational output are shown below.

```
// Program for solving an ODE by Runge-Kutta-Gill method
// Determination of mass transfer coefficient of nitrobenzene in the sulfuric acid
// Concentration of sulfuric acid = 16.7 kmol/m3; Temperature = 298 K; Stirring speed = 6.28
// rad/s
# include <iostream.h>
# include <math.h>
# include <iomanip.h>

class rkg
{
private:
        int i, n;
        double a, b, c, d, f, h, k1, k2, k3, k4, x, xf, y;
        double density_NB, mol_wt_NB, a1, vol_ini, eqlm_sol, vol_inf, area, kl;
public:
        double func (double z, double t)
```


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```
{
f=(kl*area/pow(vol_ini,2))*pow((1-(t*a1)),2)*((vol_inf*eqlm_sol)-(((vol_inf*eqlm_sol*a1)+vol_ini)*t));
return f;
}
void solution ();
};
// Main function
void main ()
{
rkg runge;
runge.solution ();
}
// Apply Runge-Kutta-Gill method
void rkg :: solution ()
{
density_NB =1200;                    // Density of nitrobenzene
mol_wt_NB =0.123;                    // Molecular weight of nitrobenzene in kg/mol
a1 = mol_wt_NB/density_NB;
area = 3.1416*pow(0.1,2)/4.0;        // Determination of interfacial area
eqlm_sol = 4528.46;                  // Equilibrium solubility of nitrobenzene
vol_ini = 300e-6;                    // Initial volume of aqueous phase
vol_inf = (vol_ini/(1-(eqlm_sol*a1))); // Infinite volume of aqueous phase
kl = 0.183e-4;                       // Value of mass transfer coefficient
x = 0; y = 0;                        // Initial condition
xf = 3000;                           // Final time
n = 100;                             // Number of divisions
h = (xf - x)/n;
a = (sqrt(2)-1)/2; b = (2-sqrt(2))/2;
c = -sqrt(2)/2; d = 1+sqrt(2)/2;
for (i=0; i<n; i++)
{       k1 = h*func (x,y);
        k2 = h*func((x+h/2),(y+k1/2));
        k3 = h*func((x+h/2),(y+a*k1+b*k2));
        k4 = h*func((x+h),(y+c*k2+d*k3));
        y += (k1+2*b*k2+2*d*k3+k4)/6;
        cout.setf(ios::fixed,ios::floatfield);
        cout<<setprecision(0)<<(x+h)<<setw(15)<<setprecision(2)<<(y)<<endl;
```


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```
        x += h;
}
}
```

The output for the aforesaid program is given below.

Time (s)	C^a_{NB} (mol/m^3)	Time (s)	C^a_{NB} (mol/m^3)	Time (s)	C^a_{NB} (mol/m^3)	Time (s)	C^a_{NB} (mol/m^3)
30	118.41	780	1914.46	1530	2748.64	2280	3236.84
60	231.03	810	1959.11	1560	2773.01	2310	3252.18
90	338.30	840	2002.52	1590	2796.89	2340	3267.27
120	440.63	870	2044.72	1620	2820.28	2370	3282.11
150	538.35	900	2085.78	1650	2843.21	2400	3296.71
180	631.81	930	2125.74	1680	2865.68	2430	3311.08
210	721.29	960	2164.64	1710	2887.71	2460	3325.22
240	807.05	990	2202.53	1740	2909.31	2490	3339.13
270	889.34	1020	2239.45	1770	2930.49	2520	3352.82
300	968.38	1050	2275.44	1800	2951.27	2550	3366.30
330	1044.36	1080	2310.52	1830	2971.66	2580	3379.57
360	1117.47	1110	2344.75	1860	2991.66	2610	3392.63
390	1187.89	1140	2378.14	1890	3011.30	2640	3405.49
420	1255.75	1170	2410.73	1920	3030.57	2670	3418.16
450	1321.21	1200	2442.55	1950	3049.49	2700	3430.63
480	1384.40	1230	2473.62	1980	3068.06	2730	3442.92
510	1445.45	1260	2503.98	2010	3086.31	2760	3455.02
540	1504.46	1290	2533.64	2040	3104.23	2790	3466.94
570	1561.53	1320	2562.64	2070	3121.83	2820	3478.68
600	1616.78	1350	2590.98	2100	3139.12	2850	3490.26
630	1670.28	1380	2618.71	2130	3156.12	2880	3501.66
660	1722.13	1410	2645.82	2160	3172.82	2910	3512.90
690	1772.40	1440	2672.36	2190	3189.24	2940	3523.97
720	1821.17	1470	2698.33	2220	3205.37	2970	3534.89
750	1868.50	1500	2723.75	2250	3221.24	3000	3545.65

B.2 Modeling of mass transfer with chemical reaction (supplementary information of Chapter 5)

The model developed in the Chapter 5 for mass transfer with chemical reaction was solved numerically using Runge-Kutta-Gill method. Using this model, the concentration profiles of the reactants and the products as well as the conversion profiles of the reactants in the aqueous phase during nitration can be predicted. For the heterogeneous nitration of

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nitrobenzene at 298 K using 14.8 kmol/m^3 concentration of sulfuric acid, a typical C++ program and computational output are shown below.

```
// Program for solving a set of ODEs by Runge-Kutta-Gill method
// Modeling of mass transfer with chemical reaction
// Determination of concentration profiles of reactant and product, and conversion profiles of
// nitric acid
// Concentration of sulfuric acid = 14.8 kmol/m3; Temperature = 298 K
# include <iostream.h>
# include <math.h>
# include <fstream.h>
# include <iomanip.h>
class s_ode
{
private:
        int i, j, l, n;
        double a, b, c, d, h, x, x1, xi, xf;
        double a1, k2, kl, mol_wt_NB, density_NB, ca0, area;
        double vol_inf, vol_h2so4, vol_hno3, vol_aq, eqlm_sol;
        double *b1, *b2, *b3, *g, *y, *y1;
public:
        s_ode ()
{
a = (sqrt(2)-1)/2; b = (2-sqrt(2))/2;
c = -sqrt(2)/2; d = 1+sqrt(2)/2;
area = 3.1416*pow(0.09,2)/4.0;
k2 =0.7e-6;                                  // Value of rate constant
kl =0.65e-5;                                 // Value of mass transfer coefficient
density_NB =1200;                            // Density of nitrobenzene
mol_wt_NB =0.123;                            // Molecular weight of nitrobenzene in kg/mol
a1 = mol_wt_NB/density_NB;
eqlm_sol = 722.4;                            // Equilibrium solubility of nitrobenzene
vol_h2so4 = 300e-6;                          // Initial volume of sulfuric acid
vol_hno3 = 42.6e-6;                          // Initial volume of nitric acid
vol_aq = vol_h2so4 + vol_hno3;
vol_inf = (vol_h2so4 / (1 – (eqlm_sol*a1)));  // Infinite volume of aqueous phase
```


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```
ca0 = 0.667/vol_aq;                          // Initial concentration of nitric acid
}
void func(double p, double *q, double *r)    //ODEs
{
r[0] = (kl*area*eqlm_sol*vol_inf*pow((1-a1*q[0]),3)/pow(vol_aq,2))-(((kl*area*(1-
(a1*q[0]))/vol_aq)+(k2*q[1]))*(1-(a1*q[0]))*q[0]);
r[1] = -(k2*q[1]*q[0])-(a1*q[1]*r[0]/(1-a1*q[0]));
r[2] = (k2*q[1]*q[0])-(a1*q[2]*r[0]/(1-a1*q[0]));
}
void solution ();                    //Function for implementing the Runge-Kutta-Gill method
        ~s_ode () { delete b1, b2, b3, g, y, y1; }
};
//main function
void main ()
{
        s_ode multivar;
        multivar.solution ();
}
void s_ode :: solution ()
{
        n = 3;                                   // Number of differential equations
        b1 = new double[n];
        b2 = new double[n];
        b3 = new double[n];
        g = new double[n];
        y = new double[n];
        y1 = new double[n];
        l = 100;                                 // Number of divisions
        xi = 0.0; y[0] = 0.0; y[1] = ca0; y[2] = 0.0; // Initial conditions
        xf = 1800.0;                             // Final time
        h = (xf-xi)/l;
        x = xi;
        for(i = 0; i<l; i++)                     // Runge-Kutta-Gill method
        {
          for(j=0; j<n; j++)
          { y1[j] = y[j]; }
          x1 = x;
```


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```
        func (x,y,g);
        for(j=0; j<n; j++)
        {
        b1[j] = g[j];
        y[j] = y1[j] + h*g[j]/2;
        }
        x = x1 + h/2;
        func (x,y,g);
        for(j=0; j<n; j++)
        {       b2[j] = g[j];
                y[j] = y1[j]+h*(a*b1[j]+b*g[j]);
        }
        func (x,y,g);
        for(j=0; j<n; j++)
        {
                b3[j] = g[j];
                y[j] = y1[j]+h*(c*b2[j]+d*g[j]);
        }
        x = x1 + h;
        func (x,y,g);

        for(j=0; j<n; j++ )
        { y[j] = y1[j]+h*(b1[j]+g[j]+2*(b*b2[j]+d*b3[j]))/6; }
        cout.setf(ios::fixed,ios::floatfield);
        cout<<setprecision(0)<<x<<setw(15)<<setprecision(2)<<y[0]<<setw(15)<<setprecision(2)<<y[
        1]<<setw(15)<<setprecision(2)<<y[2]<<setw(15)<<setprecision(2)<<(1-(y[1]/(ca0*(1-
        a1*y[0])))*100<< endl;                    // Output statement
      }
}
```

The output of the aforesaid program is given below.

Time (s)	C_{NB} (mol/m^3)	C_{HNO_3} (mol/m^3)	C_{DNB} (mol/m^3)	X_{HNO_3} (%)
18	1.46	1946.57	0.02	0.00
36	2.89	1946.23	0.07	0.00
54	4.28	1945.86	0.16	0.01
72	5.63	1945.47	0.28	0.01
90	6.94	1945.06	0.43	0.02
108	8.22	1944.62	0.62	0.03
126	9.46	1944.15	0.84	0.04

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Time (s)	C_{NB} (mol/m^3)	C_{HNO_3} (mol/m^3)	C_{DNB} (mol/m^3)	X_{HNO_3} (%)
144	10.67	1943.66	1.08	0.06
162	11.85	1943.15	1.36	0.07
180	13.00	1942.62	1.66	0.09
198	14.12	1942.06	2.00	0.10
216	15.21	1941.49	2.35	0.12
234	16.26	1940.89	2.74	0.14
252	17.30	1940.28	3.15	0.16
270	18.30	1939.64	3.58	0.18
288	19.28	1938.99	4.04	0.21
306	20.23	1938.32	4.52	0.23
324	21.15	1937.63	5.03	0.26
342	22.05	1936.92	5.56	0.29
360	22.93	1936.20	6.10	0.31
378	23.79	1935.46	6.67	0.34
396	24.62	1934.70	7.26	0.37
414	25.43	1933.93	7.87	0.41
432	26.22	1933.14	8.50	0.44
450	26.99	1932.34	9.15	0.47
468	27.73	1931.53	9.81	0.51
486	28.46	1930.70	10.50	0.54
504	29.17	1929.86	11.20	0.58
522	29.86	1929.00	11.91	0.61
540	30.54	1928.14	12.65	0.65
558	31.19	1927.26	13.40	0.69
576	31.83	1926.36	14.16	0.73
594	32.46	1925.46	14.94	0.77
612	33.06	1924.55	15.73	0.81
630	33.65	1923.62	16.54	0.85
648	34.23	1922.68	17.36	0.89
666	34.79	1921.74	18.20	0.94
684	35.34	1920.78	19.04	0.98
702	35.87	1919.81	19.90	1.03
720	36.39	1918.84	20.78	1.07
738	36.90	1917.85	21.66	1.12
756	37.39	1916.86	22.56	1.16
774	37.87	1915.85	23.47	1.21
792	38.34	1914.84	24.38	1.26
810	38.80	1913.82	25.31	1.31
828	39.24	1912.79	26.25	1.35
846	39.68	1911.76	27.20	1.40
864	40.10	1910.71	28.16	1.45
882	40.51	1909.66	29.13	1.50
900	40.92	1908.60	30.11	1.55
918	41.31	1907.54	31.10	1.60
936	41.69	1906.47	32.09	1.66
954	42.06	1905.39	33.10	1.71
972	42.43	1904.30	34.11	1.76
990	42.78	1903.21	35.13	1.81

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Time (s)	C_{NB} (mol/m^3)	C_{HNO_3} (mol/m^3)	C_{DNB} (mol/m^3)	X_{HNO_3} (%)
1008	43.13	1902.11	36.16	1.87
1026	43.47	1901.01	37.19	1.92
1044	43.80	1899.90	38.24	1.97
1062	44.12	1898.78	39.29	2.03
1080	44.44	1897.66	40.35	2.08
1098	44.74	1896.54	41.41	2.14
1116	45.04	1895.41	42.48	2.19
1134	45.34	1894.27	43.56	2.25
1152	45.62	1893.13	44.64	2.30
1170	45.90	1891.98	45.73	2.36
1188	46.17	1890.83	46.83	2.42
1206	46.44	1889.68	47.93	2.47
1224	46.70	1888.52	49.04	2.53
1242	46.95	1887.36	50.15	2.59
1260	47.20	1886.19	51.27	2.65
1278	47.44	1885.02	52.39	2.70
1296	47.68	1883.84	53.52	2.76
1314	47.91	1882.66	54.65	2.82
1332	48.14	1881.48	55.79	2.88
1350	48.36	1880.29	56.93	2.94
1368	48.57	1879.11	58.08	3.00
1386	48.78	1877.91	59.23	3.06
1404	48.99	1876.72	60.38	3.12
1422	49.19	1875.52	61.54	3.18
1440	49.39	1874.31	62.71	3.24
1458	49.58	1873.11	63.87	3.30
1476	49.77	1871.90	65.04	3.36
1494	49.95	1870.69	66.22	3.42
1512	50.14	1869.47	67.40	3.48
1530	50.31	1868.26	68.58	3.54
1548	50.49	1867.04	69.76	3.60
1566	50.65	1865.82	70.95	3.66
1584	50.82	1864.59	72.14	3.72
1602	50.98	1863.37	73.34	3.79
1620	51.14	1862.14	74.53	3.85
1638	51.30	1860.91	75.73	3.91
1656	51.45	1859.67	76.94	3.97
1674	51.60	1858.44	78.14	4.04
1692	51.75	1857.20	79.35	4.10
1710	51.89	1855.96	80.56	4.16
1728	52.03	1854.72	81.78	4.22
1746	52.17	1853.47	82.99	4.29
1764	52.30	1852.23	84.21	4.35
1782	52.44	1850.98	85.43	4.41
1800	52.57	1849.73	86.65	4.48

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APPENDIX C

ERROR ANALYSIS

The error in experimentally-measured quantities is important as it determines the accuracy of the calculation. In conducting an experiment, one generally encounters three types of errors: (i) human error, (ii) systematic error, and (iii) random error. Human error occurs when the experimenter makes a mistake. Therefore, it is experimenter's error. Systematic errors are the results of inappropriate experimental apparatus, faulty assumptions or improper analysis techniques. Random error results from random variation in the precision of measuring devices, and the slight variations that occur in successive measurements by the same observer under nearly identical conditions. In this work, care was taken to eliminate human and systematic errors by suitably designing the experiments and adopting appropriate methods for the analysis of samples. Random error cannot be eliminated. They can only be minimized by using the most accurate measuring devices and techniques available. The focus of the error analysis presented here is on the random errors in experimentally-measured quantities, and their contribution in the estimation of the overall error in the parameter, which is calculated from these measurements.

If a measurement is repeated in independent and unbiased ways, the results of the measurements will be slightly different each time. A statistical analysis of these results gives the "best" value of the measured quantity, and the "best" estimate of the uncertainty to be associated with that result. The usual method of determining the best value is to compute the "mean value" of the results.

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If $x_1, x_2, \cdots\cdots, x_N$ are the N results of the measurement of the quantity x, then the mean value of x, usually denoted as $\bar{x}$, is defined as,

$$\bar{x} \equiv \frac{x_1 + x_2 + \cdots + x_N}{N} = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad \text{(C.1)}$$

The uncertainty in the result is usually expressed as the "root-mean-squared deviation" (RMSD) which is also called the "sample standard deviation" (SSD). The sample standard deviation is computed by the following equation.

$$s = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \cdots + (x_N - \bar{x})^2}{N - 1}} \qquad \text{(C.2)}$$

The sample standard deviation is generally accepted as the "best" estimate of the measurement uncertainty. From the value of s, the % of error of estimation can be calculated by using the following equation.

$$\% \text{ of error} = \left(\frac{s}{\bar{x}}\right) \times 100 \qquad \text{(C.3)}$$

Some typical values of RMSD for experimental measurements carried out in the present work are presented in this appendix. A typical RMSD for the measurement of solubility of nitrobenzene in 15.3 kmol/m^3 sulfuric acid at 298 K is shown in Table C.1. Table C.2 shows the RMSD and the % of error for the solubility of sulfuric acid in the organic phase at 15.6 kmol/m^3 of sulfuric acid concentration at 298 K. RMSD values for experimental measurement of the distribution of isomers of dinitrobenzene at 17.1 kmol/m^3 sulfuric acid concentration at 298 K are shown in Table C.3.

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Table C.1 RMSD for measurement of solubility of nitrobenzene in the sulfuric acid

Run	Solubility of nitrobenzene in sulfuric acid (mol/m^3)	$\bar{x}$	s	% of error
1	1420.16	1406.86	12.54	0.89
2	1405.18			
3	1395.25			

Table C.2 RMSD for measurement of solubility of sulfuric acid in the organic phase

Run	Solubility of sulfuric acid in the organic phase (mol/m^3)	$\bar{x}$	s	% of error
1	224.38	222.86	5.46	2.45
2	216.80			
3	227.40			

Table C.3 RMSD for measurement of distribution of dinitrobenzene isomers

Isomers of dinitrobenzene	Distribution of isomers (mol %)			$\bar{x}$	s	% of error
	Run 1	Run 2	Run 3			
1,4-dinitrobenzene	1.03	1.01	1.00	1.01	0.02	1.51
1,3-dinitrobenzene	91.64	91.66	91.63	91.64	0.02	0.02
1,2-dinitrobenzene	7.33	7.33	7.39	7.35	0.03	0.47

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